Molybdenum(VI) *cis*-Dioxo Complexes with Chiral Schiff Base Ligands: Synthesis, Characterization, and Catalytic Applications

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Three optically active Molybdenum (VI) dioxo complexes with tetrahydro salen and substituted tetrahydro salen derivatives as ligands were synthesized and examined as catalysts for asymmetric epoxidation. Complexes of the type MoO_2(L)(Solv) and WO_2(L) (L = tridentate, *trans*-2-aminocyclohexanol derived chiral Schiff base, Solv = alcohol) were prepared and characterized by elemental analysis, NMR and IR spectroscopy. These complexes are applicable as catalysts for olefin epoxidation reactions with *tert*-butyl hydroperoxide (TBHP) being the oxidizing agent. In case of *cis*-β-methylstyrene moderate enantiomeric excesses of up to 26% can be reached when the reaction is carried out at 0 °C.

Key words: Catalysis, Chirality, Epoxidation, Molybdenum, Salen

Introduction

Enantiopure epoxides are highly valuable chiral synthons useful for the synthesis of various biologically active molecules [1]. For the preparation of chiral epoxides, the transition metal-catalyzed enantioselective epoxidation of different organic substrates is of the utmost importance and has been widely studied over the past decades [2]. The generally good catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions make this type of complexes – in principle – promising candidates for asymmetric catalysis by using chiral ligands [3]. 2'-Pyridyl alcohols and phosphino alcohols [4] have been reported to induce *ee*'s of 20 – 40% for functionalized olefins when coordinated to dioxo or peroxo molybdenum(VI) fragments. In this context, we and others have reported on the synthesis of a variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline, *cis*-diol and *cis*-8-phenylthiomenthol [5]. Recently we reported also the synthesis of some molybdenum(VI)-*cis*-dioxo complexes bearing sugar derived chiral Schiff base ligands of general formula MoO_2(L')(Solv), which showed moderate enantiomeric induction of *ca.* 30% *ee* for the epoxidation of *cis*-β-methyl styrene [6].

The pioneering studies by the groups of Katsuki [7] and Jacobsen [2] have led to a variety of chiral Mn(III) salen-based catalysts which epoxidized non-functionalized alkenes with high enantioselectivity. Manganese salen complexes are regarded as the most efficient catalysts for enantioselective epoxidation of unfunctionalized olefins [8]. More recently, chromium oxo complexes bearing salen ligands were also examined for the asymmetric epoxidation of *trans*-methylstyrene reaching *ee*'s up to 90% [9]. Although Mo(VI)-dioxo complexes bearing tetradentate salen ligands have been prepared and spectroscopically characterized 20 years ago [10, 11], to the best of our knowledge, their catalytic application for epoxidation reactions has not been, so far, explored. In this work, optically active Molybdenum (VI) dioxo complexes bearing tetrahydro salen and substituted tetrahydro salen derivatives as ligands were synthesized and tested for their catalytic activity. Additionally, some molybdenum and tungsten dioxo complexes with tridentate Schiff base ligands were prepared and their catalytic activity in olefin epoxidation was investigated.

Results and Discussion

Synthesis and spectroscopic examinations

The preparation of ligand **1** was performed according to literature procedures [12] by condensation

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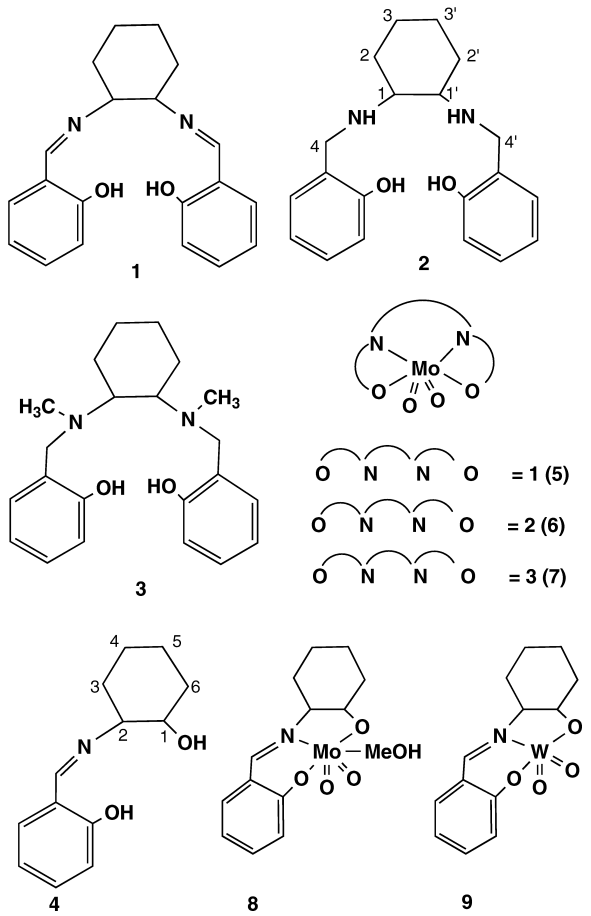

Chart 1.

of salicyl aldehyde and 1,2-diamino cyclohexane in methanol. Ligands **2** and **3** were prepared from ligand **1** by reduction with $NaBH_4$ and $Na[(CN)BH_3]$ in CH_3CN, respectively, according to literature procedures [11, 13]. The related chiral ligands were prepared using (1R, 2R)-(-)-1,2-diamino cyclohexane as starting material. The corresponding Mo-complexes **5** and **7** were synthesized by reacting $MoO_2(acac)_2$ with 1.1 equivalents of the respective ligands in methanol according to literature procedures [10, 11]. Compound **6** was prepared by a similar method. Ligand **4** was prepared by the condensation of salicylaldehyde and (+,-) *trans*-2-aminocyclohexanol in methanol. Complexes **8** and **9** were synthesized by the reaction of $MoO_2(acac)_2$ and $WO_2(acac)_2$ with ligand **4** in methanol.

All complexes are fairly air stable as solids, albeit decomposition occurs slowly in solution and the colour changes from yellow to green in the presence of moisture.

The proton signals of compounds **2, 3, 6** and **7** were determined by H-H COSY-NMR spectroscopy. Comparing the chemical shifts of ligand **2** and complex **6**, being formed after coordination of **2** to a MoO_2-moiety, the H-5 and H-5' signals are shifted to lower field, since the shielding effect of the neighbouring N atom decreases due to coordination to the Mo centre. The same effect can be observed for the chemical shifts of H-1 and H-1' as well as H-2 and H-2'. Unfortunately, it was not possible to obtain crystals of sufficient quality for determining the X-ray crystal structure of compound **6**. Nevertheless, according to the NMR and IR data the structure of **6** should be very similar to that of compounds **5** and **7**, which have been published elsewhere [10, 11].

Elementary analysis of the compounds **8** and **9** suggests that both complexes contain a dioxo metal moiety, thus giving evidence for the monomeric nature of these complexes. IR spectroscopy further shows, that the metal-oxygen bonds are in the typical M=O region for both molecules. Mass spectrometry also gave no hint for the presence of dimeric species [14] or indicative fragments, the molecular mass $m/z = 345$ and 433 was found for **8** and **9**, respectively, and there are no other peaks originating from fragments of dimeric molecules at higher molecular masses. The same products (**8** and **9**) were formed when two equivalents of ligand **4** were used in the synthesis.

Interestingly, the NMR and elemental analysis as well as the MS results indicate that in complex **8** molybdenum is hexa-coordinated, bearing a dioxo moiety, the tridentate ligand and a methanol molecule. This is in accordance with the coordination behaviour of other molybdenum dioxo complexes bearing tridentate Schiff base ligands [6]. For the tungsten analogue **9**, however, there is no hint for the presence of a coordinated solvent molecule, and both spectroscopic and elemental analysis indicated a penta-coordinated W core.

It was previously observed that during the reaction of a molybdenum(VI)-*cis*-dioxo species with a β-configurated glucosamine derived chiral Schiff base ligand an inversion of the β-configuration into α-configuration occurs [6]. This interesting configuration transformation prompted us to further examine the interaction between the molybdenum dioxo starting material and other ligands with comparable configuration to the above mentioned sugar derived ligands. Ligand **4** shows the OH and imine group in the cyclohexane ring in *trans*-configuration, *i. e.* β-configuration with

Table 1. Selected ^{1}H NMR chemical shifts and coupling constants.

	trans-2-Aminocyclohexanol hydrochloride	**4**	**8**	**9**
δ Ring H-1 [ppm]	3.49	3.64	3.67	3.69
$J_{1,2}$ [Hz]	15.88	16.38	14.18	16.64

$J_{1,2} = 16.38$ Hz. After coordination to Mo or W, the coupling constants $J_{1,2}$ are 14.18 Hz and 16.64 Hz, respectively. This suggests that in this case no configuration inversion occurs during coordination. This observations seems further to indicate that the inversion of configuration follows a ring opening mechanism of the sugar ring, which in this case is not available, since cyclohexane can not undergo ring opening reactions as can oxygen containing rings, as applied in our earlier experiments [6]. Representative chemical shifts and coupling constants are listed in Table 1.

Complexes **5 – 9** *in oxidation catalysis*

Complexes **5 – 9** were examined as catalysts in the epoxidation of cyclooctene. The chiral complexes **6 – 7** were used also in the asymmetric epoxidation both of *cis*- and *trans*-β-methylstyrene. TBHP was used as the oxidant. Details about the conditions applied are given in the experimental section. Blank runs were performed and, as expected, without catalyst, no significant epoxide formation was observed under the applied conditions.

In general, complexes **5 – 8** catalyzed the epoxidation of all three examined alkenes with moderate activity and complete stereo-retention, without significant by-product formation, the selectivity being close to 100%. When the catalyst: substrate: oxidant ratio is 1:100:200, for cyclooctene, the yield reaches after 4 h a value of 20 – 35%, and after 22 h of 65 – 70% in all examined cases. The substituent at the N atom seems to have little effect on the catalytic behaviour, as it can be seen from the performance of compounds **5 – 7**. Despite having different coordination behaviour, complexes **5** and **8** show a quite similar catalytic activity. This, however, is probably due to their poor solubility in the oxidation solution. There is a strong decrease in activity on going from molybdenum to tungsten. Accordingly, the lowest activity is found for catalyst **9**, after 4 h only 5% yield can be obtained, while 25% were reached after 24 h, when the catalyst:substrate:oxidant ratio is 1:100:200.

For the asymmetric epoxidation of *cis*- and *trans*-β-methylstyrene, the general observation is that the asymmetric induction for the *cis* substrates is much better than that for the *trans* analogues, whereas higher conversions can be obtained with the *trans* substrate. Unfortunately, at lower temperatures the conversions are rather low, when the best *ee*'s can be achieved, at higher temperatures the conversions increase considerably but the *ee*'s decrease dramatically probably due to easier ligand displacement during the catalytic cycle. The effects of solvent and the amount of catalyst used have also been studied. Within the experimental error the results are the same in both CH_2Cl_2 and toluene as solvent, although compounds **5 – 7** are more soluble in CH_2Cl_2 than in toluene. Higher amounts of catalyst also improve both *ee* and yield. Accordingly, the highest observed *ee* of *ca.* 26% could be obtained with compound **5** as catalyst at 0 °C. Compounds **6** and **7** show a poor chiral induction for *cis*- and *trans*-β-methylstyrene even at 0 °C (Table 3). This indicates that the reduction of imine to amine does not have a positive influence on the *ee* values obtained, regardless, whether a hydrogen or a methyl group is coordinated to the amine nitrogen.

Table 2. Epoxidation of cyclooctene catalyzed by complexes **5 – 9** at 55 °C.

	Conversion or yield	
Compound	4 h	22 h
5	30	65
6	20	71
7	22	66
8	35	72
9	5	25

Table 3. Epoxidation of *cis*- and *trans*-β-methylstyrene catalyzed by compounds **5 – 7** at 0 °C.

Compound	*cis*-Methylstyrene			*trans*-Methylstyrene		
	Conversion		*ee*	Conversion		*ee*
	4 h	22 h		4 h	22 h	
5	6.5	11.8	25.8	11.8	32.5	14.9
6	5.7	13.7	7.81	14.4	38.3	7.35
7	6.4	13.1	4.72	12.9	34.7	3.76

Conclusions

Three optically active molybdenum (VI) dioxo complexes bearing tetrahydro salen and substituted tetrahydrosalen derivatives ligands were synthesized and tested as catalysts for asymmetric epoxidation. With *cis*-β-methylstyrene moderate enantiomeric excesses of up to 26% can be reached with compound **5** at 0 °C. Using a chiral amine instead of an imine improves neither the catalytic activity nor the chiral induction.

Complexes of the types $MoO_2(L)(Solv)$ and $WO_2(L)$ (L = tridentate, *trans*-2-aminocyclohexanol derived chiral Schiff base) are easily prepared by the reaction of the ligand L with $MoO_2(acac)_2$ or $WO_2(acac)_2$ in alcohols as the solvent. All examined Mo compounds show good to moderate activity for olefin epoxidation, while the W analogue displays quite low epoxidation activity. A comparison of the coupling constant of $J_{1,2}$ before and after coordination to the metal, indicates that there is no inversion of configuration from β to α, as it has been observed earlier for sugar derived Schiff base ligands.

Experimental Section

All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. Solvents and substrates were dried by standard procedures, distilled, and kept under argon over molecular sieves. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching (M. Barth). ^{1}H, ^{13}C, and H-H COSY NMR spectra were obtained with a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. Mass spectra were carried out in a Finnigan MAT 311 A and a MAT 90 spectrometers.

Preparation and characterization of **1 – 9**

Ligands **1**, **2** and **3** were prepared according to literature procedures [11 – 13]. The related chiral ligands were prepared using (1R, 2R)-(-)-1,2-diaminocyclohexane as starting material. The preparation of chiral complexes **5** and **7** was performed according to established procedures [10, 11]. The proton signals of compounds **2, 3, 6** and **7** were determined by H-H COSY NMR spectroscopy. $WO_2(acac)_2$ was prepared according to [15].

2: IR (KBr): ν = 3444br (νOH), 3318w (νNH), 2930, 2850, 1590s (aryl), 1455vs, 1259vs, 1151m, 1098s, 908m, 757vs cm^{-1}; – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 – 6.76 (m, 8H, aryl-H), 4.06 (d, 2H, H-5), 3.94 (d, 2H, H-5'), 2.45 (t, 2H, H-1and H-1'), 2.14 (m, 2H, H-2) 1.69 (m, 2H, H-2'), 1.23 – 1.14 (m, 4H, H-3 and H-3'); - MS: $M^+ + 1 = 327$.

3: IR (KBr): ν = 3445br (νOH), 2943, 2863, 1580s (aryl), 1486vs, 1456m, 1365m, 1283m, 1240s, 1116w, 1022w, 763s cm^{-1}; – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 – 6.76 (m, 8H, aryl-H), 3.84 (d, 2H, N-CH_2 or H-5), 3.62 (d, 2H, N-CH_2' or H-5'), 2.70 (m, 2H, N-CH-ring or H-1and H-1'), 2.21 (s, 6H, N-CH_3), 2.00 (m, 2H, CH_2-ring or H-2), 1.79 (m, CH_2'-ring or H-2'), 1.23 – 1.12 (m, 4H, CH_2-ring or H-1 and H-1'); – MS: M^+ = 354.

4: 500 mg (3.3 mmol) of *trans*-2-aminocyclohexanol hydrochloride and 277 mg of $NaHCO_3$ were dissolved in 5 ml of water. To this solution 0.38 ml (3.6 mmol) of salicyl aldehyde were added. After a few minutes, a bright yellow solid precipitated. The mixture was further stirred for 2 h, the precipitate was collected by filtration and washed with water and then re-crystallised from methanol. Yield: 75%. – IR (KBr): ν = 3359 br s, 3048w, 2935s, 2860m, 1633vs (νC=N), 1578m, 1492s, 1461m, 1397m, 1274s, 1041s, 751vs, 734m cm^{-1}; – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.30 (s, br, OH), 8.40 (s, 1H, CH=N), 7.28 (m, 2H, aryl-H), 6.93 (m, 1H, aryl-H), 6.86 (m, 1H, aryl-H), 3.64 (six, $J_{1,2}$ = 16.38 Hz, 1H, ringH-1), 2.98 (m, 1H, ring H-2), 2.05 (m, 1H, ring-H), 1.78 (m,3H, ring H), 1.62 (m, 1H, ring H), 1.35 (m, 3H, ring H); MS: M^+ = 219. – $C_{13}H_{17}NO_2$ (219): calcd. C 71.23, H 7.76, N 6.39; found C 71.21, H 7.82 N 6.31.

6: 0.31 mmol of **2** and 0.29 mmol of $MoO_2(acac)_2$ were dissolved in 10 ml of dried MeOH yielding a clear yellow solution. After stirring for half an hour, a yellow solid precipitated. The precipitate was washed with diethyl ether twice and dried under vacuum to yield 95 mg of product. Yield: 70%. – IR (KBr): ν = 3278m, 3179s (νNH), 2928m, 2856w, 1597m, 1572m, 1482s, 1449s, 1256s, 1228s, 1098m, 1013m, 920s (νMo=O), 893sm 878s, 766m, 751m, 638s, 502m cm^{-1}; – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 – 6.80 (m, 8H, aryl-H), 5.30 (d, 2H, H-5), 4.22 (d, 2H, H-5'), 2.65 (t, 2H, H-1 and H-1'), 2.33 (m, 2H, H-2) 1.73 (m, 2H, H-2'), 1.11 – 1.06 (m, 4H, H-3 and H-3'); MS: $M^+ + 1$ = 453. – $C_{20}H_{24}O_4N_2Mo$ (452): calcd. C 53.10, H 5.31, N 6.19; found C 53.21, H 5.22 N 6.21.

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 – 6.82 (8H, m, aryl-H), 5.07 (d, 2H, H-5), 3.68 (d, 2H, H-5'), 2.65 (t, 2H, H-1 and H-1'), 2.60 (s, 6H, H-4 and H-4'), 1.82 (d, 2H, H-2), 1.64 (t, 2H, H-3), 1.15 (d, 2H, H-2'), 0.86 (t, 2H, H-3'); – ^{13}C {^{1}H}NMR (100.28 MHz, $CDCl_3$): δ = 159.26, 129.54, 129.40, 122.28, 120.68, 118.40 (aryl), 61.45 (N-CH_3), 58.14 (N-CH_2), 42.53 (CH-ring), 24.22 (CH_2-ring), 21.95 (CH_2-ring).

8: A solution of 220 mg (0.68 mmol) of $MoO_2(acac)_2$ in 10 ml dried methanol was treated with 150 mg (0.69 mmol) of **4**. After a few minutes a bright yellow precipitate formed. The mixture was stirred for further 2 h and the precipitate filtered, washed with diethyl ether and dried under vacuum. Yield: 80%. – IR (KBr): ν = 3429 br, m, 2936m, 2862w, 1637vs (νC=N), 1600m, 1556m, 1450m, 1287s, 1040m, 928vs (ν_{sym}Mo=O), 907vs (ν_{asym}Mo=O), 842s, 756m cm^{-1}; – ^{1}H NMR (400 MHz, CD_3OD): δ = 8.44 (d, J = 2.44 Hz, 1H, CH=N), 7.51 (m, 1H, aryl-H), 7.38 (m, 1H, aryl-H), 6.88 (m, 2H, aryl-H), 3.67 (six, $J_{1,2}$ = 14.18 Hz, 1H, ring H-1), 3.23 (s, 3H, CH_3 of methanol), 3.09 (m, 1H, ring H-2), 2.47 (d, 1H, ring H-3), 2.07 (d, 1H, ring H-3'), 1.86 (d, 1H, ring H-6), 1.80 (t, 1H, ring H-6'), 1.36 (m, 4H, ring H-4 and H-5); – ^{13}C {^{1}H}NMR (100.28 Hz, d^6-DMSO): δ = 161.26 (C=N), 159.90, 134.49, 134.31, 121.29, 119.26

and 119.16 (aryl), 85.43 (ring C-1), 70.34 (ring C-2), 48.63 (CH_3 of methanol), 33.82 (ring C-3), 27.68 (ring C-6), 23.89 (ring C-4), 23.62 (ring C-5); MS: M^+-CH_3OH = 345, M^+-CH_3OH +2 = 347. – $C_{14}H_{19}O_5NMo$ (377): calcd. C 44.56, H 5.04, N 3.71; found C 43.91, H 4.97 N 3.61.

9: A solution of 197 mg (0.48 mmol) of $WO_2(acac)_2$ in 25 ml dried methanol was treated with 109 mg (0.5 mmol) of **4**. After 2 – 3 minutes the clear yellow solution turned unclear and the light yellow precipitate formed more and more. The mixture was stirred for 2 h and the precipitate was filtrated and washed with diethyl ether, then dried under vacuum. Yield: 77%. – IR (KBr): ν = 3435 br m, 2936m, 2864w, 1643vs (νC=N), 1600m, 1560m, 1479m, 1451s, 1285s, 1042m, 938vs (ν_{sym} W=O), 915vs (ν_{asym} W=O), 830s, 784vs, 757vs, 686s cm^{-1}; – ^{1}H NMR (400 MHz, d^6-DMSO): δ = 8.49 (d, J = 2.04 Hz, 1H, CH=N), 7.68 (dd, 1H, aryl-H), 7.52 (m, 1H, aryl-H), 6.96 (m, 2H, aryl-H), 3.69 (six, $J_{1,2}$ = 16.64 Hz, 1H, ring H-1), 3.25 (m, 1H, ring H-2), 2.47 (d, 1H, ring H-3 was covered by DMSO), 2.01 (d, 1H, ring H-3'), 1.80 (s, 2H, ring H-6), 1.34 (m, 4H, ring H-4 and H-5); – ^{13}C {^{1}H}NMR (100.28 Hz, d^6- DMSO): δ = 160.69 (C=N), 160.24, 135.04, 134.42, 121.98, 119.85 and 119.71 (aryl), 83.82 (ring C-1), 70.54 (ring C-2), 34.36 (ring C-3), 27.56 (ring C-6), 24.02 (ring C-4), 23.60 (ring C-5); **MS**: M^+ = 433. – $C_{13}H_{15}O_4NW$ (433): calcd. C 36.04, H 3.47, N 3.23; found C 35.75, H 3.81, N 3.14.

Catalytic reactions with compounds **5** – **9** *as the catalysts*

Cyclooctene epoxidation: *cis*-cyclooctene (800 mg, 7.2 mmol), mesitylene (1g, internal standard), 1 mol% (72 μmol) of compounds **5** – **9** as catalyst were added to the reaction vessel. With the addition of TBHP (2 ml, 5.5 M – 6.0 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

Chiral epoxidation: *cis*-, or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and 1 mol% (17 μmol), 5 mol% and 10 mol% of the compounds **5** – **7** as catalysts and 2 ml toluene as solvent were added to the reaction vessel. With the addition of TBHP (450 μl, 7.5 M in toluene) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated from the area ratio of the peaks corresponding to both epoxides formed.

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