Intramolecular oxidation of the ligand 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol (Hpyramol) upon coordination with iron(II) chloride and manganese(II) perchlorate

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Abstract

The ligand Hpyramol (Hpyramol = 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol) is found to undergo an oxidative dehydrogenation of its amine function to an imine group upon coordination with iron(II) chloride and manganese(II) perchlorate. X-ray diffraction analyses for both complexes shows differences in the coordination geometry of the complexes most likely because of the two different counter-ions namely the strong coordinating chloride anions and the weak coordinating perchlorate anions. The coordination sphere of the iron(III) complex in [FeCl$_2$(pyrimol)(MeOH)](MeOH) is best described as a distorted octahedral FeN$_2$O$_2$Cl$_2$ chromophore, while the manganese(II) ions in [Mn(ClO$_4$)(pyrimol)(Hpyrimol)]$_2$ are in a distorted octahedral MnN$_4$O$_2$ environment with a 2:1 ligand to metal ratio instead of 1:1.
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1. Introduction

Iron- and manganese-catalyzed oxidation reactions play an important role, not only in synthetic organic chemistry [1,2], but also in biotransformations [3,4]. Consequently, polydentate N,O-containing ligands are continuously developed both to prepare catalysts, and to model the active site of enzymes [5,6].

Transition-metal ions can also contribute in the oxidation of coordinated organic ligands [7]. Thus, primary or secondary amino group-containing ligands can undergo a metal-assisted oxidative dehydrogenation to the corresponding imine. This phenomenon was first reported in 1971 by a few research groups, who observed it with metal ions such as copper, nickel or ruthenium [8–11].

The present paper describes the preparation and characterisation of two new potential oxidation catalysts, namely [FeCl$_2$(pyrimol)(MeOH)](MeOH) and Mn(ClO$_4$)-(pyrimol)(Hpyrimol)]$_2$, obtained from 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol (Hpyramol) [12] which was oxidized to 4-methyl-2-*N*-(2-pyridylmethylene)aminophenol (Hpyrimol) upon coordination with the metal salts (Fig. 1). This Hpyramol ligand was reported in 2002 by Wong et al. [12] as tungstate and molybdate complexes for the catalysed-epoxidation of styrene. Nevertheless, no crystal structure with this ligand could be found in the Cambridge Structural Databse (January 2004 update) [13].

2. Experimental

2.1. Materials and methods

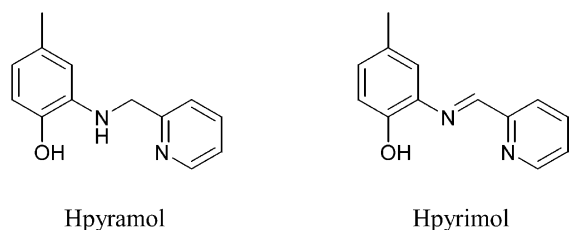All starting materials were commercially available and used as received. Infrared spectra were recorded on

Fig. 1. Reduced (Hpyramol) and oxidized (Hpyrimol) forms of the ligand.

a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond, and peaks are reported in cm^{-1}. Vis–NIR spectra were measured on a Perkin–Elmer Lambda 900 spectrophotometer, using the diffuse reflectance technique, with MgO as a reference. Mass Spectrometry experiments were performed on a Finnigan MAT TSQ-700 equipped with a custom made electropray interface (ESI). Spectra are collected by constant infusion of the analyte dissolved in methanol/water with 1% acetic acid. ^1H NMR spectra were recorded on a Jeol JNM FX-200 (200 MHz) instrument. Chemical shifts are reported in δ (parts per million) relative to an internal standard of tetramethylsilane. C,H,N-analyses were performed on a Perkin–Elmer 2400 series.

2.2. Synthesis of 4-methyl-2-N-(2-pyridylmethyl)aminophenol (Hpyramol)

The ligand Hpyramol (3) was prepared by reductive amination starting from 2-amino-4-methylphenol (1) and picolinaldehyde (2), according to the experimental procedure reported by Wong et al. [12] with slight modifications (see Fig. 2).

A solution of 12.4 g (0.1 mol) of 1 and 10.7 g (0.1 mol) of 2 in 200 mL of MeOH was refluxed for 2 h in a three-necked round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The resulting reaction mixture was cooled to 0 °C with an ice-water bath and 7.6 g (0.2 mol) of $NaBH_4$ were carefully added portion-wise during a period of 1 h (CAUTION: brisk evolution of gas took place at this stage!). After completion of the addition, the temperature was slowly raised to 65 °C and the solution was refluxed for 3 h.

After this time, the volatiles were removed under reduced pressure and a brown residue was obtained. This residue was redissolved in 100 mL of H_2O and its pH was adjusted to 7 with 25 mL of glacial acetic acid. The aqueous phase was extracted with ethyl acetate (3×150 mL) and the resulting organic extract was dried over anhydrous $MgSO_4$. A yellow-brown solid was obtained after evaporation of the solvent under reduced pressure. This solid was redissolved in 50 mL of CH_2Cl_2 and a brown precipitated appeared in. After filtration over a glass-filter, 18 g of 3 was obtained as a light brown powder.

$C_{13}H_{14}N_2O$; Mol. wt.: 214.26; Yield: 85%. ^1H NMR ($CDCl_3$, 200 MHz) δ 2.19 (s, 3H, CH_3), 4.50 (s, 2H, CH_2), 6.42 (d, 1H, C–H_{arom}), 6.44 (s, 1H, C–H_{arom}), 6.68 (d, 1H, CH_{arom}), 7.21 (dd, 1H, 5-py-H), 7.38 (d, 1H, 3-py-H), 7.67 (dd, 1H, 4-py-H), 8.58 (d, 1H, 6-py-H) ppm; IR (neat) 3393, 2918, 1595, 1524, 1446, 1215, 1008, 801, 761, 619, 404 cm^{-1}; MS (ESI): *m/z* 215 (M + H).

2.3. [FeCl₂(pyrimol)(MeOH)](MeOH) (4)

A solution of HPyramol (0.5 g, 2.33 mmol) in MeOH (20 mL) was added to a solution of $FeCl_2 \cdot 4H_2O$ (0.2 g, 1.01 mmol) in MeOH (20 mL). A green solution was formed upon addition. After a few days, 216 mg (yield: 53%) of green single-crystals of 4, suitable for X-ray crystallography, were obtained, which were collected by filtration. IR (neat) 1654, 1597, 1474, 1081, 1010, 826, 776, 668, 622 cm^{-1}. *Anal.* Calc. for $C_{15}H_{19}Cl_2FeN_2O_3$: C, 44.81; H, 4.76; N, 6.97. Found: C, 45.13; H, 4.42; N, 6.85%.

2.4. [Mn(ClO₄)(pyrimol)(Hpyrimol)]₂ (5)

A solution of HPyramol (0.3 g, 1.40 mmol) in MeOH (20 mL) was added to a solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.16 g, 0.44 mmol) in MeOH (20 mL). A dark red-brown solution was formed upon addition. After a few hours, 73.6 mg (yield: 29%) of dark-red single-crystals of 5, suitable for X-ray crystallography, were obtained, which were collected by filtration. IR (neat) 3630, 1654, 1597, 1081, 1485, 1290, 1074, 812, 668, 482 cm^{-1}. *Anal.* Calc. for $C_{26}H_{23}ClMnN_4O_6$: C, 54.04; H, 4.01; N, 9.70. Found: C, 53.52; H, 4.24; N, 9.64%.
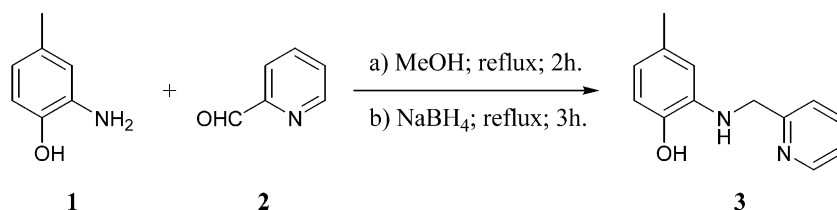

Fig. 2. Synthesis of Hpyramol (3).

2.5. X-ray structure determinations

2.5.1. Compound 4

Diffraction data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. The data were processed using the DENZO program [14]. The structure was solved by direct methods with SIR97 [15]. The positions of the hydrogen atoms were obtained from the difference Fourier maps. Full-matrix least-squares refinements on F magnitudes with anisotropic displacement factors for all non-hydrogen atoms were employed using Xtal3.6 [16]. Positional parameters of hydrogen atoms were refined together with their isotropic displacement factors. In the final cycle of the refinement, 3735 reflections and 284 parameters were used (the 'unobserved' reflections for which F_c was larger than F_o were included in the refinement).

2.5.2. Compound 5

Data collection and cell refinement were carried out on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [17] and refined with SHELXL-97 [18] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups, allowing for rotation of the Me and OH groups around the bonds linking them to the complex. The crystal structure of **5** contains two

symmetry related cavities located on crystallographic inversion centres, with a volume of 206 Å^3 each. The cavities are filled with disordered solvent for which no acceptable atomic model could be obtained. The contribution of this solvent to the structure factors has been calculated using the PLATON/SQUEEZE method [19]. A total number of 36 e was found in each cavity, corresponding to two methanol molecules per cavity (see Table 1).

3. Results and discussion

3.1. Description of the structure of [FeCl₂(pyrimol)-(MeOH)](MeOH) (4)

Reaction of $FeCl_2 \cdot 4H_2O$ in methanol with Hpyramol in air yields dark green crystalline parallelepipeds of [FeCl₂(pyrimol)(MeOH)](MeOH) (**4**). A PLATON [20] plot of **4** is given in Fig. 3. Compound **4** crystallizes in the monoclinic space group $P2_1/n$. The iron(II) atom has been oxidised to iron(III). This iron(III) center is located in a distorted octahedral environment formed by one tridentate deprotonated pyrimol ligand (N(1)–C(8) distance of 1.2771(17) Å [21]) resulting from the intramolecular oxidation of Hpyramol, two chloride anions and one methanol molecule. A mechanism for the iron-assisted oxidation of a related ligand was proposed by Morgenstern-Badarau et al. [22]. The imino form of the oxidised ligand is supported by the bond lengths and angles within the –N(1)=C(8)– moiety [21], and by the difference Fourier maps which revealed that only one H-atom was attached to C(8) and none to N(1) (see Fig. 3). Furthermore, the planarity of the ligand and the torsion angles close to 0 or 180° in the vicinity of C(8) and N(1), corroborate an sp² hybridisation of these two atoms. The distortion observed is likely due to the rigidity of the flat imine ligand. Thus, the axial angle Cl(1)$_{axial}$–Fe–O(2)$_{axial}$ is 168.74(3)°. The equatorial plane is formed by two nitrogen atoms from the organic ligand, one oxygen

Table 1
Crystal data and details of data collection and structure refinement for **4** and **5**

	Complex **4**	Complex **5**
Formula	$C_{14}H_{16}Cl_2FeN_2O_2$, CH_4O	$C_{26}H_{23}MnN_4O_2$, ClO_4[a]
Formula weight	403.08	577.87[a]
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1c$ (no. 14)
a (Å)	13.7680(2)	19.276(2)
b (Å)	7.6693(1)	16.501(2)
c (Å)	16.5857(3)	18.923(2)
β (°)	99.3263(10)	113.921(12)
V (Å^3)	1728.15(5)	113.921(12)
Z	4	8
D_c (g cm^{-3})	1.545	1.395[a]
$F(000)$	828	2376[a]
μ (mm^{-1})	1.196	0.623[a]
Crystal dimensions (mm)	$0.32 \times 0.16 \times 0.14$	$0.15 \times 0.20 \times 0.30$
Temperature (K)	150	150
$\theta_{min,max}$ (°)	2.9, 27.5	1.00, 27.48
Reflections collected	24487	138719
Independent reflections	3945	12619
$R[F_0 > 4\sigma(F_0)]$	0.031	0.050
wR_2	0.022	0.119
$\Delta\rho_{min,max}$ (e Å^{-3})	−1.15/0.52	−0.36/0.40
S	1.07	1.06

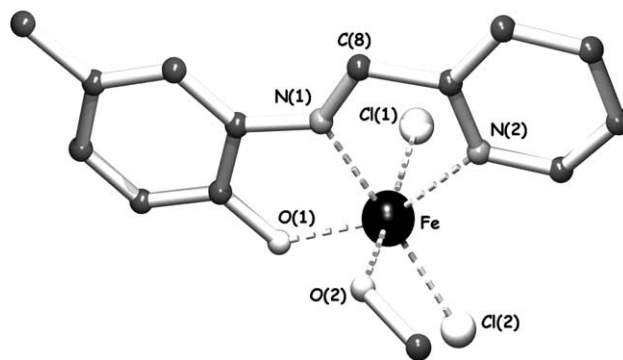[a] Excluding disordered solvent contribution.

Fig. 3. PLATON [20] projection for **4**. Hydrogen atoms are omitted for clarity.

atom from a deprotonated phenol moiety and one chloride anion.

The $N_{equatorial}$–Fe–$N_{equatorial}$, $O_{equatorial}$–Fe–$N_{equatorial}$, $O_{equatorial}$–Fe–$Cl_{equatorial}$, $Cl_{equatorial}$–Fe–$N_{equatorial}$ angles vary from 74.141(4) to 102.20(3)°. The in-plane Fe–N distances of 2.1416(10) (Fe–N(1)) and 2.1815(11) Å (Fe–N(2)) can be regarded as normal, as well as the Fe–O(1) distance of 1.9522(8) Å and the Fe–Cl(2) of 2.2601(3) Å [23]. The axial positions are occupied by Cl(1) at a distance of 2.3256(3) Å and by the oxygen atom O(2) of a coordinated methanol molecule (Fe–O(2) = 2.1566(10) Å). In addition, one methanol molecule is located in the crystal lattice.

The crystal packing is stabilized by intermolecular hydrogen bonding. Thus, the coordinated methanol molecule is hydrogen bonded to the non-coordinated methanol (O(2)$\cdots$O(3) contact distance of 2.6112(14) Å and O(2)–H...O(3) angle of 163.9(20)°). In addition, the solvate methanol is H-bonded to the O(1) atom of the ligand (O(1)$\cdots$O(3)$_{(3/2-x, 1/2+y, 1/2-z)}$ contact distance of 2.7268(17) Å and O(3)–H$\cdots$O(1) angle of 171.1(25)°) (see Table 2).

3.2. Description of the structure of $[Mn(ClO_4)(pyrimol)(Hpyrimol)]_2$ (5)

Reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ in methanol with Hpyramol yields dark-red crystalline parallelepipeds of $[Mn(ClO_4)(pyrimol)(Hpyrimol)]_2$ (**5**). A PLATON [20] plot of **5** is given in Fig. 4. Compound **5** crystallizes in the monoclinic space group $P2_1/c$. Two crystallographically independent manganese atoms with slightly different coordination geometry are located in a distorted octahedral environment formed by one neutral Hpyrimol ligand and one deprotonated pyrimol ligand. In addition, one perchlorate anion is located in the unit cell for each independent Mn complex. Once again, a metal-assisted oxidation of the ligand Hpyramol is observed. To the best of our knowledge, this is the first example of such an oxidation which involves manganese ions. The distortion of the octahedron is probably due to the rigidity of the planar imine ligand. Consequently, axial angles (O(1)–N(9)–N(12)–N(29) considered as the basal plane) around 148° are observed (Table 3). The in-plane N–Mn–N and N–Mn–O angles vary from 72.47(8)° to 117.80(8)°. The Metal-donor atom distances
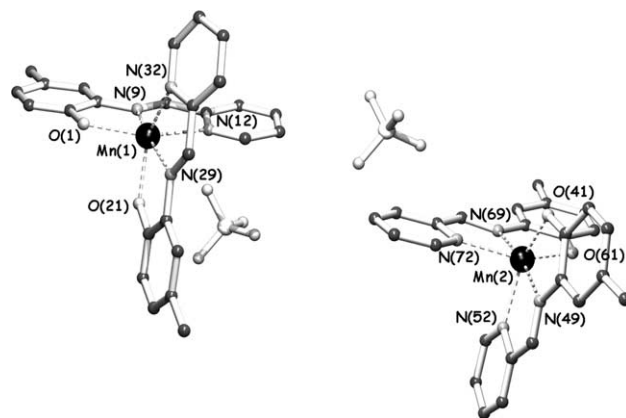

Fig. 4. PLATON [20] projection for **5**. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for **5**

	I	II
Mn(1)–O(1)	2.1606(17)	2.1699(18)
Mn(1)–O(21)	2.2092(19)	2.1345(17)
Mn(1)–N(9)	2.195(2)	2.231(2)
Mn(1)–N(12)	2.285(2)	2.277(3)
Mn(1)–N(29)	2.197(2)	2.219(2)
Mn(1)–N(32)	2.253(2)	2.264(2)
O(1)–Mn(1)–O(21)	91.48(7)	93.84(7)
O(1)–Mn(1)–N(9)	75.05(7)	73.67(7)
O(1)–Mn(1)–N(12)	148.00(7)	146.11(7)
O(1)–Mn(1)–N(29)	116.88(7)	117.80(8)
O(1)–Mn(1)–N(32)	103.72(7)	94.21(8)
O(21)–Mn(1)–N(9)	97.46(7)	109.78(7)
O(21)–Mn(1)–N(12)	95.55(8)	100.03(8)
O(21)–Mn(1)–N(29)	73.26(7)	74.48(7)
O(21)–Mn(1)–N(32)	147.25(7)	145.92(7)
N(9)–Mn(1)–N(12)	73.10(7)	72.55(8)
N(9)–Mn(1)–N(29)	114.33(8)	167.96(8)
N(9)–Mn(1)–N(32)	164.44(8)	104.27(8)
N(12)–Mn(1)–N(29)	95.01(7)	95.76(8)
N(12)–Mn(1)–N(32)	86.78(8)	91.37(8)
N(29)–Mn(1)–N(32)	73.99(8)	72.47(8)

S.u.'s are given in parentheses. Labels are given for molecule I, containing Mn(1). Add 40 to the numerical part of the O and N labels to obtain the labels of complex II, containing Mn(2).

vary from 2.195(2) to 2.285(2) Å for Mn–N and from 2.1345(17) to 2.2092(19) Å for Mn–O. This can be considered as normal for manganese(II) ions with an octahedral geometry.

Furthermore, each manganese complex is hydrogen-bonded to a crystallographically independent, adjacent complex through the hydrogen atom of its protonated ligand and the oxygen atom of the deprotonated ligand from the contiguous complex and inversally (Fig. 5). The presence of these hydrogen bonds of type [O–H$\cdots$O]$^-$ is clear from the observed O$\cdots$O distances, which are 2.439(2) and 2.448(2) Å for the bonds involving O(1) and O(21), respectively. These O$\cdots$O dis-

Table 2
Selected bond distances (Å) and angles (°) for **4**

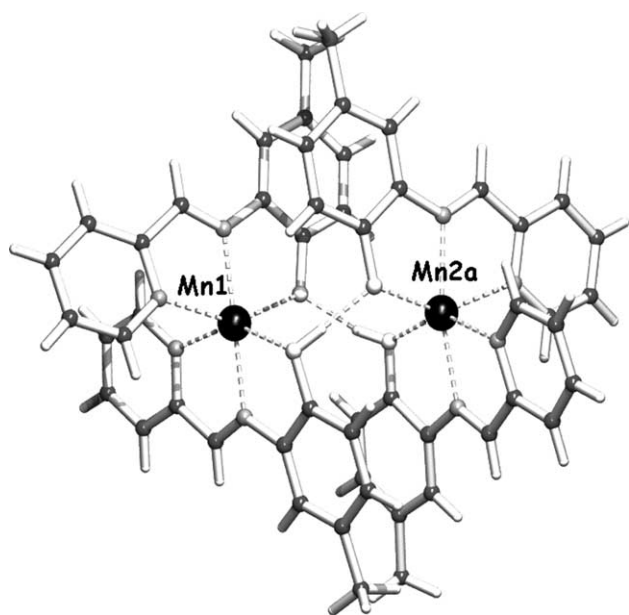| Bond distances		Bond angles	
Fe–N(1)	2.1416(10)	N(1)–Fe–N(2)	74.14(4)
Fe–N(2)	2.1815(11)	N(2)–Fe–Cl(2)	102.20(3)
Fe–Cl(1)	2.3256(3)	Cl(2)–Fe–O(2)	91.11(3)
Fe–Cl(2)	2.2601(3)	O(2)–Fe–N(1)	78.90(4)
Fe–O(1)	1.9522(8)	Cl(1)–Fe–O(2)	168.74(3)
Fe–O(2)	2.1566(10)		

Fig. 5. PLATON [20] projection of **5** showing the hydrogen-bonding between two neighbouring manganese complexes by means of their protonated (Hpyrimol) and deprotonated (pyrimol) phenol-based ligand.

tances are 0.60 and 0.59 Å shorter then the sum of the Van der Waals radii. The position of the hydrogen atoms could not be unambiguously determined, possibly due to disorder of the hydrogen atom. The hydrogen atoms were therefore arbitrarily assigned to atoms O(1) and O(61).

3.3. IR and UV–Vis spectroscopy

The IR spectra of [FeCl$_2$(pyrimol)(MeOH)](MeOH) (**4**) and of [Mn(ClO$_4$)(pyrimol)(Hpyrimol)]$_2$ (**5**) exhibit a band at 1654 cm^{-1} which can be assigned to the v (C=N) of the coordinated imine group [24]. No absorption band is observed in this area for the free amine ligand Hpyramol. In addition, the spectrum of **5** shows a strong band at 1081 cm^{-1} characteristic of perchlorate ions [25].

The electronic spectra of the two coordination compounds exhibit intense bands below 400 nm, assignable to charge-transfer transitions in the Fe(III) [26] and Mn(II) chromophores and/or intraligand π–π^* interactions. The Mn(II) ion is in a distorted octahedral environment. Therefore, according to the ligand field theory and assuming an O_h symmetry, the ground state of manganese(II) is $^6A_{1g}$. Because d–d transitions of Mn(II) ($^6A_{1g} \rightarrow {}^4T_{1g}(G), {}^4T_{2g}(G), {}^4A_{1g}$) are spin-forbidden [27], no characteristic band of manganese(II) was observed.

4. Concluding remarks

The tridentate N$_2$O ligand Hpyramol undergoes iron(II)- and manganese(II)-assisted oxidative dehydro-

genation in air forming the imine ligand Hpyrimol. The crystal structures of the resulting iron(III) complex [FeCl$_2$(pyrimol)(MeOH)](MeOH) (**4**) and the manganese(II) complex [Mn(ClO$_4$)(pyrimol)(Hpyrimol)]$_2$ (**5**) are described and compared. Only one organic ligand is coordinated to the iron atom while two ligands are coordinated to the manganese atom. This difference is probably caused by the presence of coordinating chloride anions and of non-coordination perchlorate anions, for the iron(III) complex and the manganese(II) complex, respectively. The packing of the crystal structures shows that the systems are stabilised by H-bonds.

The use of these two coordination compounds in catalytic epoxidation of alkenes is currently under investigation.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos. CCDC-216664 (**4**) and CCDC-234498 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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