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Dioxomolybdenum(VI) and dioxotungsten(VI) complexes of isomeric ONO donor ligands and the X-ray crystal structure of $[MoO_2(o\text{-}OC_6H_4CH{=}NCH_2C_6H_4O)(MeOH)]_2 \cdot MeOH$

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Abstract—Dioxomolybdenum(VI) and dioxotungsten(VI) complexes of two isomeric Schiff bases derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde and *o*-hydroxybenzylamine or *o*-aminobenzylalcohol have been prepared and characterized. ^1H NMR spectral data confirm the formation of $[MO_2L]$ (M = Mo or W, LH_2 = ligand) types of complexes except the complex of dioxomolybdenum(VI) with the ligand salicylaldehyde-*o*-hydroxybenzylamine (H_2sal-OHYBA) which forms $[MoO_2(\text{sal-OHYBA}) \cdot CH_3OH]$. An X-ray study of $[MoO_2(\text{sal-OHYBA}) \cdot CH_3OH]$ shows the presence of distorted octahedral geometry around molybdenum in which the tridentate ligand occupies meridional position where two anionic oxygens are mutually *trans* and are *cis* to the *cis* dioxo group. Generally the tungsten complex is more stable to decomposition than the molybdenum one within the same ligand. © 1997 Elsevier Science Ltd

Keywords: molybdenum and tungsten complexes; Schiff bases complexes; X-ray crystal structure.

The isomeric Schiff bases (**I** and **II**) derived from *o*-aminobenzylalcohol or *o*-hydroxybenzylamine are potential ONO donor tridentate ligands and form stable complexes with full range of transition and inner-transition metal ions [1]. However, amongst the d^0 ions of the chromium group metals, only dioxomolybdenum(VI) complexes with these ligands have been reported in the literature [2]. The reason for the lack of dioxochromium(VI) and dioxotungsten(VI) complexes with such ligands is the non-availability of suitable starting materials. The simplified synthesis of $[WO_2(acac)_2]$ (acacH = acetylacetone) [3], and its successful use as a suitable starting material has now boosted the coordination chemistry of tungsten(VI) complexes [4]. In this paper, we report the dioxotungsten(VI) complexes of the isomeric Schiff bases (**I** and **II**). As the dioxomolybdenum(VI) complexes of these ligands have not been studied in detail [2], we have also considered these complexes here, and have compared their spectral and thermal analysis pattern with dioxotungsten(VI) complexes. Single crystal X-ray study of one of the representative molybdenum complexe has also been reported.

EXPERIMENTAL

Reagents

Ammonium paramolybdate(VI) tetrahydrate, salicylaldehyde, acetylacetone, benzene and methanol were purchased from Loba Chemie (India). WO_2Cl_2 and *o*-aminobenzylalcohol were procured from Aldrich Chemical Co. (USA), while 2-hydroxy-1-naphthaldehyde was a product of Fluka A.G. (Switzerland). $[MoO_2(acac)_2]$ [5], $[WO_2(acac)_2]$ [3],

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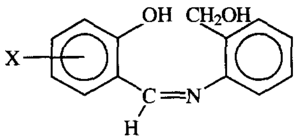

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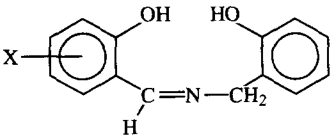

II

No.	Ligand	X	Abbreviations
1	I	H	H_2sal-OABA
2	II	H	H_2sal-OHYBA
3	I	5,6-C_4H_4	H_2hynaph-OABA
4	II	5,6-C_4H_4	H_2hynaph-OHYBA

Schiff bases **I** and **II** [2], and *o*-hydroxybenzylamine [6] were prepared by following the published procedures.

Preparation of dioxomolybdenum(VI) complexes

These complexes were prepared by the method described previously [2].

Preparation of dioxotungsten(VI) complexes. A general method

A hot solution of $[WO_2(acac)_2]$ (0.44 g, 1 mmol) in 20 cm^3 of methanol was added to the appropriate Schiff base (1 mmol) dissolved in 20 cm^3 of methanol with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a waterbath for 6 h. After concentrating the solution to *ca* 10 cm^3 and cooling to 10°C overnight, the separated coloured solid was filtered, washed with methanol and dried *in vacuo* at room temperature.

The colour, yield, analytical and physico-chemical data of the complexes are presented in Tables 1, 2 and 3.

Measurements

Elemental analyses of the complexes were carried out by the Micro Analytical section of the National Chemical Laboratory. IR spectra were recorded as Nujol mull on a Perkin-Elmer Model 1620 FT-IR spectrophotometer. Electronic spectra were recorded in DMF on a Shimadzu UV-2101PC recording spectrophotometer. ^1H NMR spectra were obtained on a Bruker WH-90 and WH-200 spectrometer in DMSO-d_6 using tetramethylsilane as an internal standard. The electrical conductance measurements were performed in 1×10^{-3} M DMF solution using a Biochem Model DC-808 digital conductivity bridge calibrated with potassium chloride solutions of various concentrations. The thermogravimetry was conducted on a Seiko Instruments Inc. TG/DTA Model 32 Thermal Analyzer.

X-ray data collection and analyses

A single crystal of $\{[MoO_2(\text{sal-OHYBA})(MeOH)]_2 \cdot MeOH\}$ suitable for X-ray structure determination was grown by slow-evaporation of a methanolic solution of the complex at ambient temperature. Data were collected on a PC-controlled Enraf–Nonius CAD-4 single crystal X-ray diffractometer. Pertinent crystal data are listed in Table 4. Accurate unit cell parameters were determined by least-squares fit of 25 machine centered reflections, $16 < 2\theta < 32°$. Three standard reflections measured every hour showed less than 4% variation in average intensity. The structure was solved by direct methods using NRCVAX [7] and refined by least-squares method using SHELX-93 [8]. Least-squares refinement of scale factor, positional and anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.036$. Coordinates of hydrogen atoms, determined geometrically and confirmed by difference Fourier, were held fixed during refinement. Each hydrogen atom was assigned the same isotropic temperature factor as the atom to which it was bonded.

RESULTS AND DISCUSSION

The dibasic tridentate ligands **I** and **II** react with $[WO_2(acac)_2]$ in a 1 : 1 molar ratio in refluxing methanol to yield the corresponding dioxotungsten(VI) complexes of the type $[WO_2L]$ where LH_2 = ligand) as follows:

$$[WO_2(acac)_2]+LH_2 \xrightarrow{MeOH} [WO_2L]+2acacH.$$

The analytical data support the above formulation of the complexes. The dioxomolybdenum(VI) complexes of these ligands have also been isolated in the similar way following the literature procedure. All the complexes have similar general formula of $[MoO_2L]$ except the complex $[MoO_2(\text{sal-OHYBA})MeOH]$ which had coordinated methanol.

All the complexes are diamagnetic as expected for the $4d^0$ molybdenum and $5d^0$ tungsten ions. They are soluble in coordinating solvents like pyridine, DMF

Table 1. Analytical and physicochemical data of the complexes

S. No.	Compounds[a] Stoichiometry	Colour	Dec.p. (°C)	Ω M[b]	Found (calc.)% C	H	N
1a	$[MoO_2(\text{sal-OABA})]$ $C_{14}H_{11}NO_4Mo$	Greenish yellow	300	3.0	47.4 (47.7)	3.5 (3.1)	3.8 (4.0)
1b	$[WO_2(\text{sal-OABA})]$ $C_{14}H_{11}NO_4W$	Bright yellow	320	4.8	38.5 (38.2)	2.3 (2.5)	3.1 (3.2)
2a	$[MoO_2(\text{sal-OHYBA})$ $(\cdot MeOH)]C_{15}H_{15}NO_5Mo$	Yellow	280	5.2	46.7 (46.9)	3.6 (3.9)	3.6 (3.6)
2b	$[WO_2(\text{sal-OHYBA})]$ $C_{14}H_{11}NO_4W$	Orange yellow	330	6.0	38.4 (38.2)	2.5 (2.5)	3.5 (3.2)
3a	$[MoO_2(\text{hynaph-OABA})]$ $C_{18}H_{13}NO_4Mo$	Brown	325	3.5	53.5 (53.7)	3.2 (3.2)	3.6 (3.5)
3b	$[WO_2(\text{hynaph-OABA})]$ $C_{18}H_{13}NO_4W$	Brown	375	3.0	44.0 (44.1)	2.4 (2.7)	2.7 (2.9)
4a	$[MoO_2(\text{hynaph-OHYBA})]$ $C_{18}H_{13}NO_4Mo$	Brown	250	7.0	53.9 (53.7)	3.1 (3.2)	3.8 (3.5)
4b	$[WO_2(\text{hynaph-OHYBA})]$ $C_{18}H_{13}NO_4W$	Bright yellow	320	4.5	44.3 (44.1)	2.5 (2.7)	2.7 (2.9)

[a] Abbreviations as listed under structures **I** and **II**.

[b] Conductance values are in Ω^{-1} mol^{-1} cm^2.

Table 2. IR and electronic spectral data (ν cm^{-1}) of ligands and complexes

Compounds[a]	IR spectra (C=N)	(O=M=O)	$(M{\cdots}O \rightarrow M)$	Electronic spectra (ε/dm^3 mol^{-1} cm^{-1})
1	1616			30300(15400), 28570(8600)
1a	1613	939	750	33890(14200), 27620(1140), 25310(690)
1b	1611	955	757	33890(3040), 27397(2410), 25970(1280)
2	1657			36360(16000), 33330(19000)
2a	1632	933, 911		36760(11600), 32780(6400), 27770(1060)
2b	1638	918	695	32250(2840), 28990(1750)
3	1621			32250(92000), 27390(76000), 22000(12300)
3a	1616	925	770	32250(38500), 27770(11600), 21800(1270)
3b	1618	946	746	32250(12000), 27770(7600), 21730(1600)
4	1650			33890(90000), 27770(45000), 23500(9600)
4a	1620	928	753	33800(16400), 27770(1450), 23800(900)
4b	1626	931	716	33890(40000), 28160(1580), 23500(1000)

[a] For abbreviations see Table 1.

and DMSO. The low molar conductance values (3–7 ohm^{-1} mol^{-1} cm^2) in DMF indicate their non-electrolytic behaviour.

Thermogravimetric analyses

The thermal analysis data for $[MoO_2(\text{sal-OHYBA})\cdot CH_3OH]$ show the loss of a methanol molecule at 170°C and invariably conversion into a stable species $[MoO_2(\text{sal-OHYBA})]$. This information is in agreement with the coordination of methanol at the sixth position site. Due to weak coordination and labile nature of such monodentate ligands in the complexes of the type $[MoO_2L(D)]$ (M = Mo or W; D = neutral monodentate ligand) they are known to undergo cleavage on heating [9]. On further heating the compound starts decomposing at 280°C and continues losing weight until it forms MoO_3 at 580°C. Other complexes are stable up to ~275°C and then decompose to give their respective oxides at ~600°C. On comparing the decomposition temperature pattern (Table 1), it may be concluded that, within the same ligand the tungsten complex decomposes at a rela-

Table 3. ^{1}H NMR spectral data (δ in ppm)[a]

Compound[b]	—CH=N—	Aromatic protons	—CH$_2$	—OH
1	8.66 (s, 1H)	6.83–7.75 (m, 8H)	4.57 (s, 2H)	13.08 (s, 1H)
1a	8.72 (s, 1H)	6.68–7.73 (m, 8H)	5.22 (s, 2H)	
1b	8.74 (s, 1H)	6.77–7.82 (m, 8H)	5.51 (s, 2H)	
2	8.60 (s, 1H)	6.65–7.50 (m, 8H)	4.70 (s, 2H)	12.50 (s, 2H)
2a	8.64 (s, 1H)	6.53–7.56 (m, 8H)	4.68 (s, 2H)	
2b	8.67 (s, 1H)	6.67–7.64 (m, 8H)	4.82 (s, 2H)	
3	8.28 (s, 1H)	6.82–7.86 (m, 10H)	4.62 (s, 2H)	9.40 (s, 1H)
3a	8.87 (s, 1H)	6.91–7.98 (m, 10H)	5.29 (s, 2H)	
3b	9.25 (s, 1H)	7.10–8.45 (m, 10H)	5.56 (s, 2H)	
4	9.04 (s, 1H)	6.48–8.02 (m, 10H)	4.68 (s, 2H)	9.73 (s, 2H)
4a	9.40 (s, 1H)	6.55–8.33 (m, 10H)	4.70 (s, 2H)	
4b	9.52 (s, 1H)	6.73–8.40 (m, 10H)	5.05 (s, 2H)	

[a] Letters given in parentheses indicate the type of signal. s = singlet, m = multiplet.
[b] For abbreviations see Table 1.

Table 4. Crystal data and structure refinement for $[MoO_2(o\text{-}OC_6H_4CH{=}NCH_2C_6H_4O)(MeOH)]_2 \cdot MeOH$

Empirical formula	$C_{31}H_{31}Mo_2N_{2011}$
Formula weight	799.46
Temperature	293(2) K
Wavelength	0.70930 Å (Mo-K$_\alpha$ radiation)
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 9.901(1)$ Å $\alpha = 94.73(2)^\circ$
	$b = 12.603(2)$ Å $\beta = 97.70(2)^\circ$
	$c = 14.545(4)$ Å $\gamma = 111.47(1)^\circ$
Volume	1656.7(6) Å^3
Z	2
Density (calculated)	1.603 Mg/m^3
Absorption coefficient	0.818 mm^{-1}
F(000)	806
Crystal size	1.0 × 1.25 × 1.88 mm
θ Range for data collection	1.42–23.42°
Index ranges	$-11 \leqslant h \leqslant 10, 0 \leqslant k \leqslant 14, -16 \leqslant l \leqslant 16$
Scan mode/Speed (°min^{-1})	$\omega/2\theta$, 1
Independent reflections	4859
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4859/0/415
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R_\perp = 0.0363$, $wR_2 = 0.1024$
R indices (all data)	$R_\perp = 0.0401$, $wR_2 = 0.0158$
Largest diff. peak and hole	0.652 and -1.219 e Å^{-3}

tively higher temperature than the corresponding molybdenum complex.

Spectral studies

The IR spectrum of [MoO$_2$(sal-OHYBA)$\cdot$CH$_3$OH](**2a**) exhibits two bands at 911 and 933 cm^{-1}, due to the ν_{asym} and ν_{sym}(O=M=O) modes, respectively. However, other complexes exhibit only one ν(O=M=O) (M = Mo or W) stretch at 918–955 cm^{-1} and a sharp but broad band at 695–770 cm^{-1} due to the weakened ν (M=O) stretch as a result of M$\cdots$O → M interaction. These observations suggest an octahedral structure for the former while an oligomeric (pseudo-octahedral) or dimeric type structure *via* M$\cdots$O → M interaction for other complexes [10].

The coordination of the ligands is optimized by the shift of their characteristic vibrational modes. For example, the ν(C=N) (azomethine) band of the free ligands appears at 1616–1657 cm^{-1}. In the spectra of the complexes, this band shifts to lower frequency by 3–30 cm^{-1} indicating the coordination of the azomethine nitrogen atom to the metal [11]. The Schiff base exhibit a medium to strong intensity band at 1515–1535 cm^{-1} due to the ν(C—O) (phenolic) vibration. This band shifts to higher frequency by 5–15 cm^{-1} in the complexes thereby indicating the coordination of the phenolic oxygen. The Schiff base **1** and **3** (i.e., derived from *o*-aminobenzylalcohol) display the ν(C—O) (alcoholic) band at 1215 and 1195 cm^{-1}, respectively [1f]. Shift of this band to lower frequency by 14–31 cm^{-1} indicates the coordination of alcoholic oxygen. The coordination of both the oxygens are further supported by the absence of any band ~3400 cm^{-1} which is present in the ligands due to the ν(OH) mode. The presence of such a band only in **2a** may be due to coordinated methanol.

The electronic spectra of the Schiff bases, **1**–**4**, have been reported in detail by Syamal *et al.* [1]. Two electronic spectral bands are observed in the Schiff bases **1** and **2** while three bands are recorded in **3** and **4** (Table 2) in the present study. All these ligand bands are also observed in the complexes but there is no systematic trend in the change of energy. However, considerable change in the extinction coefficient on going from ligand to complex indicates the coordination of ligand to metal. In addition, complexes **1a** and **1b** display a shoulder at *ca* 25,000 cm^{-1} which is assigned to the ligand → metal charge transfer (LMCT) transition between the lowest empty *d*-orbital of metal and the highest occupied ligan molecular orbital [12]. While in other complexes such a LMCT band could not be located unequivocally, due to strong absorption of the ligand in this region.

Further evidence for the coordinating mode of the ligands is obtained from the ^{1}H NMR study of the ligands and their complexes. Table 3 presents the ^{1}H NMR spectral data. The ligands exhibit a singlet at 9.40–13.08 ppm due to the phenolic proton. There is no separate signal due to the phenolic proton of the amine residue. The absence of this resonance in the spectra of the complexes indicates that the coordination of the phenolic oxygen atom(s) to metal after proton replacement. A signal due to an alcoholic proton could not be located in the 0–15 ppm region. A sharp singlet at 8.28–9.04 ppm due to the azomethine proton shifts downfield and resonate at 8.64–9.52 ppm, suggesting the coordination of the azomethine nitrogen [13]. Other resonances due to —CH$_2$ protons and aromatic protons appear at almost the same positions in the ligands as well as in their complexes. The methyl signal at 3.13 ppm present only in [MoO$_2$(sal-OHYBA)·CH$_3$OH] indicates the coordination of methanol to molybdenum. Thus the NMR data agree well with the conclusion drawn from the IR data.

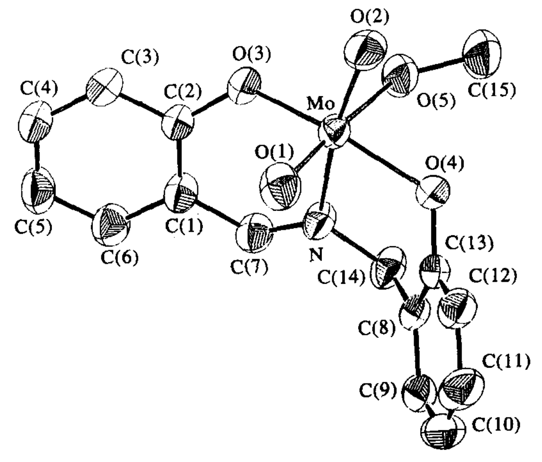

Fig. 1. ORTEP diagram of [MoO$_2$(*o*-OC$_6$H$_4$CH=NCH$_2$C$_6$H$_4$O)(MeOH)]$_2$·MeOH (one of the molecules in the asymmetric unit) along with the crystallographic numbering. Ellipsoids are drawn with 50% probability.

Crystal structure of [MoO$_2$(*o*-OC$_6$H$_4$CH=NCH$_2$C$_6$H$_4$O)(MeOH)]$_2$·MeOH

The single crystal X-ray diffraction study of the title compound revealed that the asymmetric unit consists of two [MoO$_2$(sal-OHYBA)(MeOH)] molecules having a similar conformation and a solvated methanol. An ORTEP diagram of one such molecule with crystallographic numbering of the atoms is given in Fig. 1. Table 5 gives selected bond lengths and bond angles. The complex contains a *cis* dioxo group, as was observed in a similar dioxomolybdenum(VI) complex [14]. The tridentate ligand occupies a meridional position where two anionic oxygens are mutually *trans* and are *cis* to the two oxo groups. A methanol molecule forms the sixth coordination site and is *trans* to one of the oxygens of ligand. Thus molybdenum acquires a distorted octahedral structure. The *cis* bond angles range from 75.0(1) to 106.2(2)° and the *trans* angles from 154.8(1) to 168(1)°. The Mo–ligand bond distances in the two molecules are quite similar except for the Mo—O(4) length which differs by 0.04 Å. Moreover, the C(13)—O(4) bond length also varies by 0.02 Å. These could be attributed to the fact that O(4) is involved in hydrogen bonding while O(4′) is not. The Mo—O(5) (methanol) distances are relatively longer [average 2.303(4) Å] than other Mo—O distances.

The crystal structure is stabilized by hydrogen bonding. The hydroxy group, O(6) of the solvent methanol molecule forms two hydrogen bondings; one to O(5) of coordinated methanol with a distance of 2.606 Å and the other to an oxygen of the dioxo group, O(1′) (at $1-x, 1-y, 1-z$) and distance 2.767 Å). There is another hydrogen bond (distance 2.721 Å) between O(4) and O(5′) (at $x, 1+y, z$), which suggests that the hydroxyl group of the ligand methanol is not deprotonated.

Table 5. Selected bond lengths (Å) and angles (°) for $C_{31}H_{31}Mo_2N_2O_{11}$

Mo—O(1)	1.685(3)	O(1)—Mo—O(2)	106.6(2)
Mo—O(2)	1.697(3)	O(1)—Mo—O(3)	97.15(13)
Mo—O(3)	1.942(3)	O(2)—Mo—O(3)	98.63(12)
Mo—O(4)	1.960(2)	O(1)—Mo—O(4)	96.67(13)
Mo—O(5)	2.303(3)	O(2)—Mo—O(4)	96.82(12)
Mo—N	2.313(3)	O(3)—Mo—O(4)	155.90(11)
O(3)—C(2)	1.348(4)	O(1)—Mo—O(5)	167.91(12)
O(4)—C(13)	1.362(4)	O(2)—Mo—O(5)	85.35(13)
O(5)—C(15)	1.424(5)	O(3)—Mo—O(5)	79.82(10)
N—C(7)	1.274(5)	O(4)—Mo—O(5)	83.19(10)
N—C(14)	1.479(5)	O(1)—Mo—N	92.65(13)
C(1)—C(6)	1.404(6)	O(2)—Mo—N	160.71(13)
C(1)—C(2)	1.398(6)	O(3)—Mo—N	79.26(11)
C(1)—C(7)	1.443(6)	O(4)—Mo—N	80.03(11)
C(2)—C(3)	1.397(5)	O(5)—Mo—N	75.42(10)
C(3)—C(4)	1.380(6)	C(2)—O(3)—Mo	128.9(2)
C(4)—C(5)	1.376(7)	C(13)—O(4)—Mo	123.6(2)
C(5)—C(6)	1.377(6)	C(15)—O(5)—Mo	126.5(3)
C(8)—C(9)	1.388(6)	C(7)—N—C(14)	117.9(3)
C(8)—C(13)	1.390(6)	C(7)—N—Mo	124.3(3)
C(8)—C(14)	1.504(6)	C(14)—N—Mo	117.8(2)
C(9)—C(10)	1.376(7)	C(6)—C(1)—C(2)	118.9(4)
C(10)—C(11)	1.377(8)	C(6)—C(1)—C(7)	118.9(4)
C(11)—C(12)	1.386(7)	C(2)—C(1)—C(7)	122.2(3)
C(12)—C(13)	1.380(6)	O(3)—C(2)—C(3)	118.4(3)
O(6)—C(16)	1.331(10)	O(3)—C(2)—C(1)	121.8(3)
		C(3)—C(2)—C(1)	119.7(3)
		C(4)—C(3)—C(2)	120.0(4)
		C(5)—C(4)—C(3)	120.9(4)
		C(4)—C(5)—C(6)	119.8(4)
		C(5)—C(6)—C(1)	120.8(4)
		N—C(7)—C(1)	125.1(3)
		C(9)—C(8)—C(13)	119.0(4)
		C(9)—C(8)—C(14)	123.3(4)
		C(13)—C(8)—C(14)	117.7(3)
		C(10)—C(9)—C(8)	120.4(4)
		C(11)—C(10)—C(9)	120.2(4)
		C(10)—C(11)—C(12)	120.5(4)
		C(13)—C(12)—C(11)	119.2(4)
		O(4)—C(13)—C(12)	120.1(4)
		O(4)—C(13)—C(8)	119.0(3)
		C(12)—C(13)—C(8)	120.9(4)
		N—C(14)—C(8)	108.9(3)

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