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Supramolecular structures of mononuclear and dinuclear dioxomolybdenum(VI) complexes via hydrogen bonds and $\pi - \pi$ stacking, thermal studies and electrochemical measurements

ABSTRACT

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1. Introduction

The chemistry of molybdenum has become a prospective area for research. This is due to molvbdenum's ability to form compounds with most inorganic and organic ligands, in addition to forming bi- and polynuclear compounds. These compounds have the ability to form molybdenum-molybdenum bonds as well as being complexes containing bridging ligands [1–5]. Molybdenum compounds have many and varied potential applications. Recently, molybdenum complexes have been paid great interest because of the presence of molybdenum in metalloenzymes and its significant role in hydroxylase and oxotransferase enzymes [6–12].

An exceptional feature of molybdenum is that it has versatile oxidation states, from (-2) to (6), and coordination numbers ranging from 4 to 8 [13]. It is well known that catalytic reactions of molybdoenzymes involve molybdenum in its (+6) and (+4) oxidation states [14]. Therefore, molybdenum complexes are considered to be very effective catalysts for oxidation reactions [15]. Molybdenum Schiff base complexes have continued to play the role of one of the most important models of molybdoenzymes due to their preparative accessibility [16,17]. Schiff bases derived from salicylaldehyde and amino alcohols have been widely used for the preparation of oxomolybdenum complexes containing the MoO₂²⁺ core [18,19].

The field of supramolecular frameworks has developed rapidly because of its structural diversity and potential applications [20-24]. There are large numbers of 1D, 2D and 3D supramolecular frameworks that have been studied, with various types of hydrogen bonds and π - π stacking interactions [25–27]. The selection and design of suitable ligands as a building blocks are playing key roles in the construction of supramolecular frameworks. Additionally, the coordination geometry of the metal and the orientation of the binding sites are key factors in the supramolecular design. Despite the great importance of molybdenum complexes, few articles present molybdenum complexes as supramolecular structures [28-32].

Two dioxomolybdenum(VI) complexes, $[Mo_2O_4(HBAP)_2L]$ (1) and $[MoO_2(HMBI)]$ (2) (HBAP = ((E)-2-(2-

hydroxybenzylidene)amino)phenol, HMBI = ((E)-N'-(2-hydroxy-3-ethoxybenzylidene)isonicotinohydraz-

ide) and L = (4,4'-dipyridyl), have been synthesized and structurally characterized by elemental analysis,

¹H NMR spectroscopy and X-ray single crystal diffraction analysis. In complex (1), a 1D-chain is formed through $C \cdots H \cdots O$ hydrogen-bonding interactions. In complex (2), a dimer is formed through $O \cdots H \cdots N$

hydrogen-bonding interactions. This dimer is extended into a 1D chain through secondary $C \cdots H \cdots O$

In this article, we report the synthesis and crystal structure determination of supramolecular mono and dinuclear dioxomolybdenum(VI) complexes based on Schiff base ligands. The electrochemistry of the dioxomolybdenum(VI) complexes was studied as well as the thermal degradation of the complexes.

2. Experimental

2.1. Materials

MoO₂(acac)₂, salicaldehyde, 4,4'-dipyridyl, O-ominophenol, O-vanillin and isonicotinic acid hydrazide were purchased from Aldrich. Reagent grade solvents were dried and distilled prior to use. All the starting chemicals were analytically pure and were used





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(E)-2-((2-hydroxybenzylidene) amino) phenol (HBAP)

(E)-N'-(2-hydroxy-3-methoxybenzylidene) isonicotinohydrazide (HMBI)

Fig. 1. Structure of the ligands.

Table 1

Crystal data and structural refinements for complexes (1) and (2).

Compound	Complex (1)	Complex (2)
Empirical formula	C ₃₆ H ₂₆ Mo ₂ N ₄ O ₈	$C_{15}H_{15}MoN_{3}O_{6}$
Formula weight	834.49	429.24
T (K)	100.3	100(1)
λ (Å)	0.71073	0.7107
Crystal system	monoclinic	monoclinic
Space group	P12 ₁ /c	$P12_1/n$
Unit cell dimensions		
a (Å)	10.8386(13)	6.75499(13).
b (Å)	6.5964(6)	30.2838(5)
<i>c</i> (Å)	22.722(2)	7.89920(13)
α (°)	90	90
β (°)	91.349(9)	93.3546(16)
γ (°)	90	90
V (Å ³)	1624.1(3)	1613.14(5)
Ζ	2	4
D_{calc} (Mg/m ³)	1.706	1.767
Absorption coefficient (mm ⁻¹)	0.834	0.852
F(000)	836	864
Crystal size (mm)	$0.2361 \times 0.0385 \times 0.0263$	$0.3955 \times 0.2024 \times 0.0552$
Theta range for data, collection (°)	3.57-32.51	3.63-32.05
Index ranges	$-16 \leqslant h \leqslant 15, -9 \leqslant k \leqslant 9, -34 \leqslant l \leqslant 33$	$-10 \leqslant h \leqslant 9$, $-44 \leqslant k \leqslant 44$, $-11 \leqslant l \leqslant 11$
Reflections collected	13610	20275
Independent reflections	5347 $[R_{int} = 0.0913]$	5279 $[R_{int} = 0.0312]$
Completeness to theta = 30.00°	99.90%	99.20%
Absorption correction		
Maximum and minimum transmission	0.988 and 0.936	0.956 and 0.794
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5347/36/245	5279/3/231
Goodness-of-fit (GOF) on F^2	1.049	1.11
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0668, wR_2 = 0.0853$	$R_1 = 0.0277, wR_2 = 0.0573$
R indices (all data)	$R_1 = 0.1296, wR_2 = 0.1033$	$R_1 = 0.0345$, $wR_2 = 0.0601$
Largest difference in peak and hole (e $Å^{-3}$)	0.757 and –0.866	0.543 and -0.442

without further purification. The Schiff bases were synthesized using the procedure reported in the literature [33].

2.2. Physical measurements

Elemental analyses (C, H and N) were performed using Desert Analytics (Tucson, AZ). UV-Vis spectral measurements were carried out in DMSO solution at a concentration of 1.0×10^{-3} M using a Jenway 6405 spectrophotometer with a 1 cm quartz cell, in the range 200-800 nm. ¹H NMR spectra were recorded on a Varian Unity 400 MHz NMR spectrometer and referenced to the residual solvent peaks. FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 A) as the FAB gas. IR spectra $(4000-400 \text{ cm}^{-1})$ were recorded as KBr pellets on a Bruker FT-IR spectrophotometer. Electrochemistry, cyclic voltammetry and Osteryoung squarewave voltammetry were performed with an Epsilon potentiostat from Bioanalytical Systems, Inc. in one compartment, three electrode cells using a carbon working electrode, platinum wire auxiliary electrode and a Ag wire pseudo reference electrode calibrated against the ferrocene/ferrocenium couple, FeCp2/FeCp2+, as an internal standard. Measurements were made at a rate of 100 mV/ s. The supporting electrolyte was 0.1 M nBu_4NPF_6 in spectral grade DMF. Solutions were deoxygenated by bubbling with argon, and the working electrode was manually cleaned prior to analysis. Thermogravimetric analyses (TG/DTG) were carried out at 25–800 °C under a steam of nitrogen using a TGA Q500 thermal analyzer. The experimental conditions were platinum crucible, nitrogen atmosphere with a 40 ml/min flow rate and a heating rate 10 °C/min.

2.3. X-ray crystallography

An orange-brown needle $(0.026 \times 0.038 \times 0.24 \text{ mm}^3)$ of complex (1) and an orange block $(0.06 \times 0.20 \times 0.40 \text{ mm}^3)$ of complex (2) were centered on the goniometer of an Agilent Gemini E Ultra diffractometer operating with Mo K α radiation. The data collection routine, unit cell refinement and data processing were carried out with the program CrysAlisPro [34]. The Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/c$ for complex (1) and $P2_1/n$ for complex (2). The structures were solved using SHELXS-97 [35] and refined using SHELXS-97 [35]



Fig. 2. (a) Molecular diagram for complex (1) showing the atom-labelling scheme (non-hydrogen) (50% thermal ellipsoids), (b) Molecular diagram of the asymmetric unit for complex (1) showing the atom-labelling scheme, hydrogen atoms are omitted for clarity (50% thermal ellipsoids).

Table 2Selected bond lengths (Å) and angles (°) for complex (1).

Bond lengths		Bond angles	
Mo(1)-O(1)	1.707(3)	O(1)-Mo(1)-O(3)	96.46(14)
Mo(1)-O(2)	1.705(3)	O(1)-Mo(1)-O(4)	100.57(14)
Mo(1)-O(3)	1.956(3)	O(1)-Mo(1)-N(1A)	161.82(15)
Mo(1)-O(4)	1.930(3)	O(1)-Mo(1)-N(1B)	161.9(6)
Mo(1)-N(1A)	2.275(4)	O(1)-Mo(1)-N(2)	84.65(13)
Mo(1)-N(1B)	2.27(3)	O(2)-Mo(1)-O(1)	106.77(14)
Mo(1)-N(2)	2.424(3)	O(2)-Mo(1)-O(3)	99.82(13)
O(3) - C(1)	1.352(5)	O(2)-Mo(1)-O(4)	98.95(13)
O(4)-C(13)	1.344(5)	O(2)-Mo(1)-N(1A)	90.13(14)
N(1A) - C(2)	1.442(6)	O(2)-Mo(1)-N(1B)	86.9(6)
N(1A)-C(7A)	1.290(8)	O(2)-Mo(1)-N(2)	168.57(13)
N(1B)-C(7B)	1.30(4)	O(3)-Mo(1)-N(1A)	73.55(16)
N(1B)-C(8)	1.70(3)	O(3)-Mo(1)-N(1B)	92.7(7)
N(2)-C(14)	1.331(5)	O(3)-Mo(1)-N(2)	78.13(12)
N(2)-C(18)	1.327(5)	O(4)-Mo(1)-O(3)	149.74(13)
		O(4)-Mo(1)-N(1A)	82.91(16)
		O(4)-Mo(1)-N(1B)	64.9(7)
		O(4)-Mo(1)-N(2)	78.77(12)
		N(1A)-Mo(1)-N(2)	78.49(13)
		N(1B)-Mo(1)-N(2)	82.0(6)
		C(1)-O(3)-Mo(1)	123.8(3)

via OLEX2 [36]. A 2-position disorder model was used for the Schiffbase ligand, with relative occupancies that refined to 0.844(8) and 0.156(8). The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. The anisotropic displacement parameters of the atoms in the disordered region of the Schiff base were restrained with the SIMU command. The hydrogen atom position of the CH₃OH alcohol group was located from the residual electron density map and the position refined with distance restraints.

2.4. Synthesis of the Schiff base ligands

O-aminophenol (1.09 g, 10 mmol) in methanol (30 ml) was added to salicylaldehyde (1.221 g, 10 mmol) in methanol (10 ml). The resulted deep orange solution was heated at 80 $^\circ$ C for 2 h,

concentrated and cooled to room temperature, then the orange precipitate that formed was filtered, and washed with 2 ml methanol and 5 ml diethyl ether, dried in vacuo to obtain **HBAP**, Fig. 1 (yield 87%, 1.86 g). *Anal*. Calc. for C₁₃H₁₁NO₂: C, 73.33; H, 5.20; N, 6.57. Found: C, 73.64; H, 5.17; N, 6.81%. ¹H NMR (400 MHz, DMSO-d6) δ : 8.53 (s, 1H, imine), 7.56–6.71 (m, 2 × 4H, Ph), 4.71 (s, 2 × 1H, Ph–OH). IR (KBr, in cm⁻¹): v(OH) 3324, v(C–N) 1629. The mass spectrum gave a molecular peak at 213 *m*/*z*.

HMBI was synthesized and purified by a similar method, using isonicotinic acid hydrazide instead of *O*-aminophenol, and *O*-vanillin instead of salicylaldehyde, Fig. 1 (yield 70%, 1.9 g). *Anal.* Calc. for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 62.11; H, 4.54; N, 15.87%. ¹H NMR (400 MHz, DMSO-d6) δ : 12.1 (s, 1H, imine), 8.82–7.80 (m, 4H, pyridine ring), 7.56–6.79 (m, 3H, Ph), 7.45 (s, 1H, benzylidene), 3.8 (s, 3H, OCH₃). IR (KBr, in cm⁻¹): v(OH) 3332, v(NH) 3255, v(C–N) 1639, v(C=O) 1678. The mass spectrum gave a molecular peak at 271 *m*/*z*.

2.5. Synthesis of the dioxomolybdenum(VI) complexes

2.5.1. Complex (1)

A solution of the Schiff base ligand **HBAP** (0.1 mmol, 0.213 g) in 15 ml methanol was added to a stirred solution of $MoO_2(acac)_2$ (0.1 mmol, 0.331 g) in 5 ml methanol and 2 ml dichloromethane. The reaction mixture was heated under reflux for 1 h with continuous stirring, while the color changed from yellow to orange, the linker (4,4'-dipyridyl (0.05 mmol, 0.08 g) in 5 ml methanol was added dropwise over a period of 10 min. The resulting reaction solution was heated under reflux with stirring for an addition 1 h. The solvent was removed in vacuo and the residue was dissolved in 10 ml dichloromethane. A very fine colorless precipitate was filtered over celite. The orange filtrate was recrystallized from dichloromethane and methanol. Upon standing at -5 °C and after 4 days, orange solid crystals appeared (yield 43%, 0.360 g). *Anal.* Calc. for $C_{36}H_{26}Mo_2N_4O_8$ (834.49): C, 51.81; H, 3.14; N, 6.71. Found: C, 52.23; H, 3.57; N, 6.54%.



Fig. 3. (a) Diagram for complex (1) showing the hydrogen-bonding between O2 and H7A (the hydrogen bond is represented as a black dashed line), non-bonding hydrogen atoms are omitted for clarity, (b) Packing diagram for complex (1) around the b axis, hydrogen atoms are omitted for clarity.



Fig. 4. Molecular diagram for complex (**2**) showing the atom-labelling scheme (50% thermal ellipsoids), hydrogen atoms are omitted for clarity.

2.5.2. Complex (2)

A solution of the Schiff base ligand **HMBI** (0.1 mmol, 0. 271 g) in 15 ml methanol was added to a stirred solution of $MOO_2(acac)_2$

(0.1 mmol, 0. 331 g) in 5 ml methanol and 2 ml dichloromethane. The reaction mixture was heated under reflux for 2 h with continuous stirring, while the color changed from yellow to orange, then the solvent was removed in vacuo. The residue was dissolved in 10 ml dichloromethane and 2 ml MeOH and was left for 2 days at -5 °C. Orange solid crystals suitable for X-ray single crystal analysis appeared (yield 45%, 0.196 g). *Anal.* Calc. for C₁₅H₁₅MoN₃O₆ (429.24): C, 41.97; H, 3.52; N, 9.79. Found: C, 42.13; H, 3.66; N, 9.58%.

3. Results and discussion

Two dioxomolybdenum(VI) compounds were synthesized from the reaction of the tridentate ligands **HBAP** and **HMBI** with bis-(acetylacetonate)dioxomolybdenum(VI), in the presence of 4,4'dipyridyl as a linker in the case of complex (1). In complex (2), no linker was used because the terminal nitrogen of the pyridine ring was expected to act as a linker. X-ray single crystal diffraction analysis reveals that the terminal nitrogen atom did not coordinate to the metal ion as expected, but it was involved in a hydrogen

Table 3 Selected bond lengths (Å) and angles (°) for complex (2).

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bond lengths		Bond angles	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mo(1)-O(1)	1.7127(12)	O(1)-Mo(1)-O(3)	97.41(5)
$\begin{array}{c ccccc} Mo(1)-O(3) & 2.0237(12) & O(1)-Mo(1)-O(6) & 83.75(5) \\ Mo(1)-O(4) & 1.9375(12) & O(1)-Mo(1)-N(1) & 157.43(5) \\ Mo(1)-O(6) & 2.3470(12) & O(2)-Mo(1)-O(1) & 105.34(6) \\ Mo(1)-N(1) & 2.2315(14) & O(2)-Mo(1)-O(3) & 96.41(6) \\ O(3)-C(1) & 1.330(2) & O(2)-Mo(1)-O(4) & 98.68(6) \\ O(4)-C(8) & 1.3479(19) & O(2)-Mo(1)-O(6) & 170.72(5) \\ O(5)-C(7) & 1.363(2) & O(2)-Mo(1)-N(1) & 95.85(5) \\ O(5)-C(14) & 1.437(2) & O(3)-Mo(1)-O(6) & 80.32(5) \\ O(6)-C(15) & 1.437(2) & O(3)-Mo(1)-O(6) & 80.32(5) \\ N(1)-N(2) & 1.298(19) & O(4)-Mo(1)-O(3) & 151.09(5) \\ N(1)-C(2) & 1.296(2) & O(4)-Mo(1)-O(6) & 80.86(5) \\ \end{array}$	Mo(1)-O(2)	1.7045(12)	O(1)-Mo(1)-O(4)	102.13(5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Mo(1)-O(3)	2.0237(12)	O(1)-Mo(1)-O(6)	83.75(5)
$\begin{array}{c ccccc} Mo(1)-O(6) & 2.3470(12) & O(2)-Mo(1)-O(1) & 105.34(6) \\ Mo(1)-N(1) & 2.2315(14) & O(2)-Mo(1)-O(3) & 96.41(6) \\ O(3)-C(1) & 1.330(2) & O(2)-Mo(1)-O(4) & 98.68(6) \\ O(4)-C(8) & 1.3479(19) & O(2)-Mo(1)-O(6) & 170.72(5) \\ O(5)-C(7) & 1.363(2) & O(2)-Mo(1)-N(1) & 95.85(5) \\ O(5)-C(14) & 1.436(2) & O(3)-Mo(1)-O(6) & 80.32(5) \\ O(6)-C(15) & 1.437(2) & O(3)-Mo(1)-N(1) & 72.15(5) \\ N(1)-N(2) & 1.3983(19) & O(4)-Mo(1)-O(3) & 151.09(5) \\ N(1)-C(2) & 1.296(2) & O(4)-Mo(1)-O(6) & 80.86(5) \\ \end{array}$	Mo(1)-O(4)	1.9375(12)	O(1)-Mo(1)-N(1)	157.43(5)
$\begin{array}{c ccccc} Mo(1)-N(1) & 2.2315(14) & O(2)-Mo(1)-O(3) & 96.41(6) \\ O(3)-C(1) & 1.330(2) & O(2)-Mo(1)-O(4) & 98.68(6) \\ O(4)-C(8) & 1.3479(19) & O(2)-Mo(1)-O(6) & 170.72(5) \\ O(5)-C(7) & 1.363(2) & O(2)-Mo(1)-N(1) & 95.85(5) \\ O(5)-C(14) & 1.436(2) & O(3)-Mo(1)-O(6) & 80.32(5) \\ O(6)-C(15) & 1.437(2) & O(3)-Mo(1)-N(1) & 72.15(5) \\ N(1)-N(2) & 1.3983(19) & O(4)-Mo(1)-O(3) & 151.09(5) \\ N(1)-C(2) & 1.296(2) & O(4)-Mo(1)-O(6) & 80.86(5) \\ \end{array}$	Mo(1)-O(6)	2.3470(12)	O(2)-Mo(1)-O(1)	105.34(6)
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$\begin{array}{cccc} O(5)-C(14) & 1.436(2) & O(3)-Mo(1)-O(6) & 80.32(5) \\ O(6)-C(15) & 1.437(2) & O(3)-Mo(1)-N(1) & 72.15(5) \\ N(1)-N(2) & 1.3983(19) & O(4)-Mo(1)-O(3) & 151.09(5) \\ N(1)-C(2) & 1.296(2) & O(4)-Mo(1)-O(6) & 80.86(5) \\ \end{array}$	O(5) - C(7)	1.363(2)	O(2)-Mo(1)-N(1)	95.85(5)
O(6)-C(15) 1.437(2) O(3)-Mo(1)-N(1) 72.15(5) N(1)-N(2) 1.3983(19) O(4)-Mo(1)-O(3) 151.09(5) N(1)-C(2) 1.296(2) O(4)-Mo(1)-O(6) 80.86(5)	O(5)-C(14)	1.436(2)	O(3)-Mo(1)-O(6)	80.32(5)
N(1)-N(2)1.3983(19)O(4)-Mo(1)-O(3)151.09(5)N(1)-C(2)1.296(2)O(4)-Mo(1)-O(6)80.86(5)	O(6) - C(15)	1.437(2)	O(3)-Mo(1)-N(1)	72.15(5)
N(1)-C(2) 1.296(2) O(4)-Mo(1)-O(6) 80.86(5)	N(1) - N(2)	1.3983(19)	O(4)-Mo(1)-O(3)	151.09(5)
	N(1)-C(2)	1.296(2)	O(4)-Mo(1)-O(6)	80.86(5)
N(2)-C(1) 1.298(2) O(4)-Mo(1)-N(1) 81.87(5)	N(2)-C(1)	1.298(2)	O(4)-Mo(1)-N(1)	81.87(5)
N(3)-C(11) 1.344(2) N(1)-Mo(1)-O(6) 74.89(5)	N(3)-C(11)	1.344(2)	N(1)-Mo(1)-O(6)	74.89(5)
N(3)-C(12) 1.345(2) C(1)-O(3)-Mo(1) 118.46(10)	N(3)-C(12)	1.345(2)	C(1)-O(3)-Mo(1)	118.46(10)
C(8)-O(4)-Mo(1) 136.03(11)			C(8) - O(4) - Mo(1)	136.03(11)
C(7)-O(5)-C(14) 116.56(14)			C(7)-O(5)-C(14)	116.56(14)
C(15)–O(6)-Mo(1) 122.52(11)			C(15) - O(6) - Mo(1)	122.52(11)
N(2)–N(1)–Mo(1) 115.78(10)			N(2)-N(1)-Mo(1)	115.78(10)
C(2)–N(1)–Mo(1) 129.10(12)			C(2)-N(1)-Mo(1)	129.10(12)

bonding interaction instead. The complexes were isolated as orange crystals. They are insoluble in weak polar solvents, only sparingly soluble in strong polar solvents (acetonitrile, CH_2Cl_2)

3.1. The structure of complex (1)

Complex (1) crystallized in the monoclinic space group $P2_1/c$, Table 1. The molecular structure is shown in Fig. 2a, with relevant bond distances and angles collected in Table 2. The coordination geometry around the Mo(VI) centre is distorted octahedral. The asymmetric unit of the compound consists of a [MoO₂(HBAP)] moiety and half of a 4,4'-dipyridyl molecule, Fig. 2b. The Schiff base ligand is bonded to the $Mo(VI)O_2^{2+}$ ion in the *xy*-plane through two phenoxide oxygen donor atoms, an imine nitrogen atom and a nitrogen atom of 4,4'-bipyridine. Two[MoO₂(HBAP)] moieties are linked together via the 4,4'-dipyridyl ligand to form a dinuclear dioxomolybdenum complex. The [MoO₂(HBAP)] moiety occupies the equatorial plane. The terminal nitrogen of 4,4'-dipyridyl and the second oxo ligand (O) occupy the axial positions. The ligand coordinates to the Mo ion, forming five and six member chelate rings with O(3)-Mo(1)-N(1A) and O(4)-Mo(1)-N(1A) bite angles of 73.55(16) and 82.91(16)°, respectively. The non-bonding interatomic Mo...Mo separation within the dimeric cation is 11.96 Å. The Mo-O, Mo-N and Mo=O bonds are within the normal ranges and are comparable to those observed in similar dioxomolybdenum(VI) complexes [37,38].



Fig. 5. (a) Molecular diagram illustrating the formation of the dimer as result of hydrogen bonding between H6 and N3, (b) Diagram illustrating the formation of the infinite one dimensional hydrogen bonded chain in complex (**2**). Hydrogen bonding between two molecules to form a dimer is represented by a dashed blue line (N3 \cdots H6), the extended hydrogen bond is represented by a dashed black line (H2 \cdots O2), non-bonding hydrogen atoms are omitted for clarity.



Fig. 6. (a) Crystal packing of complex (2) around the *a* axis. (b) Structure diagram of complex (2) showing the intermolecular π - π stacking interactions between two pyridine rings, hydrogen atoms are omitted for clarity.



Fig. 7. TGA curves of the Mo complexes (1) and (2).

A hydrogen bond was observed in the packing structure, Fig. 3a, between the oxo ligand of molybdenum (O2) and H7A (a hydrogen atom of a methylene group) with bond lengths O2…H7A 2.35 Å, O2…C7A 3.14 Å and angle O2…H7A…C7A 140.6°, forming a 1D chain (ladder structure), Fig. 3b. The hydrogen bond distance and angle values are in good agreement with previously reported values [5].

3.2. The structure of complex (2)

The coordination geometry around the Mo ion in the structure of complex (**2**) can be described as slightly distorted octahedral. The molecular structure of complex (**2**) is shown in Fig. 4. The Schiff base ligand is bonded to the $Mo(VI)O_2^{2+}$ ion in the *xy*-plane through one phenoxide oxygen donor atom, the ketone oxygen of

the isonicotinic moiety and an imine nitrogen atom, with one methanol molecule completing the distorted octahedral geometry. The methanol ligand and the second oxo ligand occupy the axial positions. The complex crystallizes in the spacegroup $P12_1/n1$, Table 1. Selected bond lengths and angles are given in Table 3. The Mo ion forms five and six member chelate rings with bite angles of 72.15(5) and $81.87(5)^{\circ}$, respectively. The ligand is coordinated in the enol form, which is evident from the O(3)–C(1) and N(2)–C(1) bond lengths, with values of 1.330(2) and 1.298(2) Å, respectively. In the crystal packing structure of complex (2) it is obvious that adjacent molecules are linked through O···H bonds to form a dimer. The hydrogen bond exists between the hydroxyl group of a coordinated methanol molecule and the nitrogen atom of a pyridine ring to form an intermolecular O6···H6···N3 hydrogen bonding interaction, as shown in Fig. 5a, with bond lengths



Fig. 8. Electrochemical measurements of the Mo complexes (1) and (2).

H6…N3 1.84 Å, N3…O6 2.701 Å and angle N3…H6…O6 165°. This dimer is extended into a 1D chain through hydrogen bonding, Fig. 5b, between the oxo ligand of molybdenum (O2) and a hydrogen atom of a methylene group, O2…H2, with bond lengths O2…H2 2.303 Å, O2…C2 3.20 Å and angle O2…H2…C2 167°. In addition to the hydrogen bond, the crystal packing structure of complex (**2**), Fig. 6a, shows further stabilisation via π – π stacking interactions, centroid–centroid distance 3.52 Å, face-to-face, with a dihedral angle of 0°, Fig. 6b, and this value is similar to the values reported for other π – π interactions [21,39].

3.3. Thermal studies

The thermal behaviors of the complexes have been studied. TGA experiments were performed under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ in the temperature range 25–800 °C. The thermal curves are exhibited in Fig. 7. The TGA curve of complex (1) reveals that the complex is stable up to 252 °C. Decomposition of the organic part is within the range 252–370 °C. The final product, consisting of two Mo atoms, was formed above 400 °C.

Complex (2) is thermal stable up to 306 °C. The weight loss in the first stage is due to the release of the methanol molecule, in the range 120–170 °C. Decomposition of the organic part is within the range 306–700 °C. The final product was formed above 700 °C, consisting of MoO_2 and one carbon residue, with an estimated mass loss of 33.34% (calculated mass loss 33.07%). As expected, the complexes have high thermal stability due to the formation of the hydrogen bonds.

3.4. Electrochemical measurements

The electrochemical behavior of the two dioxomolybdnum(IV) complexes has also been studied. The reduction process has been observed in DMF in the range +1.0 to -2.5 V. The electron transfer behavior of the two complexes shows two irreversible reduction processes (-1 to -2 V), which may be attributed to the elimination of oxo ligands as OH⁻ or as H₂O in the case of complex (**1**), and the elimination of an oxo ligand and the methanol ligand in the case of complex (**2**), which depends on the existence of protons. On the other hand, no oxidation peak was observed. For complex (**1**) the reduction peaks are at -1.15 and -1.86 V, whilst for complex (**2**) the reduction peaks are at -1.04 and -1.56 V, Fig. 8.

4. Conclusions

Supramolecular mononuclear and dinuclear dioxomolybdenum(VI) complexes have been synthesized and characterized. A hydrogen bond was observed in the packing structure of complex (1) between an oxo ligand of molybdenum (O2) and H7A (a hydrogen atom of a methylene group) to form a 1D chain. It is obvious that complex (2) forms a dimer via hydrogen bonding, and this dimer is extended into a 1D chain via a second hydrogen bond and π - π stacking interactions. The presence of π - π stacking interactions in complex (2) is due to the existence of an electron-withdrawing nitrogen atom, which reduces the π -electron density in the ring and consequently the π -electron repulsion. These complexes show thermal stability up to 252 and 306 °C for complexes (1) and (2), respectively. The electrochemical measurements of the two complexes show two irreversible reduction processes (-1 to -2 V) and no oxidation peaks were observed.

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Appendix A. Supplementary data

CCDC cs1753 and cs1943 contains the supplementary crystallographic data for complex (1) and complex (2). 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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