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Syntheses, characterization, and crystal structures of few dioxomolybdenum(VI) complexes incorporating tridentate hydrazones



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ABSTRACT

Three new *cis*-dioxomolybdenum(VI) complexes, $[MOO_2(L^1)(CH_3OH)]$ (1), $[MOO_2(L^2)(CH_3OH)]$ (2), and $[MOO_2(L^3)(CH_3OH)]$ (3) have been synthesized using three different tridentate hydrazone Schiff bases, (E)-*N'*-(4-oxopentan-2-ylidene)isonicotinohydrazide (H_2L^1) , (E)-*N'*-(4-oxo-4-phenylbutan-2ylidene)isonicotinohydrazide) (H_2L^2) , and (E)-*N'*-(2,3-dihydroxybenzylidene)benzohydrazide (H_2L^3) , respectively. The ligands and their metal complexes were characterized by different physicochemical techniques. The molecular structures of the complexes were conclusively established by single crystal X-ray diffraction which reveals that six coordinated molybdenum(VI) atom adopts distorted octahedral geometry. The tridentate hydrazone coordinates to the metal centers in their di-anionic form. The crystal packing of the complexes also reveals that classical hydrogen bonding between adjacent units result in stair-like 1D structure for 1 while an interlocked dimer for 2 and 3, respectively. Crystal packing also reveals that further non-classical interactions lead to 2D (for 1 and 3) and 3D (for 2) supramolecular structures in their solid state. Hirshfeld surface analyses were carried out to get insight to the intermolecular interactions. Thermal stabilities and electrochemical behavior of the complexes have also been investigated.

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1. Introduction

Metal complexes involving supramolecular interactions are attracting the interest of the researchers due to their wide variety of properties, such as magnetic [1], catalytic [2], redox [3], electrical [4], sensing [5] or non-liner optical [6] and therefore appear as very attracting materials in connection with several possible applications [7]. They can self-assemble as different suitable building blocks either in solution or in solid states or in both [8]. Therefore metal complexes with coordinatively unsaturated metal atoms or those with labile coordination sites achieved special interest [9]. In this context, hydrazone Schiff bases acquired considerable attention due to their versatile coordination modes [10] and potential for leading different kinds of supramolecular interactions [11]. Numerous versatile complexes of different geometries and nuclearities [12] are generated by critically designing the arylhydrazone Schiff base ligands [13], exhibiting different weak interactions [14]. These complexes also serve as potential building blocks either as metalloligands (linkers) or as nodes (connectors) in the crystal engineering of polymeric frameworks [15].

In this respect, molybdenum-Schiff base complexes also gained interest due to their potential to construct varieties of supramolecular architectures [16]. Moreover, due to its various stable and accessible oxidation states and versatile coordination chemistry [17] molybdenum plays a significant role in industrial [18] and biological reactions [19]. Particularly, molybdenum(VI) complexes containing a cis- $[MoO_2]^{2+}$ core became a fascinating class of compounds and extensively studied due to their easy preparation, structural flexibilities, and high stabilities [20,21]. Moreover, molybdenum(VI) complexes have attracted considerable interest due to their relevance to the active sites of the majority of molybdo-enzymes [22,23]. Oxo-peroxo and dioxo complexes of molybdenum(VI) with polydentate nitrogen, sulfur and oxygen donor ligands are considered valuable models for the active site of several molybdenum enzymes [24-26]. They have been shown to be very effective for oxygen transfer reactions of a wide class of substrates, including olefin epoxidation, oxidation of saturated hydrocarbons, oxidation of alcohol, and oxidation of sulfides [27-30].

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Herein we report the syntheses, spectral and structural characterizations of three new dioxomolybdenum(VI) complexes, $[MoO_2(L^1)(CH_3OH)]$ (1), $[MoO_2(L^2)(CH_3OH)]$ (2) and $[MoO_2(L^3)(CH_3OH)]$ (3) derived from three different ONO-donor hydrazone ligands; H_2L^1 ((E)-N'-(4-oxopentan-2-ylidene)isonicotinohydrazide), H_2L^2 ((E)-N'-(4-oxo-4-phenylbutan-2-ylidene)isonicotinohydrazide), and H_2L^3 ((E)-N'-(2,3-dihydroxybenzylidene) benzohydrazide) respectively (Scheme 1). Structural characterization reveals that molybdenum atom displays octahedral geometry associated with different degrees of distortion. The tridentate ligands bind the metal atoms as di-negative ion in these complexes. Crystal packing supported by Hirshfeld surface analyses reveals that intermolecular interactions play a dominant role on the solid state structure of the complexes. Thermal stabilities and redox behavior of the complexes are also investigated.

2. Experimental

2.1. Materials

Acetylacetone, benzoylacetone, 2,3-dihydroxybenzaldehyde, isonicotinic hydrazide, and benzhydrazide were purchased from sigma Aldrich Co. MoO₂(acac)₂ was synthesized following the literature procedure [31]. All other chemicals and solvent used for the syntheses were of AR grade and used without further purification.

2.2. Syntheses of ligands and complexes

2.2.1. Synthesis of (E)-N'-(4-oxopentan-2-

ylidene)isonicotinohydrazide (H_2L^1)

A 10 mL methanolic isonicotinic hydrazide (0.686 g, 5 mmol) was added to 10 mL methanolic acetylacetone (0.501 g, 5 mmol). The mixture was refluxed with vigorous stirring for 2 h and the colorless solution changed to yellow, indicating the formation of the Schiff base ligand. The resulting solution was cooled and analyzed by TLC, which revealed the presence of some starting materials along with the Schiff base. The Schiff base ligand was isolated by column chromatography over silica gel (SRL) 60–120 mesh size, using a mixture of light petroleum and ethyl acetate (v/v, 2:3);

subsequent evaporation of this eluent yielded the ligand in solid form, which was dried and stored *in vacuo* over fused CaCl₂ for subsequent use. Yield: 0.935 g (80%). *Anal.* Calc. for C₁₁H₁₃N₃O₂ (MW: 219.24): C, 60.26; H, 5.88; N, 19.17. Found: C, 60.20; H, 5.80; N, 19.14%. ¹H NMR (CDCl₃, 300 MHz). δ 1.95 (s, 3H), 2.03 (s, 3H), 2.84 (d, *J* = 18.5 Hz, 1H), 3.08 (d, *J* = 18.5 Hz, 1H), 7.64–7.69 (m, 2H), 8.72 (brs, 2H) ppm (Scheme 2; see also Fig. S1 (ESI)). ESI-MS, *m/z*: [M+H]⁺ = 220.1132 (Fig. S7 (ESI)). IR bands (KBr, cm⁻¹): 3392–3226 (N–H str.), 2924–2840 (C–H str.), 1620 (C=N). UV– Vis bands (λ /nm): 274 ($\pi \rightarrow \pi^*$), 330 and 412 ($n \rightarrow \pi^*$).

2.2.2. Synthesis of (E)-N'-(4-oxo-4-phenylbutan-2-ylidene) isonicotinohydrazide (H_2L^2)

Solid benzoylacetone (0.811 g, 5 mmol) was added to a 10 mL methanolic solution of isonicotinic hydrazide (0.686 g, 5 mmol) and refluxed for 2 h. The resulting mixture turned to orange color indicating the formation of the ligand. The mixture was cooled to room temperature. The bright yellow precipitate was filtered and washed with cold methanol and dried in air. Yield: 1.180 g (79%). Anal. Calc. for C₁₆H₁₅N₃O₂ (MW: 281.31): C, 68.31; H, 5.37; N, 14.94. Found: C, 68.28; H, 5.33; N, 14.95%. ¹H NMR (CDCl₃, 300 MHz): δ 2.09 (s, 3H), 3.01 (d, J = 18.7 Hz, 1H), 3.34 (d, *J* = 18.7 Hz, 1H), 7.28–7.36 (m, 1H), 7.39–7.41 (m, 2H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.76–7.78 (m, 2H), 8.73–8.74 (m, 2H) ppm (Scheme 2; see also Fig. S2 (ESI)). ESI-MS, m/z: $[M+H]^+$ = 282.1317 (Fig. S8 (ESI)). IR bands (KBr, cm⁻¹): 3477(N-H), 3224–3060 (C–H str.), 1650 (C=N). UV–Vis bands (λ/nm): 272 $(\pi \rightarrow \pi^*)$, 332 and 410 $(n \rightarrow \pi^*)$.

2.2.3. Synthesis of (E)-N'-(2,3-dihydroxybenzylidene)benzohydrazide (H_2L^3)

A 10 mL methanolic solution of isonicotinic hydrazide (0.686 g, 5 mmol) was added to a 10 mL methanolic solution of 2,3-dihydroxybenzaldehyde (0.691 g, 5 mmol). The resulting solution was refluxed with vigorous stirring for 2 h and consequently the mixture changed its color from pale yellow to bright yellow. The solution was then allowed to cool to room temperature. The pale yellow crystals were separated by filtration and washed with cold methanol and dried in air. Yield: 1.020 g (75%). *Anal.* Calc. for $C_{14}H_{12}N_2O_3$ (MW: 256.257): C, 65.62; H, 4.72; N, 10.93. Found:



Scheme 1. Synthetic scheme of the hydrazone ligands $(H_2L^1, H_2L^2, and H_2L^3)$.



Scheme 2. Proton numbering scheme of H_2L^1 , H_2L^2 , and H_2L^3 .

C, 65.60; H, 4.68; N, 10.90%. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 6.74 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 6.8 Hz, 1H), 6.95 (d, *J* = 6.9 Hz, 1H), 7.54 (d, *J* = 7.54 Hz, 1H), 7.59 (d, *J* = 7.0, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 8.58 (s,1H), 9.20 (s, 1H), 11.14 (s, 1H), 12.09 (s, 1H) ppm (Scheme 2; see also Fig. S3 (ESI)). ESI-MS, *m/z*: [M+H]⁺ = 257.1000, [M+Na]⁺ = 279.0808 (Fig. S9 (ESI)). IR bands (KBr, cm⁻¹): 3411 (O-H), 3193–2921 (C-H str.), 1680 (C=O), 1623(C=N). UV–Vis bands (λ /nm): 280 ($\pi \rightarrow \pi^*$), 327 and 390 ($n \rightarrow \pi^*$).

2.2.4. Synthesis of $[MoO_2(L^1)(CH_3OH)]$ (1)

A mixture of $MoO_2(acac)_2$ (0.164 g, 0.5 mmol) and H_2L^1 (0.110 g, 0.5 mmol) in methanol (20 mL) was refluxed for 3 h. A small amount of precipitate was formed during reflux which was separated by filtration. The filtrate was kept undisturbed at room temperature for slow evaporation of the solvent. X-ray diffraction quality dark red colored prism shaped single crystals of 1 were obtained after fifteen days. The crystals were filtered, washed with diethyl ether and dried in air. Yield: 0.161 g (85% with respect to metal substrate). Anal. Calc. for C₁₂H₁₅MoN₃O₅ (MW: 377.21): C, 38.21; H, 4.01; N, 11.14. Found: C, 38.19; H, 3.98; N, 11.12%. ¹H NMR (CDCl₃, 300 MHz). δ 2.13 (s, 3H), 2.42 (s, 3H), 3.49 (s, 3H), 5.53 (s, 1H), 7.73 (d, J = 4.8 Hz, 2H), 8.52 (d, J = 4.6 Hz, 2H) ppm (see also Fig. S4 (ESI)). ESI-MS, m/z: $[MoO_2(C_{11}H_{11}N_3O_2)+H]^+ =$ 348.0026 (Fig. S10 (ESI)). IR bands (KBr, cm⁻¹): 3410 (O-H), 1601(C=N), 943 and 905 (*cis* O=Mo=O). UV-Vis bands (λ /nm): 232 and 271($\pi \rightarrow \pi^*$), 313 ($n \rightarrow \pi^*$), 416 (LMCT).

2.2.5. Synthesis of $[MoO_2(L^2)(CH_3OH)]$ (2)

A mixture of MoO₂(acac)₂ (0.164 g, 0.5 mmol) and H₂L² (0.141 g, 0.5 mmol) in methanol (20 mL) was stirred for 1 h at 50 °C. A small amount of red precipitate was formed during stirring which was filtered off and the resulting filtrate was kept undisturbed at room temperature for slow evaporation of the solvent. X-ray diffraction quality dark red colored prism shaped single crystals of **2** were obtained after twelve days. The crystals were filtered, washed with diethyl ether and dried in air. Yield: 0.154 g (70% with respect to metal substrate). *Anal.* Calc. for C₁₇H₁₉MoN₃O₅ (MW: 439.28): C, 46.24; H, 4.34; N, 9.52. Found: C, 46.22; H, 4.30; N, 9.48%. ¹H NMR (CDCl₃, 300 MHz) δ 2.56 (s, 3H), 3.49 (s, 3H), 6.28

(s, 1H), 7.42–7.48 (m, 3H), 7.79–7.82 (m, 4H), 8.59 (brs, 2H) ppm (see also Fig. S5 (ESI)). ESI-MS, m/z: $[MoO_2(C_{16}H_{15}N_3O_2)+H]^+ = 410.0175$ (Fig. S11 (ESI)). IR bands (KBr, cm⁻¹): 3454 (O–H), 1617 (C=N), 944 and 898 (*cis* O=Mo=O). UV–Vis bands (λ /nm): 230 and 272 ($\pi \rightarrow \pi^*$), 330 ($n \rightarrow \pi^*$), 445 (LMCT).

2.2.6. Synthesis of $[MoO_2(L^3)(CH_3OH)]$ (3)

A mixture of MoO₂(acac)₂ (0.164 g, 0.5 mmol) and H_2L^3 (0.124 g, 0.5 mmol) in acetonitrile (20 mL) was refluxed for 2 h. A small amount of precipitate was formed during reflux. The precipitate was filtered off and the resulting filtrate was kept undisturbed at 10 °C for slow evaporation of the solvent. X-ray diffraction quality orange colored plate shaped single crystals of 3 were obtained after twenty days. The crystals were filtered, washed with diethyl ether and dried in air. Yield: 0.155 g (75% with respect to metal substrate). Anal. Calc. for C₁₅H₁₄MoN₂O₆ (MW: 414.23): C, 43.49; H, 3.41; N, 6.76. Found: C, 43.45; H, 3.39; N, 6.74%. ¹H NMR (DMSO-d₆, 300 MHz): δ 6.90 (t, 1H), 7.09 (d, 1H), 7.19(d, 1H), 7.49-7.59 (m, 2H), 7.99 (t, 2H), 8.94 (s, 1H), 9.5 (s, 1H) ppm (see also Fig. S6 (ESI)). ESI-MS (m/z): $[MoO_2(C_{14}H_{10}N_2O_3)+H]^+ =$ 384.9858 (Fig. S12 (ESI)). IR bands (KBr, cm⁻¹): 3341 (O-H), 1613 (C=N), 921 and 907 (cis-O=Mo=O). UV-Vis bands (λ /nm): 225 and $295(\pi \to \pi^*)$, $362(n \to \pi^*)$.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen, and nitrogen) were carried out using a Perkin-Elmer 2400 II elemental analyzer. The Fourier transform infrared spectra of the ligands and complexes were recorded (4000–400 cm⁻¹) on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr disc. The electronic spectra were recorded on a Perkin-Elmer Lambda 40 UV–Vis spectrophotometer using spectroscopic grade methanol. ¹H NMR spectra of H₂L¹, H₂L², **1** and **2** were recorded on a Bruker 300 MHz FT-NMR spectrometer using tetramethylsilane as internal standard in CDCl₃ while ¹H NMR spectra of H₂L³ and **3** were recorded on the same instrument with the same internal standard in DMSO-*d*₆. The positive ion ESI-MS were performed in a QTOF micro mass spectrometer using spectroscopic grade methanol. Electrochemical measurements were performed using a PAR VersaStat-potentiostat/Galvanostat II electrochemical analysis system under dry argon using conventional three electrode configurations in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. Platinized platinum millielectrode and saturated calomel electrode (SCE) were used as working and reference electrodes, respectively, along with a platinum counter electrode in cyclic voltammetry performed at a scan rate of $v = 150 \text{ mV s}^{-1}$. Thermogravimetric analyses were carried out at a heating rate of 10 °C/min with a Mettler-Toledo Star TGA/SDTA-851e thermal analyzer system in a dynamic atmosphere of N_2 (flow rate: 40 mL min⁻¹), the sample was in an alumina crucible and the temperature range was 25-800 °C.

2.4. X-ray crystallography

Diffraction quality prism shaped red crystals of **1** and **2** were mounted on Bruker APEX-II CCD diffractometer, equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å) from a fine focus sealed tube radiation source while a plate shaped orange crystal of 3 was mounted on an Oxford Diffraction Gemini diffractometer equipped with graphite monochromated Mo K α radiation $(\lambda = 0.71069 \text{ Å})$ from a rotating anode radiation source. Intensity data for 1, 2 and 3 were collected at room temperature using the ω scan technique. Multi-scan absorption corrections were applied empirically to the intensity values ($T_{max} = 0.938$ and $T_{min} = 0.855$ for **1**, $T_{max} = 0.940$ and $T_{min} = 0.878$ for **2**) using SADABS [32] while for **3** analytical absorption correction was applied to the intensity values ($T_{\text{max}} = 0.940$ and $T_{\text{min}} = 0.878$) [33]. Data reductions for 1 and 2 were performed using program SAINT [34] while for 3 the CRYSALIS [34] program was used. All the structures were solved by direct methods using the program sir-97 [35] and refined with full-matrix least-squares based on F^2 using program SHELXL-97 [36] (for 1 and 2) or CRYSTALS (for 3) [34]. All non-hydrogen atoms





Fig. 1. An ORTEP view of 1 with displacement ellipsoids drawn at the 50% probability level.



Fig. 2. An ORTEP view of 2 with displacement ellipsoids drawn at the 50% probability level.

Parameters for	1	2	3
Empirical formula	C ₁₂ H ₁₅ MoN ₃ O ₅	C ₁₇ H ₁₇ MoN ₃ O ₅	C ₁₅ H ₁₄ MoN ₂ O ₆
Formula weight	377.21	439.28	414.23
Crystal dimension (mm ³)	$0.07 \times 0.13 \times 0.26$	$0.09 \times 0.12 \times 0.22$	$0.12\times0.23\times0.29$
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>Cc</i> (No. 9)	$P2_1/n$ (No. 14)	<i>P</i> 1̄ (No. 2)
a (Å)	14.2744(8)	14.3684(17)	7.7643(6)
b (Å)	7.6972(4)	8.4149(10)	10.9440(8)
c (Å)	14.1195(8)	15.990(2)	10.9479(8)
α (°)	90	90	97.405(6)
β(°)	112.3488(7)	113.6104(17)	107.998(7)
γ (°)	90	90	107.916(7)
$V(Å^3)$	1434.82(14)	1771.5(4)	815.66(10)
Z	4	4	2
T (K)	293	294	293
$\lambda_{Mo K\alpha}$ (Å)	0.71073	0.71073	0.71073
D_{calc} (g cm ⁻³)	1.746	1.647	1.687
$\mu (\text{mm}^{-1})$	0.939	0.774	0.837
F(000)	760	888	416
θ range (°)	3.1-30.7	1.6-26.0	2.9-29.1
Total data	11093	20075	4433
Unique data	4366	3484	3166
Observed data $[I > 2\sigma(I)]$	3748	3156	2692
$N_{\rm ref:} N_{\rm par}$	4366, 197	3484, 241	2460, 217
R ^a	0.0213	0.0243	0.0325
wR	0.0557 ^b	0.0722 ^b	0.0762 ^c
Flack parameter ^d	0.00(3)		
R _{int}	0.020	0.023	0.018
Goodness-of-fit, S	1.053	1.069	1.130
$\Delta \rho_{\rm max} ({ m e}{ m \AA}^{-3})$	0.35	0.63	0.60
$\Delta ho_{ m min}$ (e Å ⁻³)	-0.29	-0.30	-0.46

b

 $R = \sum (|F_o - F_c|) / \sum |F_o|,$ $wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{\frac{1}{2}}$

 $wR = \{\sum [w(|F_{o} - F_{c}|)^{2}] / \sum [w|F_{o}|^{2}]\}^{\frac{1}{2}}.$

^d 2147 Friedel pairs.

Table 2			
Selected bond	lengths (Å) and	d angles (°) for	1, 2 and 3 .

1			
Mo1-01	1.9589(17)	Mo1-04	1.6839(17)
Mo1-02	2.0159(13)	Mo1-05	2.3514(15)
Mo1-03	1.7047(15)	Mo1-N1	2.2194(16)
C6-02	1.3190(2)	C2-01	1.3360(3)
01-Mo1-02	151.91(6)	02-Mo1-05	80.39(5)
01-Mo1-03	101.97(8)	03-Mo1-04	105.39(8)
01-Mo1-04	98.14(9)	O3-Mo1-O5	81.30(7)
01-Mo1-05	81.53(7)	O3-Mo1-N1	155.51(7)
01-Mo1-N1	82.21(6)	O4-Mo1-O5	173.18(7)
02-Mo1-03	96.33(7)	04-Mo1-N1	97.76(8)
02-Mo1-04	97.29(8)	-	-
2			
Mo1-01	1.9493(14)	Mo1-04	1.6910(19)
Mo1-02	1.9964(14)	Mo1-05	2.3674(18)
Mo1-03	1.7017(16)	Mo1-N1	2.2450(17)
C7-01	1.334(2)	C11-02	1.329(3)
01-Mo1-02	150.13(6)	O2-Mo1-N1	72.52(6)
01-Mo1-03	100.71(7)	03-Mo1-04	105.19(8)
01-Mo1-04	99.34(8)	03-Mo1-05	83.54(7)
01-Mo1-05	80.53(6)	O3-Mo1-N1	158.02(7)
01-Mo1-N1	81.39(6)	04-Mo1-05	171.07(7)
02-Mo1-03	98.33(7)	04-Mo1-N1	95.94(7)
02-Mo1-04	97.61(8)	05-Mo1-N1	75.18(6)
02-Mo1-05	78.97(6)	-	-
3			
Mo1-01	1.921(2)	Mo1-04	1.683(3)
Mo1-02	2.007(2)	Mo1-05	2.359(3)
Mo1-03	1.702(2)	Mo1-N1	2.245(2)
C8-02	1.309(4)	-	-
01-Mo1-02	148.95(9)	O2-Mo1-N1	71.16(8)
01-Mo1-03	102.57(10)	03-Mo1-04	106.14(14)
01-Mo1-04	98.45(13)	03-Mo1-05	82.79(12)
01-Mo1-05	81.59(9)	O3-Mo1-N1	158.05(13)
01-Mo1-N1	81.17(8)	04-Mo1-05	170.75(9)
02-Mo1-03	98.29(10)	04-Mo1-N1	94.52(10)
02-Mo1-04	97.51(11)	O5-Mo1-N1	76.32(8)
02-Mo1-05	78.49(9)	-	-

were refined anisotropically. The hydroxy hydrogen atoms in **1** and **2** and the amine hydrogen atoms in **3** were located in a difference Fourier map and refined isotropically. All other hydrogen atoms in **1**, **2**, and **3** were first located in the Fourier difference map, then positioned geometrically and allowed to ride on their respective parent atoms. The molecular graphics and crystallographic illustrations for **1**, **2** and **3** were prepared using the SCHAKAL99 [37], ORTEP [38], and CAMERON [39] programs. Relevant crystallographic data and structure refinement parameters of the complexes are summarized in Table 1.

3. Results and discussion

3.1. Fourier transform infrared spectra

The FTIR spectra of the complexes **1–3** were analyzed in comparison with those of the free ligands, $H_2L^1-H_2L^3$ (Fig. S13-S18 (ESI)), respectively. In the IR spectra of hydrazone ligands $(H_2L^1,$ H_2L^2 and H_2L^3), the imine $(v_{C=N})$ stretching bands appeared at 1622, 1646, 1629 cm⁻¹ whereas they are shifted to lower stretching frequencies in the spectra 1, 2, and 3, and observed at 1610, 1611, and 1608 cm⁻¹, respectively, indicating the coordination of the imine nitrogen to the metal center [40]. A sharp doublet observed at 905 and 943 cm^{-1} , 898 and 944 cm^{-1} , 907 and 921 cm^{-1} for **1**. **2**. and **3**. respectively, which is related to the symmetric and anti-symmetric stretching vibrations of cis-MoO₂²⁺ moiety which appeared at 897 and 943 cm⁻¹ in the spectra of the precursor complex MoO₂(acac)_{2.} This indicates that symmetric and anti-symmetric stretching vibrations of MoO_2^{2+} are independent on either electron donating or accepting capacity of the ligands [41,42]. This data also support the existence of cis-MoO₂²⁺ moiety in these complexes since $trans-MoO_2^{2+}$ moiety would normally show only one $v_{Mo=O}$ asymmetric stretching vibration [42]. Bands in the range 2923–3057 cm^{-1} may be assigned to



the -CH₂- stretching frequency of methyl/methylene moiety of the free/coordinated ligands.

3.2. Electronic spectra

UV-Vis spectra of the free ligands (Fig. S19) and their complexes (Fig. S20) were recorded at room temperature using spectroscopic grade methanol. The absorption bands of the free ligands can be classified into three regions. Band in the range 271-280 nm in the spectra of ligands is characteristic for the $\pi \rightarrow \pi^*$ transition of the aromatic rings of the ligands. Other two bands observed between 320 and 450 nm are probably due to the $n \rightarrow \pi^*$ transition of the -C=N- and -C=O- moieties of the ligands [43]. In the spectra of complexes the bands of the azomethine chromophore $(n \rightarrow \pi^*)$ transition are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion. In addition 1 and 2 also show a broad band at ca. 443 and 423 nm, which is assignable to a ligand to metal charge transfer (LMCT) due to the promotion of an electron from the highest occupied molecular orbital (HOMO) of the ligand to the lowest unoccupied molecular orbital (LUMO) of molybdenum atom [44]. Complex **3** does not show any LMCT band.

3.3. ¹H NMR spectra of the ligands and complexes

The proton numbering scheme of the ligands are represented in Scheme 2 while ¹H NMR spectra of these ligands $(H_2L^1, H_2L^2, and H_2L^3)$ and their complexes are represented in Figs. S1–S3 (ESI)

Table 3

Hydrogen bonding parameters (Å, °) in 1.

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
05–H50…N3*	0.815(18)	1.878(18)	2.686(2)	171(2)
C11–H11…O3#	0.93	2.46	3.283(3)	148

Symmetry code: * -1/2 + x, -1/2 - y, -1/2 + z; # x, -1 + y, z.

and Figs. S4–S6 (ESI), respectively. ¹H NMR spectroscopy has been used to extract information regarding the formation of the ligands and their mode of coordination to the MoO_2^{2+} moiety in the complexes. In the ¹H NMR spectra of H₂L¹ and H₂L² two geminal-coupled doublets for the $-CH_2$ - group (H⁴ for H₂L¹ and H⁶ for H₂L²) (δ = 2.84–3.08 ppm) substantiated the presence of two π -acceptor carbonyl groups. The peaks between δ = 7.64–8.74 ppm correspond to the aromatic protons of H_2L^1 (H^6 , H^7) and H_2L^2 (H^1 , H^2 , H^3 , H^8 , H⁹). In the ¹H NMR spectra of **1** and **2**, two doublets for the protons of the methylene group are absent at δ = 3.7–3.9 ppm, thus indicating deprotonation of the methylene group [45,46]. This also confirms that both ligands coordinate to the molybdenum center in the enolic form. Moreover, it is clearly observed that the signals of aromatic hydrogen are broadened compared to the free ligands $(H_2L^1 \text{ and } H_2L^2)$ possibly due to spin-lattice relaxation caused by paramagnetic impurities in the complexes. The ¹H NMR spectra of **1** and **2** contain one additional singlet at δ = 3.49, tentatively assigned to the coordinated CH₃OH molecule.

The ¹H NMR spectrum of H₂L³ displays two signals at δ = 8.58 (H⁷) and 9.20 (H⁶) which can be attributed to azomethylene and —NH=N— protons confirming the formation of the hydrazone. The aromatic proton signals (H³, H⁴, H⁵, H⁸, H⁹ and H¹⁰) were observed in the range δ = 6.74–7.93 ppm. Moreover, peaks at δ = 11.14 and 12.09 ppm can be attributed to two phenonolic hydrogen atoms. The ¹H NMR spectrum of **3** resembled to that of H₂L³ very much except that the signal of the phenolic-OH proton was absent which supported its deprotonation during complexation. The results of the ¹H NMR spectra are in good agreement with the structure of the complexes.

3.4. Structure description of the complexes 1, 2, and 3

Complexes **1** and **2** crystallize in the monoclinic space group *Cc* and $P2_1/n$, respectively. An ORTEP view of the asymmetric unit of **1** and **2** with atom labels are shown in Figs. 1 and 2 and relevant bonding parameters are listed in Table 2. The asymmetric units



Fig. 4. Crystal packing of 2 showing the formation of centrosymmetric dimers via pairs of O-H···N hydrogen bonds (dashed lines).

Table 4Hydrogen bonding parameters (Å, °) in 2.

D–H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
05–H50…N3*	0.79(4)	1.92(4)	2.706(3)	171(3)
C4–H4…O5#	0.93	2.60	3.475(3)	157
C14–H14…O4\$	0.93	2.58	3.140(3)	119

Symmetry code: *1 - x, 1 - y, 1 - z; # -x, -y, 1 - z; \$ 1/2 - x, 1/2 + y, 1/2 - z.



Fig. 5. An ORTEP view of 3 with displacement ellipsoids drawn at the 50% probability level.

Table	5
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Hydrogen bonding parameters (Å, °) in 3.

D–H…A	d(D-H)	$d(H \cdots A)$	$d(D \cdots A)$	∠(DHA)
06–H1…03* C7–H41…04\$ C12–H101…06**	0.85 0.96 0.96	1.90 2.60 2.57	2.753(4) 3.314(4) 3.425(4)	180 132 149

Symmetry code: * 1 – x, 1 – y, 1 – z; -z; \$ –x, 1 – y, -z; ** x, -1 + y, -1 + z.

of both complexes consist of one molybdenum(VI) atom, one dianionic tridentate hydrazone Schiff base $(L^1)^{2-}$ (for **1**) or $(L^2)^{2-}$ (for 2), two oxo ligands, and one coordinated methanol. The coordination geometry around the Mo center in these complexes can be described as distorted octahedron in which the tridentate ligand coordinate through the anionic alkoxo oxygen (O1), the imine nitrogen (N1), and the anionic carboxamido oxygen (O2) and adopt *mer*-arrangement with two anionic oxygen atoms mutually *trans* while they remain as *cis* with respect to the two oxygen atoms (O3 and O4) of cis-dioxo group (Figs. 1 and 2). The octahedral geometry of the molybdenum center is completed by the oxygen atom of the coordinated methanol (05). The metal atom is displaced from the best equatorial plane formed by the O1, N1, O2, O3 atoms (maximum deviation from the planarity of 0.068(2) Å for O1 in **1** and 0.025(2) Å for N1 in **2**) toward the O4 apical atom by 0.3350(5) and 0.3330(2) Å in **1** and **2**, respectively.

The two *transoid* basal angles (O3–Mo1–N1 and O1–Mo1–O2) deviate significantly from the ideal value (180°) while the axial *trans* angle (O4-Mo1-O5) is very close to the ideal value. The C2–O1, C6–O2 and C7–O1, C11–O2 bond lengths (Table 2) in 1 and 2 are comparable to other *enolato* C–O bond lengths found in the complexes reported earlier [47,48], thus indicating that carbonyl functionality coordinates in *enolic* form in both cases.

A detailed investigation of the crystal structure of **1** reveals that the alkoxo oxygen of the coordinated methanol molecule acts as hydrogen donor to the acceptor pyridyl nitrogen (N3) of an adjacent complex molecule resulting in the formation of a one dimensional stair-like chain structure propagating along the crystallographic [101] direction (Fig. 3). Furthermore these stairlike chains are interlinked by non classical C–H…O hydrogen bond (Table 3) leading to a 2D supramolecular structure.

In the crystal packing of **2** (Fig. 4) molecules related by center of inversion interlocked into dimer through pairs of O5–H50…N3 hydrogen bonds (Table 4), forming a ring of $R_2^2(18)$ graph-set motif according to Etter's notation [49]. A comparison of the crystal



Fig. 6. Crystal packing of 3 showing the formation of centrosymmetric dimers via pairs of O-H···O hydrogen bonds (dashed lines).



Fig. 7. Hirshfeld surface mapped with d_{norm} (a), *shape index* (b), and *curvedness* (c) for **1**, **2** and **3**.

structures of complexes **1** and **2** indicates that the replacement of a methyl group by a phenyl group leads to a drastic change in the hydrogen bonding pattern probably due to steric effect of the bulky phenyl ring. In addition, the dimers in **2** are interwoven by non-classical C–H…O hydrogen bond (Table 4) to form a 3D network.

Complex 3 crystallized in triclinic space group P1. An ORTEP view of **3** is shown in Fig. 5 and relevant bonding parameters are summarized in Table 2. Alike 1 and 2, the asymmetric unit of 3 also consists of a molybdenum(VI) atom, one di-negative tridentate hydrazone Schiff base $(L^3)^{2-}$, two oxo ligands and a methanol. The coordination polyhedron around Mo1 is best described as distorted octahedron where the best equatorial plane is defined by O1, N1, O2 and O3 atoms leaving O4 and O5 at the two apexes. All donor atoms in the mean equatorial plane are almost coplanar (maximum displacement 0.022(3) Å for atom O2 and N1) with the Mo1 atom protruding by 0.3264(4) Å towards the apical O4 oxygen atom. The Mo=O bond lengths and the O=Mo=O angles are in the expected range for *cis* dioxomolybdenum(VI) complexes. The *enolic* nature of the C8-O2 bond is evident from its similarities to other enol C-O bond distances observed in the reported complexes [47,48].



Fig. 8. Fingerprint plots of 1, 2 and 3.

The conformation of complex **3** is stabilized by (Table 5) pairs of cooperative O–H…O interactions operating between the phenolic-OH (O6–H1) and the oxo (O3) groups of centrosymmetrically-related molecules leads to a dimeric structure (Fig. 6) forming a ring of $R_2^2(12)$ graph-set motif according to Etter's notation [49]. The supramolecular dimers are further connected by non-classical C–H…O hydrogen bonds as well as $\pi...\pi$ stacking interactions (centroid-to-centroid distances of 3.679(3) Å) to form 2D layer parallel to the [101] plane.

3.5. Hirshfeld surface analyses

Intermolecular interactions are conveniently viewed and quantified by mapping a Hirshfeld surface onto a fragment of each complex using the program CrystalExplorer3.1 [50] and then generating the corresponding 2D fingerprint plot. The Hirshfeld surfaces of the title complexes are depicted in Fig. 7, showing surfaces that have been mapped over $d_{\rm norm}$ (-0.5 to 1.5 Å), shape index and curvedness. d_{norm} surfaces of **1** and **2** with the large circular gloominess visible on the surfaces are indicative of strong O-H...N interactions between the oxygen atom of the coordinated methanol and the nitrogen atom of the pyridine ring. Intense red gloominess on d_{norm} surface of complex **3** can be assigned to strong O-H…O interactions among phenoxo and hydroxyl groups, methanolic hydrogen. Other visible spots in the surfaces are because of H…H contacts. The O…H/H…O intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Fig. 8). Complementary regions are visible in the fingerprint plots where one molecule act as donor $(d_e > d_i)$ and the other as an acceptor $(d_e < d_i)$. The fingerprint plots can be decomposed to highlight particular atoms pair close contacts [51]. The proportions of O.-.H/H...O interaction are 29.9, 25.6, and 35.1% of the Hirshfeld surfaces for each molecule of 1, 2, and 3, respectively. The O.-.H interactions are represented by a spike $(d_i = 1.3, d_e = 1.3 \text{ Å in } 1, d_i = 1.1, d_e = 1.4 \text{ Å in } 2$ and $d_i = 0.7$, $d_e = 1.1$ Å in **3**) in the bottom left (donor) area of the fingerprint plot (Fig. 8). No significant C–H \cdots π interaction is observed in these complexes while the C.-.H close contacts are 11.6%, 18.7%, and 12.6% in 1, 2, and 3, respectively. Percentage contribution of a variety of contacts in the molybdenum complexes are listed Table 6.

The inspections on the Hirshfeld surface of **1** and **2** do not show adjacent red and blue triangles on the shape-index surfaces (Fig. 7). Moreover no flat region toward the bottom of both sides of benzene and pyridine moiety is evident on the curvedness surface (Fig. 7). However **3** shows adjacent red and blue triangles on shape-index surface as well as flat region toward the bottom of both sides of benzene and pyridine moieties on curvedness surface. These clearly indicate that **1** and **2** have no π ... π stacking in the solid state but **3** possess π ... π stacking interaction.

3.6. Electrochemical studies

Electrochemical properties of the complexes were studied at room temperature in HPLC grade acetonitrile using cyclic voltammetry at a platinum electrode with tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 150 mV s⁻¹ within the potential range 0 to -1.75 V. During the cathodic scan an irre-

Table 6

Summary of the various contacts percentage contributions to the Hirshfeld surface area in 1, 2 and 3.

Complexes	0−H…H− 0	N−H…H− N	C−H…H− C	H…H	C…C	C-0…0- C
1	29.9	8.4	11.6	42.4	3.0	2.2
2 3	25.6 30.6	7.5 1.9	18.7 12.6	40.9 41.2	4.8 7.9	0.1 0.7



Fig. 9. Cyclic voltammograms of complexes 1, 2 and 3, recorded at a scan rate 150 mV $s^{-1}.$



Fig. 10. TGA curves of complexes 1, 2 and 3.

versible reduction peak at -1.149, -0.913, and -1.121 V were observed for **1**, **2**, and **3**, respectively (Fig. 9) corresponds to Mo(VI)/Mo(V) redox couple [8,52]. For the complexes, no oxidation peak is observed during anodic scan on cyclic voltammetry.

3.7. Thermogravimetric analyses

Thermogravimetric analysis curves (Fig. 10) for complexes 1, 2, and 3 were recorded in the temperature range 25–800 °C with a heating rate of 10 °C min⁻¹ in dynamic nitrogen atmosphere which reveal their thermal stabilities. The samples were purged by a stream of dry nitrogen flowing at 40 mL min⁻¹. All three complexes undergo decomposition in two well defined stages. The loss of weakly coordinated methanol molecule occurred in between 170, 195, 130 °C for 1, 2, and 3, respectively [53]. The second stage of decomposition took place in the temperature range of 180–434, 300–597, and 240–750 °C for 1, 2, and 3 corresponding to loss of the coordinated hydrazone ligands. The final residue in the decomposition of each complex was identified as MoO_2 by qualitative analysis.

4. Conclusions

In this paper we have reported the syntheses and spectral characterization of three new *cis*-dioxomolybdenum(VI) complexes incorporating different tridentate hydrazone ligands. Structural characterization reveals that all the complexes consist of a MoO_2^{2+} core incorporating a coordinated tridentate hydrazone in di-negative form. In all the complexes the molybdenum(VI) atom displays distorted octahedron geometry. Several weak interactions are present in the complexes and play an important role in their crystal packing which is supported by Hirshfeld surface analyses. An electrochemical study shows an irreversible redox behavior of the complexes. The relatively long molybdenum-oxygen (methanolic) bond distances, thermal analyses and ESI-MS analyses reveal that the coordinated methanol is loosely held to the MoO_2^{2+} core of the complexes suggesting their potential use as catalysts [27–30].

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Appendix A. Supplementary data

CCDC 988880-988882 contain the supplementary crystallographic data for 1–3. 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2014.12.017.

References

- [1] W. Xu, Y. Zhou, D. Huang, W. Xiong, M. Su, K. Wang, S. Han, M. Hong, Cryst. Growth Des. 13 (2013) 5420.
- [2] M.R. Sambrook, S. Notman, Chem. Soc. Rev. 42 (2013) 9251.
- [3] P.A. Ochoa, R.J. Aparicio, J. Perles, M.R. Torres, M. Gennari, F. Zamora, Cryst. Growth Des. 13 (2013) 4977.
- [4] A.N. Gupta, V. Singh, V. Kumar, A. Rajput, L. Singh, M.G.B. Drew, N. Singh, Inorg. Chim. Acta 408 (2013) 145.
- [5] B.E. Aroussi, L. Guénée, P. Pal, J. Hamacek, Inorg. Chem. 50 (2011) 8588.
- [6] Z. Zheng, Z.-P. Yu, M.-D. Yang, F. Jin, L.-N. Ye, M. Fang, H.-P. Zhou, J.-Y. Wu, Y.-P. Tian, Dalton Trans. 43 (2014) 1139.
- [7] H. Zhang, Y. Zhao, Chem. Eur. J. 19 (2013) 16862.
- [8] V. Vrdoljak, B. Prugovečki, D.M. -Čalogović, J. Pisk, R. Dreos, P. Siega, Cryst. Growth Des. 11 (2011) 1244.
- [9] N.K. Ngan, K.M. Lo, C.S.R. Wong, Polyhedron 30 (2011) 2922.
- [10] M. Sutradhar, T.R. Barman, J. Klanke, M.G.B. Drew, E. Rentschler, Polyhedron 53 (2013) 48.
- [11] D. Sadhukhan, A. Ray, G. Pilet, C. Rizzoli, G.M. Rosair, C.J. Gómez-García, S. Signorella, S. Bellú, S. Mitra, Inorg. Chem. 50 (2011) 8326.

- [12] W.-T. Deng, J.-C. Liu, J. Cao, Inorg. Chem. Commun. 35 (2013) 315.
- [13] S. Shit, S.K. Dey, C. Rizzoli, E. Zangrando, G. Pilet, C.J. Gómez-García, S. Mitra, Inorg. Chim. Acta 370 (2011) 18.
- [14] H.D. Yin, S.W. Chen, Inorg. Chim. Acta 359 (2006) 3330.
- [15] V. Vrdoljak, B. Prugovecki, D.M. Calogovic, R. Dreos, P. Siega, C. Tavagnacco, Cryst, Growth Des. 10 (2010) 1373.
- [16] V. Vrdoljak, B. Prugovecki, D.M. Calogovic, J. Pisk, CrystEngComm 13 (2011) 4382
- [17] K. Hüttinger, C. Förster, T. Bund, D. Hinderberger, K. Heinze, Inorg. Chem. 51 (2012) 4180.
- [18] H. Li, J. Wu, X. Huang, G. Lu, J. Yang, X. Lu, Q. Xiong, H. Zhang, ACS Nano 7 (2013) 10344.
- [19] C. Wang, M. Yu, A.F. Kyle, P. Jakubec, D.J. Dixon, R.R. Schrock, A.H. Hoveyda, Chem. Eur. J. 19 (2013) 2726.
- [20] P. Basu, B.W. Kail, A.K. Adams, V.N. Nemykin, Dalton Trans. 42 (2013) 3071.
- [21] M. Bagherzadeh, M. Zare, V. Amani, A. Ellern, L.K. Woo, Polyhedron 53 (2013) 223.
- [22] M.J. Pushie, J.J. Cotelesage, G.N. George, Metallomics 6 (2014) 15.
- [23] J. Wilcoxen, R. Hille, J. Biol. Chem. 288 (2013) 36052.
- [24] K.C. MacLeod, P.L. Holland, Nat. Chem. 5 (2013) 559.
- [25] H. Sugimoto, S. Tatemoto, K. Toyota, K. Ashikari, M. Kubo, T. Ogura, S. Itoh, Chem. Commun. 49 (2013) 4358.
- [26] H. Sugimoto, M. Sato, L.J. Giles, K. Asano, T. Suzuki, M.L. Kirk, S. Itoh, Dalton Trans. 42 (2013) 15927.
- [27] M.E. Judmaier, C.H. Sala, F. Belaj, M. Volpe, N.C.M. Zanetti, New J. Chem. 37 (2013) 2139.
- [28] J.-I. Park, J.-K. Lee, J. Miyawaki, S.-H. Yoon, I. Mochida, J. Ind. Eng. Chem. 17 (2011) 271
- [29] B. Gao, M. Wan, J. Men, Y. Zhang, Appl. Catal. A 439-440 (2012) 156.
- [30] R.D. Chakravarthy, K. Suresh, V. Ramkumar, D.K. Chand, Inorg. Chim. Acta 376 (2011) 57.
- [31] G.J.-J. Chen, J.W. McDonald, W.E. Newton, Inorg. Chem. 15 (1976) 2612.
- [32] Bruker, sADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- [33] CRYSALIS CCD and CRYSALIS RED, Version 1.171.33.52 Oxford Diffraction Ltd., England, 2009.
- [34] Bruker, SAINT, Software Reference Manual, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.
- [35] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
- [36] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [37] E. Keller, J.-S. Pierrard, SCHAKAL99, University of Freiburg, Germany, 1999.
- [38] L.J. Farrugia, ORTEP3 for windows, J. Appl. Crystallogr. 30 (1997) 565.
- [39] D.J. Walker, C.K. Prout, F.J. Bearch, CAMERON Program, Chemical Crystallographic Laboratory, Oxford University, UK, 1996. [40] N.K. Ngan, K.M. Lo, C. Seng, R. Wong, Polyhedron 33 (2012) 235.
- [41] R.M. Ramadan, L.H. Abdel-Rahman, M. Ismael, T.A. Youssef, S.A. Ali, J. Mol. Struct. 1049 (2013) 7.
- [42] M.R. Maurya, S. Dhak, F. Avecilla, Polyhedron 67 (2014) 145.
- [43] S. Banerjee, S. Mondal, W. Chakraborty, S. Sen, R. Gachhui, R.J. Butcher, A.M.Z. Slawin, C. Mandal, S. Mitra, Polyhedron 28 (2009) 2785.
- [44] T.J. Korstanje, E. Folkertsma, M. Lutz, J.T.B.H. Jastrzebski, R.J.M.K. Gebbink, Eur. I. Inorg. Chem. (2013) 2195
- [45] H.H. Monfared, R. Bikas, P.M. Anarjana, A.J. Blake, V. Lippolis, N.B. Arslan, C. Kazak, Polyhedron 69 (2014) 90.
- [46] P. Singh, A.K. Singh, V.P. Singh, Polyhedron 65 (2013) 73.
- [47] K.R.S. Gowda, H.S.B. Naik, B.V. Kumar, C.N. Sudhamani, H.V. Sudeep, T.R.R. Naik, G. Krishnamurthy, Spectrochim. Acta, Part A 105 (2013) 229.
- [48] M. Sutradhar, M.V. Kirillova, M. Fátim, C.G. da Silva, C.-M. Liu, A.J.L. Pombeiro, Dalton Trans. 42 (2013) 16578.
- [49] M.C. Etter, J.C. MacDonald, Acta Crystallogr., Sect. B 46 (1990) 256.
 [50] S.K. Wolff, D.J. Grimwood, J.J. Mckinnon, M.J. Turner, D. Jayatilaka, M.A.
- Spackman, Crystal Explorer 3.0., University of Western Australia, 2012
- [51] M.A. Spackman, D. Jayatilaka, CrystEngComm 11 (2009) 19.
 [52] N.K. Ngan, K.M. Lo, C. Seng, R. Wong, Polyhedron 30 (2011) 2922.
- [53] R. Takjoo, A. Hashemzadeh, H.A. Rudbari, F. Nicolo, J. Coord. Chem. 66 (2013) 345.