Synthesis, characterization and spectrochemical studies on a few binuclear μ-oxo molybdenum(V) complexes of pyrimidine derived Schiff base ligands

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Abstract. Ten new binuclear singly oxo-bridged molybdenum complexes (complexes **1–10**) were prepared using five pyrimidine derived Schiff base ligands and two Mo(V) precursors $(NH_4)_2MoOCl_5$ and $(NH_4)_2MoOBr_5$. The ligands are prepared by the condensation of 4,6-dimethyl 2-hydrazino pyrimidine with salicylaldehyde (for HL_1), *o*-hydroxy acetophenone (for HL_2) and substituted salicylaldehydes (for HL_3, HL_4 and HL_5) respectively. These ligands are already reported as good donors for Mo(VI) state. The μ-oxo Mo(V) complexes reported here bears a distorted octahedral geometry around each Mo atom with either N_2O_2Cl or N_2O_2Br chromophores. Fine variations in the spectroscopic behaviour of the complexes are observed in accordance with the varying electron donating properties of the ligands. All the complexes are unstable in solution and X-ray quality crystal of complex **1** could be isolated. All the complexes are characterized by IR and UV-Vis spectra.

Keywords. Molybdenum(V); Schiff base; crystal structure; binuclear complex; spectral study.

1. Introduction

The chemistry of molybdenum is quite interesting because of its large number of accessible oxidation states as well as its ability to form stable complexes with oxygen, nitrogen and sulphur containing ligands with diverse coordination numbers and stereo-chemistries.[1] Perhaps this versatility is what qualifies it for use by nature in various essential life processes as constituent part of several metalloenzymes.[2] In fact, Mo is the only essential trace element of the second transition series and is an integral part of oxotransferase[3] and nitrogenase enzymes.[4]

Several molybdoenzymes consist of two Mo atoms per molecule suggesting binuclear Mo sites and joined by one or two oxo or sulphido bridges. The Mo atom alternates +VI and +IV states with the involvement of transient Mo(V) state also.[5] Though the active site of the fully oxidized (Mo^{6+}) and reduced form (Mo^{4+}) of metalloenzymes has already

been determined crystallographically the understanding of the transient Mo(V) state is still heavily dependant on spectroscopy.[6] With the knowledge of approximate coordination sphere of Mo in the metalloenzymes at hand, several attempts have been made to model the active sites of these enzymes and study their enzyme mimetic activity. From the last quarter of twentieth century the literature has been flooded with reports of model complexes mostly containing the Mo(VI) state and Schiff base ligands.[7] The Mo(V) complexes are less described and compared to the Mo(VI) species. In fact, up to the first half of this decade only a few crystal structures of Mo(V) complexes with Schiff bases[8] could be found at the Cambridge structural Database (version 5·26, November 2004).[9] The chemistry of Mo(V) is dominated by spin paired oxo-bridged dimers with $Mo_2O_3^{4+}$ or $Mo_2O_4^{2+}$ cores. Mononuclear paramagnetic Mo(V) complexes are not so common in literature. Because of a tendency of Mo(V) species to form oxo-bridged binuclear complexes preparation of mononuclear complexes requires careful choice of the ligands

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which stereochemically hinders formation of binuclear Mo core.[10] In nature, however, the pterin bound enzymes such as DMSO reductase are common in microbial systems and are mononuclear in nature.[11]

Apart from their utility as model compounds for enzymes the Mo(V) complexes have also found use as catalysts for oxygen transfer. Mo(V) complexes are known to 'speed up' the transfer of oxygen from DMSO or pyridine-N-oxide to triphenyl phosphine.[12]

In the present work, we have continued our endeavour to explore the chemistry of Mo complexes with heterocycle based ligands and synthesized ten new μ-oxo binuclear Mo complexes of pyrimidine derived Schiff base ligands. These complexes are prepared from two standard Mo(V) precursors $(NH_4)_2MoOCl_5$ and $(NH_4)_2MoOBr_5$. The complexes bear octahedral arrangement about each Mo center using the tridentate NNO donor ligand, two oxo groups (one terminal and the other bridging) and a loosely bound halide moiety. Previously we have shown that difference in electron donating abilities of Schiff base ligands affect the spectroscopic properties in the corresponding Mo(VI) complexes with justifiable correlations.[13] Here also, we have found that similar effects are observed for a series of Mo(V) complexes.

2. Experimental

$(NH_4)_2MoOCl_5$ and $(NH_4)_2MoOBr_5$ were prepared as described in the literature.[14] Reagent grade solvents were used as received. 4,6-dimethyl 2-hydrazino pyrimidine was prepared as described in the literature.[15] Salicylaldehyde, 5-bromo salicylaldehyde, 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde and *o*-hydroxyacetophenone were purchased from Aldrich Chemical Company, USA and used as received. The ligands HL_1, HL_2 were prepared as described in our previous publication.[16] HL_3, HL_4 and HL_5 were prepared using a similar technique by condensation of 10 mmol of 5-bromo salicylaldehyde, 5-chlorosalicylaldehyde or 5-nitrosalicylaldehyde with 10 mmol of 4,6-dimethyl 2-hydrazino pyrimidine in each case.

HL_3: m.p. 167°C. Yield: 2·68 g (80%). IR (KBr pellet) v/cm^{-1}: 3321 (N–H), 3187 (O–H), 1535·2 (C=N), 1612 (C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS) δ/ppm: (6·62) (s, 1H, –C$_5$–H Pyrimidine), (6·9–7·6) (*m*, 4H, –C$_6$H$_4$), (8·2) (*s*, 1H, –CH=N–), (12·8) (s, 1H, aromatic-OH), (2·28) (s, 1H, (N–H of hydrazone), (2·46–2·53) (*m*, 6H, CH$_3$).

HL_4: m.p. 165°C Yield: 1·70 g (60%). IR (KBr pellet) v/cm^{-1}: 3275 (N–H), 3191 (O–H), 1528 (C=N), 1610 (C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS) δ/ppm: (6·63) (*s*, 1H, –C$_5$–H pyrimidine), (6·9–7·8) (*m*, 4H, –C$_6$H$_4$), (8·2) (*s*, 1H, –CH=N–), (12·8) (*s*, 1H, aromatic-OH), (2·28) (*s*, 1H, N–H of hydrazone), (2·46–2·53) (*m*, 6H, (CH$_3$).

HL_5: m.p.: above 200°C Yield: 2·28 g (80%). 3321 (N–H), 3187 (O–H), 1535·2 (C–N), 1612 (C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS) δ/ppm: (6·62) (s, 1H, –C$_5$–H pyrimidine), (6·9–7·6) *m*, 4H, –C$_6$H$_4$), (8·2) (*s*, 1H, –CH=N–), (12·8) (*s*, 1H, aromatic-OH), (2·28) (*s*, 1H, N–H of hydrazone), (2·46–2·53) (*m*, 6H, CH$_3$).

2.1 *Synthesis of the complexes* **1–10**

The complexes $[Mo_2O_3(L_1)_2Cl_2]$ (**1**), $[Mo_2O_3(L_2)_2Cl_2]$ (**2**), $[Mo_2O_3(L_3)_2Cl_2]$ (**3**), $[Mo_2O_3(L_4)_2Cl_2]$ (**4**) and $[Mo_2O_3(L_5)_2Cl_2]$ (**5**) were synthesized by adding an ethanolic solution (10 mL) of $(NH_4)_2MoOCl_5$ (0·5 mmol, 0·160 g) as the common reagent with ethanolic solutions of HL_1 (0·5 mmol, 0·122 g), HL_2 (0·5 mmol, 0·136 g), HL_3 (0·5 mmol, 0·201 g) and HL_4 (0·5 mmol, 0·158 g) and HL_5 (0·5 mmol, 0·167 g) respectively. A deep magenta colouration of the solution developed immediately on mixing the two components. The respective complex separated as a violet microcrystalline compound on refluxing the reaction mixture for 15 min at water bath temperature. It was filtered, washed with ethanol and dried over fused CaCl$_2$.

X-ray quality crystals of **1** were grown by slow diffusion of a dilute ethanolic solution of $(NH_4)_2MoOCl_5$ into a dilute ethanolic solution of ligand HL_1 in a sealed glass tube. When the solution of the two precursors diffused into one another crystals of **6** formed and deposited on the inner wall of the glass tube.

Preparation of complexes **6–10** were affected by taking equimolar proportion of $(NH_4)_2MoOBr_5$ and the respective ligands and applying the same method.

$[Mo_2O_3(L_1)_2Cl_2]$ (**1**): Yield 0·130 g (33%). Elemental analysis: Anal. Calc. (%) for C$_{26}$N$_8$O$_5$H$_{26}$Mo$_2$Cl$_2$: C: 39·39 H: 3·28 N: 14·14; Found C: 38·91 H: 3·25 N: 14·05.

$[Mo_2O_3(L_2)_2Cl_2]$ (**2**): Yield 0·143 g (35%). Elemental analysis: Anal. Calc. (%) for C$_{28}$N$_8$O$_5$H$_{30}$Mo$_2$Cl$_2$: C: 40·97 H: 3·65 N: 13·65; Found C: 40·61H: 3·52N: 13·30.

$[Mo_2O_3(L_3)_2Cl_2]$ **(3)**: Yield 0·166 g (35%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_8O_5H_{24}$ $Mo_2Cl_2Br_2$: C: 32·84H: 2·52N: 11·78; Found C: 32·45H: 2·38N: 11·50.

$[Mo_2O_3(L_4)_2Cl_2]$ **(4)**: Yield 0·129 g (35%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_8O_5H_{24}$ Mo_2Cl_4: C: 36·23H: 2·78N: 13·00; Found C: 35·91H: 2·65N: 12·70.

$[Mo_2O_3(L_5)_2Cl_2]$ **(5)**: Yield 0·132 g (30%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_{10}O_9H_{24}$ Mo_2Cl_2: C: 35·37H: 2·72N: 15·87; Found C: 35·33H: 2·61N: 15·66.

$[Mo_2O_3(L_1)_2Br_2]$ **(6)**: Yield 0·132 g (30%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_8O_5H_{26}$ Mo_2Br_2: C: 35·45H: 3·40N: 12·72; Found C: 35·51H: 3·27N: 12·50.

$[Mo_2O_3(L_2)_2Br_2]$ **(7)**: Yield 0·159 g (35%). Elemental analysis: Anal. Calc. (%) for $C_{28}N_8O_5H_{30}$ Mo_2Br_2: C: 37·00H: 3·30N: 12·33; Found C: 36·90H: 3·22N: 12·30.

$[Mo_2O_3(L_3)_2Br_2]$ **(8)**: Yield 0·182 g (35%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_8O_5H_{24}$ Mo_2Br_4: C: 30·05H: 2·31N: 10·78; Found C: 29·61H: 2·29N: 10·30.

$[Mo_2O_3(L_4)_2Br_2]$ **(9)**: Yield 0·166 g (35%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_8O_5H_{24}$ $Mo_2Cl_2Br_2$: C: 32·80H: 2·78N: 11·77; Found C: 32·51H: 2·61N: 11·41.

$[Mo_2O_3(L_5)_2Br_2]$ **(10)**: Yield 0·145 g (30%). Elemental analysis: Anal. Calc. (%) for $C_{26}N_{10}O_9H_{24}$ Mo_2Br_2: C: 32·16H: 2·47N: 14·43; Found C: 32·04H: 2·30N: 14·52.

2.2 *Physical measurements*

Elemental analyses (C, H and N), IR spectra (KBr discs, 4000–200 cm^{-1}), of the ligands and the complexes and UV-Vis spectra (DMF) of the complexes were done with a Perkin-Elmer Model 240°C CHN analyzer, a Jasco FTIR model 420 spectrophotometer and a Hitachi U-3501 spectrophotometer, respectively. Cyclic voltammetry (CV) experiments were carried out using Sycopel Model 77 AEW2 1820F/S instrument. The measurements were performed at 300 K in a DMF solution containing 0·2 M TEAP and $10^{-3}–10^{-4}$ M Mo(VI) complexes **1–5** and **11** deoxygenated by bubbling with nitrogen. A platinum wire, a platinum coil and a SCE were used as a working, a counter and reference electrodes, respectively. Magnetic susceptibility measurements for complex **1** was carried out on polycrystalline samples, at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the range 2–300 K under magnetic field of approximately 500 G (2–30 K) and 1000 G (35–300 K). Diamagnetic corrections were estimated from Pascal tables. The EPR spectra on **1–10** have been recorded on X-band Bruker Spectrometer (ESR 300E), working with an oxford helium liquid cryostat for variable temperature.

2.3 *Crystallographic measurement*

The crystal of complex **1** was measured on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation ($\lambda = 0·71073$ Å) and a graphite monochromator at –80°C. The unit cell dimensions were obtained from a least squares fit to the setting angles of 25, accurately determined reflections. The data were collected using a $\omega - 2\theta$ scan technique with a 2θ range of 4–55° and were corrected by an empirical method for absorption and Lorentz and polarization effect. Calculations were carried out using a XCAD-49 (data reduction), SHELXTL (absorption corrections, structure solution refinements and molecular graphics). The structures were solved using direct methods and refined on F^2 using full matrix least squares techniques with anisotropic displacement factors for all non-hydrogen atoms. Positions of the Hydrogen atom were calculated from the geometry of the molecular skeleton and their thermal displacement parameters were refined isotropically on a group-wise basis. Crystal parameters of complex **1** are provided in table 1. Selected bond distances and bond angles are provided in table 2.

3. **Results and discussion**

3.1 *Synthesis and spectroscopic analysis*

The ligands HL_n ($n = 1–5$) have been used to prepare the μ-oxo molybdenum(V) complexes **1–5** by reacting them with the Mo(V) precursor $(NH_4)_2MoOCl_5$. Similarly, using $(NH_4)_2MoOBr_5$ with the same series of ligands complexes **6–10** were prepared (scheme 1). All the ligands despite of their varying e donating ability, are found to be good donors towards both Mo(V) species. The reaction between the metal precursors and ligand solutions take place with immediate colour change at room temperature and precipitation of the respective complexes within an hour.

The complexes are spin paired oxo-bridged binuclear units. The binuclear nature of the complexes is a result of an inherent property of the Mo(V) that it is inclined to produce oxo-bridged complexes with $Mo_2O_3^{4+}$ or $Mo_2O_4^{2+}$ cores, often regardless of the ligands used. Mononuclear complexes of Mo(V) are comparatively less described. Changes in the reaction conditions such as carrying out the reactions at room temperature did not alter the composition of the products. Characterization of these complexes was however hampered considerably by their low solubility in common organic solvents and their low stability in oxygenated solvents as DMF and DMSO. IR spectra of the ligands (HL_n, $n = 1–5$) show broad bands at 3170–3191 cm^{-1} for H-bonded ν (O–H)

Table 1. Crystal parameters for complex **1**.

Identification code	Complex **6**
Empirical formula	$C_{26}H_{26}Cl_2Mo_2N_8O_5$
Formula weight	793·33
Temperature (K)	203(2)
Wavelength (Å)	0·71073
Crystal system	Orthorhombic
Space group	*Pnca*
Unit cell dimensions	$a = 15·3153(5)$ Å
	$\alpha = 90°$
	$b = 13·7183(6)$ Å
	$\beta = 90°$
	$c = 14·1143(5)$ Å
	$\gamma = 90°$
Volume (Å^3)	2965·41(19)
Z	8
Density (calc) (gm/cm^3)	1·777
Absorption coefficient (mm^{-1})	1584
$F(000)$	1584
Crystal size (mm^3)	$0·55 \times 0·43 \times 0·31$
Thetarange for data collection	4·77 to 30·63°
Index ranges	$-21 \le h \le 21$,
	$-19 \le k \le 15$,
	$-20 \le l \le 18$
Reflections collected	17220
Independent reflections	4195 [R(int) = 0·0481]
Completeness to theta	98·9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1·00000 and 0·70959
Refinement method	Full-matrix least-squares on $F2$
Data/restraints/parameters	4195/0/197
Goodness-of-fit on F^2	0·998
Final R indices	$R1 = 0.0404$, $wR2 = 0·0905$
[$I > 2$ sigma(I)]R indices (all data)	$R1 = 0.0904$ $wR2 = 0·1075$
Largest diff. peak and hole (eÅ^{-3})	0·708 and $-0·868$

stretch. The peaks for ν (N–H) of hydrazone are observed at 3275–3321 cm^{-1}.[16] In complexes **1–10** the ν (O–H) bands are found absent as a result of deprotonation of the ligands to form these complexes. All the ligands and the complexes contain the peaks for ν (C=N) and ν (C=C) stretch.[18] However, when these peaks from the ligands are compared to those in the complexes a slight blue shift (by a maximum of 35 cm^{-1}) may be observed. In the ligands the ν(C=N) appears at 1528–1546 cm^{-1}. In the complexes the C=N stretch values are found to appear at lower energy zones at around 1523–1539 cm^{-1}. In the oxo-bridged Mo(V) complexes **1–5** the ν(Mo=O) (terminal) is observed at 935–959 cm^{-1}.[19] Here the effects of the donating capacity of the ligands are very obvious. It is found that the lowest energy stretching band is observed in complex **2** where the ligand is HL_2, the most electron donating one. With the reduction of the electron donation capacity of the ligands this stretching frequency value gradually undergoes blue shift in **1**, **3**, **4** and finally has the highest value in **5** (same trend of values are observed for complexes **6–10**). The antisymmetric and symmetric stretching values for bridging Mo–O are found at 799–832 cm^{-1} and 757–772 cm^{-1}.[20] Here also the same correlation may be drawn. However there is not much difference in these peaks when the chloro complexes are compared to the bromo complexes of the same ligand showing that both the chloro and bromo donors are weakly bound and contributes little to the stability of the complexes.
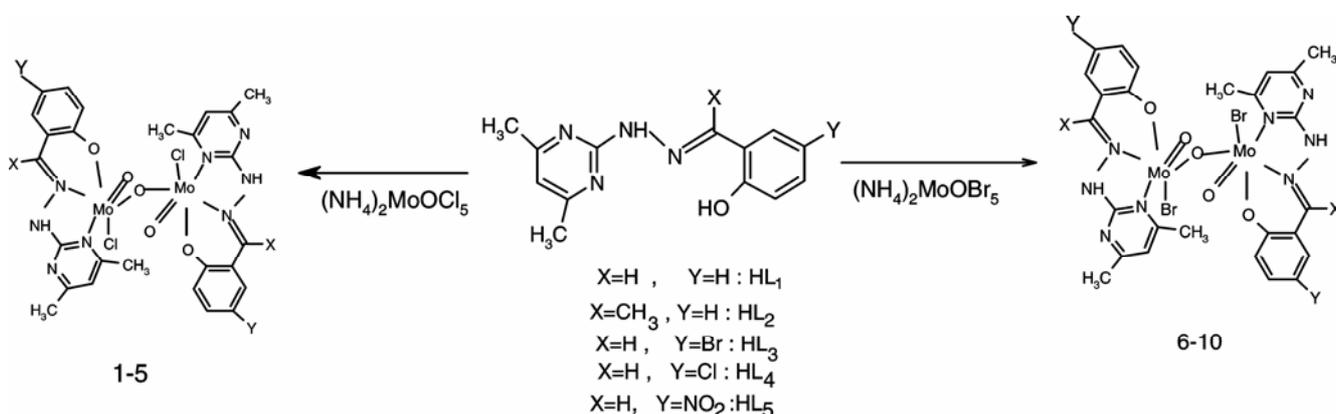
Electronic spectra of the complexes **1–10** in DMF display two strong absorption bands in the region 293–312 nm and 329–355 nm. These peaks may be assigned as charge transfer transitions of the type N($p\pi$)–Mo($d\pi$) LMCT and O($p\pi$)–Mo($d\pi$) LMCT respectively,[21] as the ligand based orbitals are either N or O donor types. The slight change in λ values within each set of peaks going from **1** to **5** (and from **6** to **10** as well) may be due to the difference in electron donating capacity of the ligands. When HL_1 is compared to HL_3 and HL_4 and HL_5, i.e. salicylaldehyde derived ligand compared to its 5-bromo-salicylaldehyde, 5-chlorosalicylaldehyde and 5-nitro-salicylaldehyde counterparts, the ligands HL_3, HL_4 and HL_5 are gradually less electron-rich due to the electron withdrawing nature of the substituents. This makes HOMO of HL_3, HL_4 and HL_5 higher in energy compared to that of HL_1. As a result, the electronic transitions in the respective complex (**3**, **4** and **5**) experience a red shift compared to those in **1**. On

Table 2.   Selected bond angles and bond distances of complex **1**.

Selected bonds		Values (Å)	Selected angles				(°)
Mo	–Cl	2·5098(10)	Cl	–Mo	–O1		89·81(8)
Mo	–O1	1·969(3)	Cl	–Mo	–O2		165·63(9)
Mo	–O2	1·8792(3)	Cl	–Mo	–O3		91·11(10)
Mo	–O3	1·676(3)	Cl	–Mo	–N1		79·16(7)
Mo	–N1	2·296(3)	Cl	–Mo	–N3		82·98(7)
Mo	–N3	2·188(3)	O1	–Mo	–O2		93·36(8)
N1	–N2	1·380(4)	O1	–Mo	–O3		101·80(11)
			O1	–Mo	–N1		80·02(10)
			O1	–Mo	–N3		151·93(10)
			O2	–Mo	–O3		101·93(13)
			O2	–Mo	–N1		87·59(12)
			O2	–Mo	–N3		87·69(8)
			O3	–Mo	–N1		170·13(12)
			O3	–Mo	–N3		105·41(11)
			N1	–Mo	–N3		72·00(9)
			Mo	–O2	–Mo_a		177·78(19)

Scheme 1.   Scheme showing method of preparation of complexes **1–10**.

the other hand, HL_2 being more e donating than HL_1, the CT bands for **2** are more blue shifted compared to **1**. Electronic spectra of all the complexes **1–10** in DMF solution shows another CT band at 518–556 nm[22] which is characteristic of binuclear μ-oxo Mo(V) complexes. None of these peaks are stable in DMF solution and disappears over a period of 24 h indicating solvolysis in DMF solvent. The diffuse reflectance spectra (DRS) of these complexes show a broad band implying several prominent transitions with maxima between 522 and 565 nm. Spectroscopic characters of individual complexes are given in table S2 in the (Supplementary Information).

All the complexes were diamagnetic at room temperature and their spin paired nature did not alter with variation of temperature either. All the com-

plexes were found to be EPR silent. Study of the electrochemical behaviour of the complexes was attempted using cyclic voltammetry but the results were unsatisfactory due to the instability of the complexes in DMF and DMSO.

3.2   *Structure of complex* **1**

The neutral μ-oxomolybdenum(V) complex **1** (figure 1) bears a distorted octahedral geometry around each Mo atom. The ligand HL_1, in its deprotonated form occupies three of the six coordination sites at the metal centre. One terminal oxo atom, one bridging oxo atom and a chloride ion complete the coordination spheres. The tridentate monoanionic donor ligand (L_1^-) binds the molybdenum(V) centre through a pyrimidine nitrogen (N3), the azomethine

nitrogen (N1) and the enolate oxygen (O1). The ligand forms a five-membered and a six-membered chelate ring at the metal centre in the equatorial XY plane.[23] One oxo group (O3) is present in the same plane *trans* to the azomathine nitrogen. The bridging oxo group (O2) is present in the axial plane with the chloride donor. The molybdenum atoms are found to be deviated from the mean equatorial plane towards the bridging oxo group by 0·119 Å at one end of the bridge and by 0·098 Å at the other end. A dihedral angle of 16·77°–17·10° between the pyrimidine and the phenyl ring in the bound ligand reveals that considerable deviation from planarity has taken place in the ligand to facilitate chelation. However, it may be noted that all the ligand atoms which form the two chelate rings maintain remarkable planarity to ensure adequate electron delocalization (maximum deviation 0·150 Å from their mean plane). This is unlike our previously reported dioxomolybdenum(VI) complex of the same ligand[16] where the phenolate oxygen was found to be deviated by (0·29 Å) from the mean plane. The Mo=O bond distances are unexceptional.[24] As expected, the axial Mo–O bond which is also bridging in nature is longer than the equatorial one by ca. 0·203 Å. The Mo–O1 bond (1·96 Å) is longer than both Mo–O2 and Mo–O3. Between the two bonds Mo–N1 and Mo–N3 the former is a little longer due to the trans effect of the oxo group.[25] The Mo–Cl bond length of 2·51 Å shows that the chloride is loosely bound.[26] The bond lengths in the coordination sphere are not appreciably different from those in the previous dioxomolybdenum(VI) complex despite of the change in Mo oxidation state. Among the angles in

the coordination sphere N1–Mo–O3 bears the highest value of 170·13°. Values of all the other angles support in favour of distorted octahedral structure. VSEPR theory can explain the order O3–Mo–O1~O3–Mo–N3 > N1–Mo–N3 ~ N3–Mo–O1 and also O3–Mo–Cl > Cl–Mo–N1. The Mo–O2–Mo bridge angle may have values ranging from 148° to 180°. The low value of this angle is often associated with the presence of Mo–Mo bonding. However, higher the value, the lower is the probability of Mo–Mo bonding. Here the bridge angle value is 177·78°, almost linear arrangement as in many other singly oxo-bridged Mo(V) complexes.[27] This rule out any Mo–Mo bonds. The distance between the two Mo atoms (3·759 Å) supports non bonded arrangement.

A two-fold intermolecular H-bonding interaction is observed in the complex involving the hydrogen bound to the azomethine nitrogen and the chloride donors, i.e. N2–H2A···Cl in the complex (figure S1). This creates an infinite one-dimensional array of H-bonded molecules organized in a zigzag fashion. Three other unconventional[28] H-bonding interactions of even lesser strength helps to build the three dimensional packing in the crystal. These are C10–H10C···O3 (intramolecular), C11---H11A···Cl and C13---H13B···O3 (both intermolecular) (see table SI supplementary information). Among these three nonconventional weak H bonding interactions the latter two are noteworthy as the distance of interaction and the angle falls within the range required for significant contribution to the 3D structure (distance between 3·0–4·0 (Å) and angle 150°–180°) (table SI in supplementary information). These two interactions create the binding force between the infinite one-dimensional H-bonded molecular strand. An interesting feature is the contribution made by one of the coordinated Cl⁻ ions which gets involved in two types of weak bond interactions. A favourable configuration of the ligands bound to the Mo centers enables a two-fold intramolecular π–π interaction between the pyrimidine and phenyl rings of the ligands with centroid to centroid distances of 3·52 Å.

4. Conclusion

Ten new Mo(V) complexes are prepared which are useful additions in the literature of binuclear oxo-bridged Mo(V) chemistry as they are based on Schiff bases derived from the biologically important heterocycle, pyrimidine. Only one of these complexes could be fully characterized as preparation of their single crystals are heavily hampered by their poor

Figure 1. Structural representation of complex **1**.

solubility and stability in common organic solvents. The complexes exhibit slight but perceivable changes in their spectroscopic characteristics depending on the variations of electron donating abilities of the used ligands.

Supplementary information

CCDC-678941 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A figure showing one-dimensional H bonding array of complex 1, table showing H-bonding parameters and spectroscopic characterization table have been presented as supplementary materials as figure S1, tables S1 and 2 (see www.ias.ac.in/chemsci).

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