Two New Hydrogen-bonded Supramolecular Dioxo-molybdenum(VI) Complexes Based on Acetyl-Hydrazone Ligands: Synthesis, Crystal Structure and DFT Studies

Monami Maiti Conceptualization; Methodology; Writing- Original draft preparation Santarupa Thakurta Conceptualization; Writing- Reviewing and Editing, Guillaume Pilet Software; Data Curation, Antonio Bauzá, Antonio Frontera Software; Formal analysis; Writing- Reviewing and Editing

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- Two new Mo(VI) complexes based on acetyl-hydrazone ligands have been synthesized.
- Molecular structures of the complexes have been conclusively accomplished by single crystal X-ray diffraction.
- H-bonding and $\pi \pi$ interactions play an important role in the packing of the complexes in their solid state.
- The relative stability of the supramolecular networks is rationalized by computational studies at the BP86-D3/def2-TZVP level of theory.

Journal Prevention

Two New Hydrogen-bonded Supramolecular Dioxo-molybdenum(VI) Complexes Based on Acetyl-Hydrazone Ligands: Synthesis, Crystal Structure and DFT Studies

Monami Maiti^{*a}, Santarupa Thakurta^b, Guillaume Pilet^c, Antonio Bauzá^d, Antonio Frontera^d

^aDepartment of Chemistry, Narasinha Dutt College, Howrah 711101, West Bengal, India.

^bDepartment of Chemistry, Prabhu Jagatbandhu College, Howrah 711302, West Bengal, India.

^cGroupe de Cristallographie et Ingénierie Moléculaire, Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS-Université Claude Bernard Lyon 1, Bât. Chevreul, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

^dDepartament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Balears), Spain.

*Corresponding author: Tel.: +91 9433968520 (M. Maiti)

Email address: monami.maiti@gmail.com (M. Maiti)

Abstract

Two new *cis*-dioxomolybden(m(VI) complexes [MoO₂L¹(H₂O)] (1) and [MoO₂L²(H₂O)] (2) have been synthesized using two different tridentate hydrazone Schiff base ligands, L¹H₂ [(*E*)-N-(2-hydroxybenzylidene)acetohydrazide] and L²H₂ [(*E*)-N-(2-hydroxy-3-methoxybenzylidene)acetohydrazide], respectively. The ligands and their corresponding Mo complexes are thoroughly characterized by different physicochemical techniques. Molecular structures of the complexes have been conclusively accomplished by single crystal X-ray diffraction. All the experimental findings reveal that both complexes have a distorted octahedral geometry around the Mo(VI) centre. The tridentate hydrazones coordinate to the metal centres in their enolic form in both **1** and **2**. Hydrogen bonding and π - π interactions play an important role in the packing of the complexes in their solid state. Computational studies are also performed using DFT calculations at BP86-D3/def2-TZVP level of theory to understand the relative stability of the supramolecular networks.

Key words: Molybdenum(VI) complexes; Hydrazone ligand; Schiff base; X-ray crystal Structure; Non-covalent interactions; Density functional calculations.

1. Introduction

Supramolecular chemistry deals with weak and reversible non-covalent interactions between molecules. These forces include hydrogen bonding, metal coordination, hydro-phobic forces, van der Waals forces, π - π interactions, CH- π interactions, electrostatic effects, and so on. The self-assembly of multimetallic complexes held together by intermolecular forces (hydrogen bonds, van der Waals forces etc.) is greatly dependent on the metal ions [1]. Metal ions can read the information coded in the organic ligands according to their coordination algorithm [2] and thereby give rise to metal-organic ligand complex species that are simultaneously assembled via complementary inter-ligand hydrogen bonding forming supramolecular multimetallic assemblies.

Hydrazone ligands are a special branch of Schiff bases which can accommodate with different coordination modes and oxidation states according to the demand of variable geometries and valences of metal ions in coordination complexes. Moreover, they form interesting hydrogen bonded self-assembly in metal-free state as well as in complexes, mainly due to the presence of the N-H functionality adjacent to the azomethine (C=N) chromophore [3]. Moreover, the electron withdrawing N-H group makes imidic C=N bond highly acidic, hence apart from hydrogen bonding the imidic C=N bond of the metalcoordinated Schiff base ligand can also interact with electron rich atoms and develop distinct supramolecular interaction. Transition metal complexes derived from hydrazone Schiff bases can serve as potential building blocks either as metalloligands (linkers) or as nodes (connectors) in the crystal engineering of polymeric frameworks [4-6] and are attracting the attention of the researchers due to several potential applications in potential biological, catalytic, and industrial field [7,8]. Many recent reports show that they are good candidates for the development of new drugs as well as their usage in other biochemical processes like enzyme inhibition, or the simulation of antimicrobial, anti-cancer, anti-malarial activities [9,10].

In this respect, molybdenum-Schiff base complexes have a unique place in the development of coordination chemistry due to their potential to construct varieties of supramolecular architectures [11,12]. Moreover, due to its various stable and accessible oxidation states and versatile coordination chemistry [13] molybdenum plays significant role in industrial [14] and biological reactions [15]. In spite of the important role of molybdenum in biological processes, its high potential as catalyst has made it even more attractive. Oxo–peroxo and dioxo complexes of Mo(VI) with polydentate nitrogen, sulphur and oxygen ligands are

considered valuable models for the active site of several molybdenum enzymes [16-18]. Mo(VI) is stabilized through formation of MoO_2^{2+} [19]. An important characteristic of coordination compounds containing MoO_2^{2+} is their ability to participate in reversible oxo-transfer reactions in aqueous aerobic media for nitrogenase, aldehyde oxidase, xanthine dehydrogenase, nitrate reductase, etc. [20-25]. This property has made them popular as oxidase or reductase catalyst in industrial and biochemical process. Oxygen transfer reactions are catalysed by Mo(VI)-cofactor-containing enzymes in many organisms and occur in DMSO reductase, sulfite oxidase, nitrate reductase, and aldehyde oxidoreductase reactions [26-28]. Synthesis and characterization of molybdenum(VI) compounds are important because they are relevant in industrial and biological research.

Herein we report the syntheses, spectral and structural characterizations of two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(H_2O)]$ (1) and $[MoO_2L^2(H_2O)]$ (2) derived from hydrazone ligands, L^1H_2 : two different tridentate Schiff base [(*E*)-N-(2- L^2H_2 : hydroxybenzylidene)acetohydrazide] and [(E)-N-(2-hydroxy-3methoxybenzylidene)acetohydrazide], respectively (Scheme 1). Structural characterization of each complex reveals that the tridentate ligand binds the central metal atom in the respective enolic form and molybdenum atom displays distorted octahedral geometry. Both the complexes exhibit supramolecular architectures through hydrogen bonding and π - π interactions in their solid state. The binding energies through supramolecular forces and the individual contributions of each kind of hydrogen-bonding (N-H···O, O-H···O, and C-H···O) and $\pi - \pi$ interactions to the binding energies have been quantitatively estimated by DFT calculations at the BP86-D3/def2-TZVPD level of theory.



Scheme 1: Synthesis of hydrazone ligands.

2. Experimental

2.1. Materials and Physical measurements

All chemicals and solvents employed for the syntheses were of analytical grade and used as received without further purification. Salicylaldehyde, o-vanillin (i.e. 2-hydroxy-3-methoxybenzaldehyde) and acetic hydrazide were reagent grade and purchased from Sigma-Aldrich. Glacial acetic acid, methanol, HPLC grade acetonitrile were purchased from LOBA Chemie. MoO₂(acaca)₂ was prepared and purified according to reported method [29].

The FT-IR spectra of the compounds were recorded on a Perkin-Elmer RX I FT-IR spectrometer with KBr pellets in the range 4000–400 cm⁻¹. The electronic spectra in HPLC grade acetonitrile were recorded at 300 K on a Perkin-Elmer Lambda 40 (UV-Vis) spectrometer in a 1 cm quartz cuvette in the range 200-800 nm. C, H, and N microanalyses were carried out with a Perkin-Elmer 2400 II elemental analyzer.

2.2. Syntheses

2.2.1. Synthesis of the Hydrazone ligands $[L^{1}H_{2} \text{ and } L^{2}H_{2}]$

The ligand L^1H_2 [(*E*)-N-(2-hydroxybenzylidene)acetohydrazide] was prepared by the condensation of acetic hydrazide (0.74 g, 10 mmol) with salicylaldehyde (1.221 g, 10 mmol) in presence of a single drop of glacial acetic acid in methanol medium (100 mL). By refluxing the methanolic solution for 5 h a colourless solution was obtained. The solvent was removed under reduced pressure, and the white residue was purified by recrystallization to obtain colourless shiny crystals. Yield 1.55 g (87%). Anal. Calcd. (%) for C₉H₁₀N₂O₂ (M = 178.1 g/mol): C, 60.66; H, 5.66; N, 15.72. Found: C, 60.55; H, 5.59; N, 15.63.

The ligand L^2H_2 [*(E*)-N-(2-hydroxy-3-methoxybenzylidene)acetohydrazide] was prepared by the condensation of acetichydrazide (10 mmol, 0.74 g) with o-vanillin (10 mmol, 1.525 g) in presence of few drops glacial acetic acid in methanol medium (200 mL). On refluxing the methanolic solution for 5 h a pale-yellow colouration was observed. The colour indicated the formation of the hydrazone ligand. The solvent was removed under reduced pressure and the residue was purified by recrystallisation to give pale yellow crystals. Yield 1.85 g (89%). Anal. Calcd. (%) for C₁₀H₁₂N₂O₃ (M = 208.2 g/mol): C, 57.68; H, 5.81; N, 13.45. Found: C, 57.62; H, 5.76; N, 13.44.

2.2.2. Synthesis of the complexes

 $2.2.2.1. [M_0O_2L^1(H_2O)] \qquad (1)$

A mixture of MoO₂(acac)₂ (0.164 g, 0.5 mmol) and L^1H_2 (0.089 g, 0.5 mmol) in methanol (20mL) was refluxed for 1 hour to give a dark orange solution. After 2 days, yellow needle shaped suitable single crystals appeared on slow evaporation of solvent. The resulting product was isolated, and dried in air. Yield 0.114 g (71%). Anal. Calcd. (%) for C₉H₁₀Mo₁N₂O₅ (M: 322.13 g/mol): C, 33.56; H, 3.13; N, 8.70. Found: C, 33.49; H, 3.19; N, 8.68.

2.2.2.2. $[MoO_2L^2(H_2O)]$ (2)

Complex 2 was prepared following a similar procedure as for 1, using 0.5 mmol of L^2H_2 (0.104 g) in methanol. Yellow plate shaped single crystals suitable for X-ray diffraction were obtained after six days. Crystals were isolated by filtration and were air dried. Yield: 0.132 g (75%). Anal. Calcd. (%) for C₁₀H₁₂Mo₁N₂O₆ (M: 352.16 g/mol): C, 34.11; H, 3.43; N, 7.95. Found: C, 34.18; H, 3.47; N, 8.01.

2.3. X-ray data collection and refinement

Intensity data of both **1** and **2** were collected at 293 K using Mo-K α radiation (λ =0.71069 Å) with an Oxford Diffraction Gemini diffractometer. Data collection and reduction were performed with the CrysAlis program [30]. The structures were solved by direct methods using the program SIR97 [31] programs and refined by full-matrix least-squares methods with programs CRYSTALS [32]. All the H atoms were generated geometrically and included in the refinement in the riding model approximation, except those of the aqua ligands in **1** and **2** detected in the Fourier map and refined. Selected crystallographic data, experimental conditions, and relevant features of the structural refinements for the compounds are summarized in Table 1.

Parameters	1	2	
Empirical formula	$C_9H_{10}Mo_1N_2O_5$	$C_{10}H_{12}Mo_1N_2O_6$	
Formula weight	322.13 g/mol	352.16 g/mol	
Temperature	293 K	293 K	
Crystal system	Orthorhombic	Monoclinic	
Space group	P _{bca}	P 1 21/n 1	
a (Å)	13.6159(8)	8.9157(9)	
<i>b</i> (Å)	7.1939(5)	8.2994(8)	

Fable	1: Cr	ystal	structure	parameters	of the	complexes	1	and	2
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<i>c</i> (Å)	22.9578(16)	17.2194(18)
α (°)	90	90
β (°)	90	102.428(11)
γ (°)	90	90
$V(\text{\AA}^3)$	2248.8(2)	1244.3(2)
Ζ	8	4
Dcalc (Mg m ⁻³)	1.898	1.880
$\mu (\mathrm{mm}^{-1})$	1.175	1.079
<i>F</i> (000)	1280	704
θ range (deg)	2.9–29.2	2.7–29.2
Total data	7778	6585
Unique data	2657	2909
Obs data $[I > 2\sigma(I)]$	2026	2195
$R1[I > 2\sigma(I)]$	0.0297	0.0700
$wR2[I > 2\sigma(I)]$	0.0514	0.0731
GoF	1.0174	1.0332
R _{int}	0.028	0.055
Residuals (e.Å ⁻³)	0.34, -0.33	2.14, -2.28

2.4. Theoretical Methods

The geometries of the complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory using the crystallographic coordinates within the TURBOMOLE program [33]. We have used this methodology (X-ray coordinates) since it is convenient to evaluate the interactions of several synthons as they stand in the solid state [34-36]. This level of theory that includes the latest available dispersion correction (D3) is adequate for studying non-covalent interactions dominated by dispersion effects like π -stacking [37]. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method [38]. The "atoms-in-molecules" (AIM) analysis [39] of the electron density has been performed at the same level of theory using the AIMAII program [40].

3. Results and discussion

Most of the works on transition metal complexes derived from hydrazone Schiff bases are based on aryl-hydrazone ligands. Very few metal complexes of hydrazone-Schiff bases derived from alkyl hydrazides are reported in literature [5,6,41-43]. The synthesis and spectroscopic studies of L^2H_2 [(*E*)-N-(2-hydroxy-3-methoxybenzylidene)acetohydrazide] was first reported by Mitra *et al.* [44]. In another paper by the same group, the crystal structure and spectroscopic characterization of L^1H_2 [(*E*)-N-(2-hydroxybenzylidene)acetohydrazide] was discussed [45]. However, in both the previous reports, the ligands chelated in keto form during complex formation with copper(II) and manganese(II). But in the present case, the ligands exhibit their respective enol forms to generate the dioxo-Mo(VI) complexes. The high oxidation state of the central metal ion can be considered as the driving force for the enolisation of the ligands. To the best of our knowledge, Mo(VI) complexes of acetyl hydrazones with extensive supramolecular weak interactions has not been published so far.

3.1. Fourier transform infrared spectra

The FT-IR spectra of the complexes **1** and **2** (Figure S1 and S2: ESI) are analyzed in comparison with that of the free ligands, $L^{1}H_{2}$ and $L^{2}H_{2}$. The IR spectra of the ligands show intense band at 1625–1640 cm⁻¹ due to C=N stretching frequency, which are shifted towards lower energy by 10–30 cm⁻¹ in the complexes, indicating coordination through the azomethine nitrogen. The hydrazone ligands display the v(C=O) and the v(N–H) absorption band at 1645–1662 cm⁻¹ and 3185–3250 cm⁻¹, respectively. Both of these bands disappear on complexation, indicating the enclisation of the [–NH–C=O] moiety [46]. The new stretching frequencies appearing at 1090–1120 cm⁻¹ for both complexes are attributed to the coordinated C–O groups. Each spectra of the complexes exhibit two strong bands in the region 900–930 cm⁻¹ corresponding to the symmetric and asymmetric stretching frequencies of [O=Mo=O]. This IR data is characteristic of the *cis*-[MoO₂] fragment [47]. The broad bands centered at 3325 cm⁻¹ for **1** and 3320 cm⁻¹ for **2** are attributable to v_{str}(O–H) vibrations of the coordinated water molecule [48]. The O–H stretching vibration for water appears generally above 3400 cm⁻¹. The shift of this band towards lower wave number and its broadness confirms the presence of strong hydrogen bonding in each complex.

3.2. Electronic spectra

The electronic spectrum of each complex (Figure S3 and S4: ESI) (displays absorptions at about 238 nm and 365 nm corresponding to intra-ligand π - π * transition and n- π * transition, respectively [49]. In both Mo(VI) complexes, the bands appearing at about 432 nm are due to

 $O(p\pi)$ -Mo(d π) charge transfer (LMCT) transitions. This phenomenon is usually observed in *cis*-MoO₂ complex [50].

3.3. Crystal structure descriptions of $[MoO_2L^1(H_2O)]$ (1) and $[MoO_2L^2(H_2O)]$ (2)

The crystallographic independent units of **1** and **2** are shown in Figure 1 and 2, respectively, and the bonding parameters are listed in Table 2. The asymmetric unit of both the complexes are built up of ONO donor set of the respective ligands and the *cis*-MoO₂²⁺ metal-oxo unit. The dianionic enolate ligands meridionally coordinate from the equatorial plane. The bond lengths C11–O12 [1.325(3) Å] and C11-N10 [1.288(4) Å] in complex **1** and C13–O14 [1.303(7) Å] and C13-N12 [1.288(7) Å] in complex **2** indicate with the presence of $\{=N-N=C(O^{-})-\}$ moiety. The C-O single bond and C=N double bond character confirming the enolic form of the ligands in the complexes.



Figure 1: Perspective view of the asymmetric unit of 1 with potential hydrogen-bonding groups.



Figure 2: Perspective view of the asymmetric unit of 2 with potential hydrogen-bonding groups.

The coordination geometry around the Mo centre in both the complexes can be best described as a distorted octahedron in which the azomethine-N, enolic–O and phenolic-O of the dianionic ligand occupies meridional position with two anionic oxygens remaining mutually *trans*. One oxido group is located *trans* to the imine nitrogen in the same plane and the other oxido group occupies one of the axial positions. The other axial position is coordinated by a water molecule completing the octahedral geometry of molybdenum centre. In the structures of both complexes, the tridentate Schiff base ligands form a fused six and five-membered metalacyclic chelate rings. The dihedral angle between the mean planes of five- and six-coordination rings is 5.29° and 9.80° for complex 1 and 2, respectively. It is noteworthy that the six-membered metallacycle in complex 1 is almost planar while the same in complex 2 is significantly twisted with atom O9 having the largest deviation from coplanarity [0.199 Å]. This structural difference between the complexes can be attributed to the steric hindrance caused by the methoxy side-arm present in complex 2.

The Mo centre in the complexes **1** and **2** are displaced towards the axial oxido atom by 0.318 and 0.330 Å, respectively from the cavity provided by donor atoms present in the equatorial plane. The twelve *cis* angles $[71.84(9)-105.9(1)^{\circ}$ for **1**; $71.4(2)-105.7(3)^{\circ}$ for **2**] and three *trans* angles $[151.23(9)-170.3(1)^{\circ}$ for **1**; $148.3(2)-167.5(2)^{\circ}$ for **2**] surrounding the central Mo1 atom show significant deviations from the ideal octahedral bond angles. Due to lone pair repulsion, the O=Mo=O angles in both **1** and **2** have values greater than 90° (Table 2), which are in the expected range for *cis*-dioxomolybdenum(VI) complexes [51]. The two

oxido groups (O21, O22) in complexes **1** and **2** exhibit typical Mo-O double bond distances 1.700(2) and 1.694(3) Å for **1**; and 1.690(6) and 1.703(5) Å for **2** [52,53]. Mo-O single bond lengths vary from 1.909(2) to 2.019(2) Å, and Mo-N distances vary from 2.233(2) to 2.243(5) Å. The longest Mo-O bonds are Mo-O_{water}, ranging from 2.320(5) to 2.336(3) Å.

Complex 1		Complex 2			
Bond distances					
Mo1–O1	1.907(2)	Mo1–O9	1.934(3)		
Mo1012	2.019(2)	Mo1-O14	2.014(4)		
Mo1–O21	1.700(2)	Mo1–O22	1.703(5)		
Mo1–N9	2.232(2)	Mo1–N11	2.243(5)		
Mo1-O22	1.694(3)	Mo1-O21	1.690(6)		
Mo1-O31	2.335(2)	Mo1-O31	2.321(5)		
Bond angles		X			
O1-Mo1-N9	82.1(1)	O9-Mo1-N11	81.2(2)		
O1-Mo1-O12	151.2	O9-Mo1-O14	148.3(2)		
O1-Mo1-O21	103.7(1)	O9-Mo1-O21	99.6(2)		
O1-Mo1-O22	100.4(1)	O9-Mo1-O22	104.4(2)		
O1-Mo1-O31	82.56(9)	O9-Mo1-O31	79.3(2)		
O12-Mo1-N9	71.84(9)	O14-Mo1-N11	71.4(2)		
O12-Mo1-O21	96.0(1)	O14-Mo1-O21	97.9(2)		
O12-Mo1-O22	94.0(1)	O14-Mo1-O22	96.0(2)		
O12-Mo1-O31	79.57(8)	O14-Mo1-O31	78.0(2)		
O21-Mo1-N9	156.4(1)	O21-Mo1-N11	93.4(2)		
O21-Mo1-O22	105.9(1)	O21-Mo1-O22	105.7(3)		
O21-Mo1-O31	82.2(1)	O21-Mo1-O31	167.5(2)		
O22-Mo1-N9	95.3(1)	O22-Mo1-N11	158.6(2)		
O22-Mo1-O31	170.3(1)	O22-Mo1-O31	86.2(2)		
O31-Mo1-N9	75.86(8)	O31-Mo1-N11	74.0(2)		

Table 2: Selected bond distances (Å) and angles (deg) for 1 and 2 $\,$

The extensive ligand-based hydrogen-bonding interactions in the respective mononuclear complexes have resulted in two different intriguing supramolecular architectures. The hydrogen-bond parameters are listed in Table 3. A detailed investigation of the crystal structure reveals that complex **1** forms a self-assembled H-bonded dimer. The coordinated water molecule of one unit acts as hydrogen bond donor to the acceptor enolic oxygen atom (O12) of an adjacent unit through cooperative O31-H311...O12 hydrogen bond interaction forming a dimer. Furthermore, adjacent dimers are connected by O31-H312...N10 hydrogen bonds involving the imidic N atom (Figure 3a). As a consequence of the interplay of such intermolecular hydrogen bonds a 2D supramolecular assembly is developed along the ab plane (Figure 3b) which is further stabilized by $\pi \cdots \pi$ stacking interaction.



Figure 3: Two-dimensional hydrogen bonded network in 1 viewed along the (a) *ac* and (b) *bc* planes

In 2, the crystal packing is different from 1 due to the presence of a methoxy group in the ligand moiety which acts as a better hydrogen bond acceptor than the enolic oxygen. The coordinated water molecule of one unit forms hydrogen bonding interaction with the methoxy oxygen atom (O2) of an adjacent unit and with the imidic nitrogen atom N12 of a second adjacent unit along the b axis. As a consequence, an infinite supramolecular 1D chain (Figure 4) is generated through two H-bonding interactions (O31_r-H100···O2 and O31–H101···N12).



Figure 4: One-dimensional hydrogen bonded chain in 2 viewed along the (a) *ab* and (b) *bc* planes.

Complex 1						
D-H···A	d(D-H) Å	d(H···A) Å	$d(D\cdots A)$ Å	<(DHA)°		
С3-Н31…О22	0.929	2.544	3.262(5)	134.41		
C13-H131O21	0.954	2.374	3.321(5)	171.76		
O31-H311…N10	0.808	2.079	2.839(5)	156.64		
O31-H312···O12	0.801	2.019	2.819(5)	177.00		
Complex 2						
D-H··· A	d(D-H) Å	d(H···A) Å	$d(D\cdots A)$ Å	<(DHA)°		
O31-H100····O2	0.807	2.019	2.826(9)	179.8(3)		
O31-H101…N12	0.799	1.974	2.773(9)	179.6(3)		

Table 3. Hydrogen bond dimensions for 1 and 2

3.4. Theoretical study

In the theoretical study we have analysed the hydrogen bonding interactions involving the Mo-coordinated water molecule that is a strong H-bond donor due to the enhanced acidity of the hydrogen atoms of the water upon coordination to the Mo(VI) metal centre. Actually, the enhanced acidity of the water protons in numerous d-block metal complexes has been demonstrated by theory and experiment [54]. In addition, we have also analysed the π - π stacking interactions in compound 1 (Figure 5A). The absence of such interaction in 2 is due

to the crucial role of the methoxy substituent of the arene (Figure 5B). These interactions are vital for understanding the final 3D architecture of the complexes.



Figure 5. X-ray fragments of compounds 1 (A) and 2 (B). Distances in Å.

In Figure 6 we have shown the theoretical models and the interaction energies of three different dimers, retrieved from the crystallographic coordinates of complexes 1 and 2. For complex 1 we have computed the interaction energy of the self–assembled dimer (Figure 6A) that is large and negative ($\Delta E_1 = -22.8$ kcal/mol), confirming the strong hydrogen bond donor ability of the coordinated water molecule. These self–assembled dimers are connected to each other by a combination of the Ow-H…N bonding and π – π stacking interactions (Figure 5A and Figure 6B). The binding energy of this dimer (Figure 6B) is also very large and negative ($\Delta E_2 = -24.6$ kcal/mol). The sum of the interaction energies of both types of dimeric motifs (shown in Figure 6A and B) is $\Delta E_1 + \Delta E_2 = -47.4$ kcal/mol.

As aforementioned, complex 2 forms infinite 1D supramolecular chains in the solid state, which are stabilized by two Ow–H···O(N) hydrogen bonds involving both hydrogen atoms of the coordinated water molecule. We have computed the interaction energy of a dimeric fragment retrieved from this supramolecular 1D chain (Figure 6C), and the result is $\Delta E_3 = -25.3$ kcal/mol that corresponds to both Ow–H···O and Ow–H···N hydrogen bonding interactions. Each asymmetric unit of compound 2 in the solid state interacts with two adjacent molecules as a consequence of the formation of the 1D the infinite chain. Thus, to compare the 1D infinite chain of compound 1 (self-assembled dimers connected by H-bond and π -stacking) to the one of compound 2, twice the energy of ΔE_3 needs to be used ($2 \times \Delta E_3 = -50.6$ kcal/mol). Therefore, the 1D supramolecular chain is more favourable in 2 than in 1.

Remarkably, the presence of the methoxy group in the organic ligand of complex 2 allows it to form a combination of H-bonds that is more stable than the combination of H-bond and π -stacking observed in 1. The energetic analysis is thus useful to explain the different behaviour of both complexes in the solid state.



Figure 6. Theoretical model used to calculate the π - π and hydrogen bonding interactions in complexes 1 and 2. Distances in Å.

Finally, we have also computed the AIM distribution of critical points in the H-bonding and $\pi - \pi$ stacking assemblies observed in complex 1 in order to corroborate the existence of the interactions and to evaluate the individual contribution of the H-bonds by using the kinetic energy (Vr) predictor developed by Espinosa *et al* [55]. The expression used to estimate the HB dissociation energy is $E_d = -\frac{1}{2}V(r)$ at the bond CP. At this point is should be emphasized that this energy predictor is basically sensitive to the distance of the H-bonds but it is not to strong electrostatic effects. That is, we have recently demonstrated [56,57] that the dissociation energies of charge assisted H-bonds, which are very strong, estimated using the V(r) predictor are identical to those of neutral H-bonds, thus evidencing that the V(r)predictor has to be used in those cases where the H-bonds are not electrostatically enhanced. The distribution of critical points and bond paths for the self-assembled H-bond dimer is shown in Figure 7b. It can be observed that the QTAIM analysis (Table S1: ESI) reveals that in addition to the conventional O-H···O interactions described above, two additional and symmetrically equivalent C-H···O are also formed. Each H-bond is characterized by a bond CP and bond interconnecting the H and O-atoms. The V(r) values in a.u. are also indicated in Figure 7a and the estimated dissociation energies. They indicate that the $C-H\cdots O$ HB is very weak (0.6 kcal/mol) and the $O-H\cdots O$ H-bond is moderately strong (4.5 kcal/mol). Therefore, the total contribution of the H-bonds estimated using the V(r) energy predictor is 10.2 kcal/mol, which is half of the interaction energy computed using the supramolecular

approach (Figure 6). This confirms the fact that the V(r) energy predictor is not sensitive to electrostatic effects that are important in **1**. These are the enhanced acidity of the coordinated water molecule and the anionic nature of the ligand. Figure 7b shows the QTAIM analysis of the HB/ π - π dimer of compound **1**. It confirms the existence of the stacking interaction that is characterized by the presence of two bond critical points (red spheres) that connect two aromatic carbon atoms of one complex with two aromatic carbon atoms of the other complex. In addition, the interaction is further characterized by the presence of a bond critical point that connects one aromatic carbon atom of one molecule with the imidic carbon atom of the other complex. Therefore, the conjugated C=N bond also participated in the π - π interaction. As a consequence of the bond critical points that emerge upon complexation, several ring critical points (yellow spheres) also characterize the interaction. We have also estimated the contribution of the H-bond using the V(r) value at the bond CP that connects the H and N atoms. The V(r) and Ed values are very similar to that observed for the O-H…O interaction in the H-bonded self-assembled dimer.



Figure 7. Distribution of critical points and bond paths in the self-assembled H-bonded simer (a) and $\pi - \pi$ /H-bonded complex (b) observed in the solid state of compound 1. The values of V(r) and the bond CPs are given in a.u.

4. Concluding remarks

We have synthesized two new Mo(VI) complexes from two different acetyl-hydrazone ligands. Structural characterization reveals that both the complexes consist of a cis-MoO₂²⁺ core incorporating coordinated tridentate hydrazone in enolic form. Both the compounds develop hydrogen-bonded assemblies of different dimensionalities and architectures. DFT energetic calculations have demonstrated that the metal coordination of the water enhances the H-bonding interaction. In complex 1, π - π interactions also contribute significantly to the overall binding energies of the supramolecular assemblies. The presence of a methoxy group

in the ligand backbone of compound 2 provokes an energetically favourable supramolecular architecture in the solid state which is also rationalized by means of the theoretical study.

Supplementary materials

CCDC 2001209 and 2001210 contain the supplementary crystallographic data for complex 1 2, and respectively. 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 Email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

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Graphical Abstract

Two New Hydrogen-bonded Supramolecular Dioxo-molybdenum(VI) Complexes Based on Acetyl-Hydrazone Ligands: Synthesis, Crystal Structure and DFT Studies

Monami Maiti, Santarupa Thakurta, Guillaume Pilet, Antonio Bauzá, Antonio Frontera

Two new Mo(VI) complexes from two related acetyl-hydrazone ligands have been synthesized and characterized. These complexes have very unique extensive supramolecular interactions. Hydrogen bonding and π - π interactions play an important role in the packing of the complexes in their solid state. Computational studies are performed using DFT calculations at BP86-D3/def2-TZVP level of theory to understand the relative stability of the supramolecular networks.



Complex 1

Complex 2

Credit Author Statement

Monami Maiti: Conceptualization; Methodology; Writing- Original draft preparation

Santarupa Thakurta: Conceptualization; Writing- Reviewing and Editing

Guillaume Pilet: Software, Data Curation

Antonio Bauzá: Software

Antonio Frontera: Software; Formal analysis; Writing- Reviewing and Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.