SYNTHESIS OF PYRIDINE *N*-IMINE COMPLEXES OF METHYLCOBALOXIME AND REACTIONS OF BIS(DIMETHYLGLYOXIMATO)METHYL(PYRIDINE *N*-IMINE)COBALT WITH ACID ANHYDRIDES AND ACETYLENEDICARBOXYLIC ACID DIMETHYL ESTER

YASUSHI TSURITA, TARO SAITO * and YUKIYOSHI SASAKI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113 (Japan)

Summary

Pyridine *N*-imine complexes of methylcobaloxime, $CH_3Co(Hdmg)_2(R^1—C_5H_nN^+—N^-H)$ ($n = 4$; R^1 = H, 2-CH_3, 3-CH_3, 4-CH_3: $n = 3$; R^1 = 2,6-CH_3), have been synthesized by the reaction of $CH_3Co(Hdmg)_2S(CH_3)_2$ with a pyridine *N*-imine which is generated from a pyridine, hydroxylamine-*O*-sulfonic acid and K_2CO_3. The reactions of $CH_3Co(Hdmg)_2(C_5H_5N^+—N^-H)$ with acid anhydrides form new methylcobaloxime complexes with N-substituted pyridine *N*-imines, $CH_3Co(Hdmg)_2(C_5H_5N^+—N^-R^2)$ R^2 = COPh, COMe, COEt). With maleic anhydride, (pyridine *N*-acryloylimine)carboxylic acid is formed. With acetylenedicarboxylic acid dimethyl ester, 1,3-dipolar cycloaddition of the ligand gives pyrazolo[1,5-a]pyridine-2,3-dicarboxylic acid dimethyl ester.
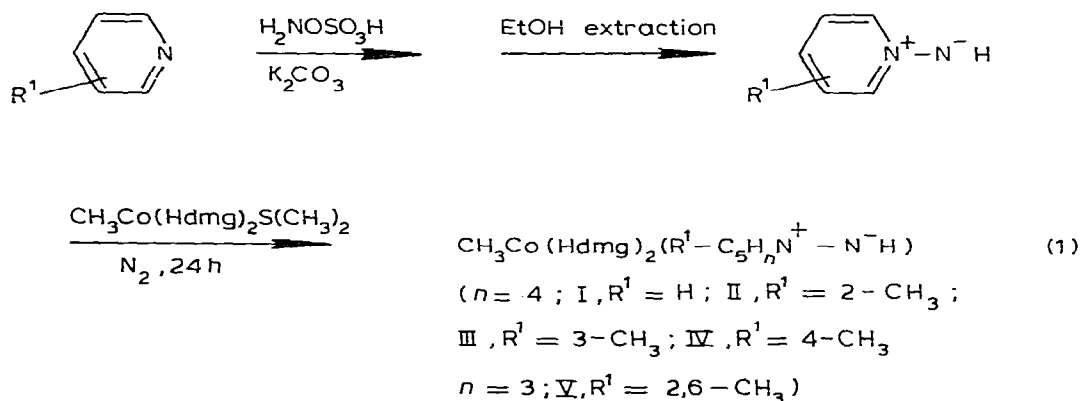
Introduction

Recently, we have reported cobaloxime complexes with pyridinium ylide ligands, $R—C_5H_4N^+—C^-H—COPh$ [1,2]. We report here methylcobaloxime complexes of pyridine *N*-imines which have zwitterionic structures, $R^1—C_5H_4N^+—N^-—R^2$, isoelectronic with pyridinium ylides and which may thus be regarded as ylide analogs [3]. The N-substituted derivatives which have a keto-stabilized substituent already have been used as ligands. For example, *ortho*-metallated palladium, platinum and rhodium complexes with pyridine *N*-benzoylimine have been reported [4]. Pyridine *N*-imine $C_5H_5N^+—N^-H$, which is isoelectronic also with pyridine *N*-oxide, seems to be unstable and has not been isolated in the pure state [5—7]. This compound usually is generated from its onium salts and is treated with a substrate *in situ* in the preparations of some heterocyclic compounds [6,7]. The aim of the present study has been to stabilize pyridine

N-imine as a ligand in transition metal complexes and to perform some reactions on the coordinated pyridine N-imine with acid anydrides and an acetylene dicarboxylate in order to compare the reactivities of the free and coordinated ligands. As well as the products of these reactions, a few new methylcobaloxime complexes of substituted pyridine N-imines have also been prepared. We have described the X-ray structure determination of $CH_3Co(Hdmg)_2(C_5H_5N^+-N^-H)$ in a previous paper [8].

Results and discussion

The methylcobaloxime complexes of pyridine N-imine and its derivatives (I—V) were prepared by the substitution of the dimethyl sulfide ligand in $CH_3Co(Hdmg)_2S(CH_3)_2$ by a pyridine N-imine which had been generated *in situ* in the intermediate stage of 1-aminopyridinium iodide preparation [9], (eq. 1).

$$R^1 - \text{(pyridine N)} \xrightarrow[\text{K}_2\text{CO}_3]{\text{H}_2\text{NOSO}_3\text{H}} \xrightarrow{\text{EtOH extraction}} R^1 - \text{(pyridine)} N^+ - N^- H$$

$$\xrightarrow[\text{N}_2, 24\,h]{\text{CH}_3\text{Co(Hdmg)}_2\text{S(CH}_3)_2} \quad CH_3Co\,(Hdmg)_2(R^1 - C_5H_nN^+ - N^-H\,) \qquad (1)$$

$$(n = 4 ;\ \text{I}, R^1 = H;\ \text{II}, R^1 = 2 - CH_3 ;$$

$$\text{III}, R^1 = 3 - CH_3;\ \text{IV}, R^1 = 4 - CH_3$$

$$n = 3 ;\ \text{V}, R^1 = 2,6 - CH_3\,)$$

Complex I was obtained also from the pyridine N-imine that had been generated by base (KOH) treatment of commercial 1-aminopyridinium iodide but the yield was low (ca. 5%). Therefore complexes II—V were prepared by the former method only. These complexes are stable in air both in the solid state or in solution and have been identified by elemental analyses and spectroscopic data (Tables 1—3). No signal assignable to NH was observed in the ^{1}H NMR spectra of complexes I—V but the IR spectra of I, III and IV indicated strong peaks at 3270—3279 cm^{-1} which were assigned to ν(N—H). Similar peaks at 3336 cm^{-1} for II and at 3322 cm^{-1} for V shifted to higher wave numbers and their intensities were much weaker, which probably reflects a steric influence of the *ortho*-methyl group(s) in the pyridine ring. The chemical shifts of Co—CH$_3$ protons of I—V have values similar to each other ($\delta \simeq 0.6$ ppm). The Co—CH$_3$ chemical shifts have been suggested to be indicative of the basicity of the axial ligand in various methylcobaloxime complexes [10]. If these observations are applied to the present complexes, it may be argued that the basicity of pyridine N-imine ($\delta = 0.63$ ppm) is near that of piperidine ($\delta = 0.63$ ppm) and is larger than that of pyridine ($\delta = 0.81$ ppm). The methyl group(s) on the pyridine ring do not seem to exert much electronic influence upon the cobalt atom, because the Co—CH$_3$ chemical shifts of the substituted pyridine N-imine complexes are not much different from that of the pyridine N-imine complex I.

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I—IX, $CH_3Co(Hdmg)_2(R^1—C_5H_nN^+—N^-—R^2)$ [a]

	R^1	R^2	Analysis found(calcd.)(%)		
			C	H	N
I	H	H	42.11	6.09	21.17
			(42.22)	(5.82)	(21.10)
II	2-CH_3	H	43.53	6.34	20.61
			(43.69)	(6.11)	(20.38)
III	3-CH_3	H	43.40	6.38	20.15
			(43.69)	(6.11)	(20.38)
IV	4-CH_3	H	43.47	6.20	20.27
			(43.69)	(6.11)	(20.38)
V	2,6-CH_3	H	45.10	6.58	19.50
			(45.07)	(6.38)	(19.71)
VI	H	COPh	49.96	5.45	16.75
			(50.20)	(5.42)	(16.73)
VII	H	COMe	43.34	5.86	19.00
			(43.64)	(5.72)	(19.09)
VIII	H	COEt	44.96	6.22	18.35
			(44.94)	(5.99)	(18.50)
IX	H	CO_2Et	43.19	5.83	17.63
			(43.41)	(5.79)	(17.87)

[a] $n = 4$ except for V($n = 3$).

TABLE 2

^{1}H NMR DATA FOR COMPLEXES I—IX

	δ(ppm)(CDCl₃, TMS)				
	Co—CH_3 [a]	dmg—CH_3 [b]	py—CH_3 [c]	py ring	OH [d]
I	0.63	2.02		~7.1, 7.65	18.1
II	0.60	2.10	2.40	7.02, 8.37	18.2
III	0.60	1.99	2.25	6.80, 7.47	17.9
IV	0.57	2.00	2.32	6.91, 7.53	18.1
V	0.57	2.00	2.49 [e]	6.76	18.0
VI	0.47	1.82		7.2—8.0 [f], 8.46	18.9
VII	0.65	2.10		7.6—8.1	17.8
VIII	0.64	2.08		7.3—8.1	17.6
IX	0.70	1.97		~7.6, 7.95	17.7

[a] Singlet, 3 H. [b] Singlet, 12 H. [c] Singlet, 3 H. [d] Broad. [e] Singlet, 6 H. [f] Pyridine + phenyl ring.
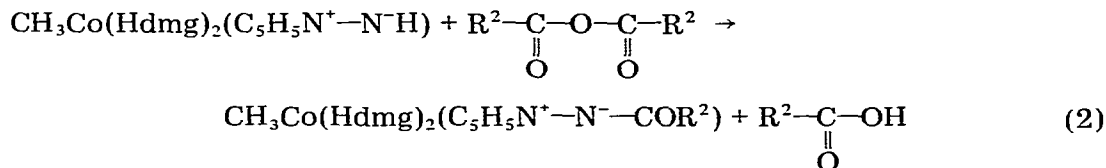
TABLE 3

IR DATA FOR COMPLEXES I—IX (cm^{-1}, KBr DISC)

|	ν(NH)	ν(CH) [a]	ν(CO)	ν(CN)	ν(NO)	ν(Co—N)
I	3270s	2895		1568	1238, 1094	520
II	3336w(br)	2896		1567	1239, 1096	521
III	3279s	2900		1565	1239, 1094	520
IV	3279s	2898		1564	1238, 1092	520
V	3322w	2897		1565	1237, 1094	519
VI		2902	1590(1556) [b]	1567	1239, 1093	520
VII		2912	1604(1560) [b]	1562	1239, 1093	520
VIII		2918	1597(1565) [b]	1561	1238, 1095	520
IX		2901	1644(1642) [b]	1560	1239, 1092	520

[a] Co—CH_3. [b] Free ligand.

The lack of the long-range influence of the methyl group(s) can be inferred also from the IR spectra which indicate that the $\nu(C=N)$, $\nu(NO)$ and $\nu(Co-N)$ of the dimethylglyoxime are not changed appreciably by the methyl substitution [11].

When complex I was treated with benzoic anhydride, acetic anhydride and propionic anhydride in chloroform, complexes VI, VII and VIII, respectively, were formed. In the reaction of benzoic anhydride with I, benzoic acid also was obtained in 36% yield. The reaction seems to have proceeded in such a way that the N^- in complex I attacked an acyl group of the acid anhydride and the resultant carboxylate anion abstracted the hydrogen atom of N—H, (eq. 2).

$$CH_3Co(Hdmg)_2(C_5H_5N^+-N^-H) + R^2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R^2 \rightarrow$$

$$CH_3Co(Hdmg)_2(C_5H_5N^+-N^--COR^2) + R^2-\underset{\underset{O}{\|}}{C}-OH \qquad (2)$$

(VI, R^2 = COPh; VII, R^2 = COMe; VIII, R^2 = COEt)

Complexes VI—VIII were identified by their elemental analyses, and ^{1}H NMR and IR spectra (Tables 1—3). Complex VI was prepared also from CH_3Co-$(Hdmg)_2S(CH_3)_2$ and $C_5H_5N^+-N^--COPh$. As an example of the nucleophilic reactions of pyridine N-imine, deketene is known to give X [5,12] (eq. 3).
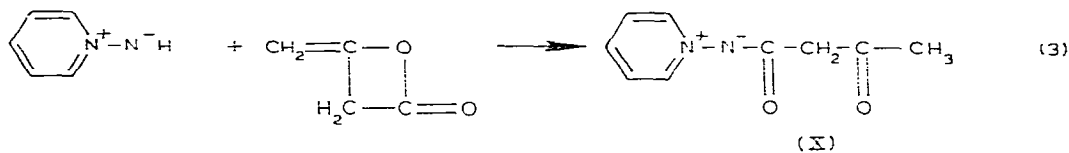
Thus, the reactivity of the coordinated and free pyridine N-imine as a nucleophile seems to be similar. Incidentally, the free ligands $C_5H_5N^+-N^--COR^2$ ($R^2 = CH_3$, C_2H_5) are very hygroscopic and difficult to isolate in air but VII and VIII are indefinitely stable in air.

The ligands in VI—VIII may be described in terms of the canonical resonance forms A and B. In complex formation, either N^- (A) or O^- (B) coordinates to a metal. The carbonyl stretching frequencies, $\nu(CO)$, normally shift to higher

(A)   (B)

wave numbers in A and to lower wave numbers in B upon coordination. In the Pd, Pt and Rh complexes of $C_5H_5N^+-N^--COPh$, the ligand coordinates to the metal in type A fashion and the $\nu(CO)$ frequencies shift to higher wave numbers [4]. X-ray structure determinations confirmed the type A coordination in the ylide complexes of cobaloxime, $XCo(Hdmg)_2(C_5H_5N^+-C^-H-COPh)$ (X = Cl,

Ch$_3$), which also showed higher frequency shifts [1,2]. The wave number shifts of 32—44 cm^{-1} in the complexes VI –VIII suggest that type A coordination is also present in these complexes. In complex IX, CH$_3$Co(Hdmg)$_2$(C$_5$H$_5$N$^+$ –N$^-$ —COOEt), which was prepared from CH$_3$Co(Hdmg)$_2$S(CH$_3$)$_2$ and C$_5$H$_5$N$^+$ –N$^-$ —COOEt, the shift is only 2 cm^{-1}. Since ν(CO) of the free ligand (1642 cm^{-1}) in IX is considerably higher than those of the ligands in VI—VIII (1556—1565 cm^{-1}), the type A contribution is probably already dominant in free C$_5$H$_5$N$^+$—N$^-$—COOEt.

Complex I reacted with maleic anhydride to give XI and methylcobaloxime dimer (XII), (eq. 4). In the ^{1}H NMR spectrum of XI, the OH signal appears at

$$CH_3Co\,(Hdmg)_2(C_5H_5N^+\!-N^-H) \quad + \quad$$

$$(XI)$$

$$+ \qquad \tfrac{1}{2}\left\{CH_3Co(Hdmg)_2\right\}_2 \qquad (4)$$

$$(XII)$$
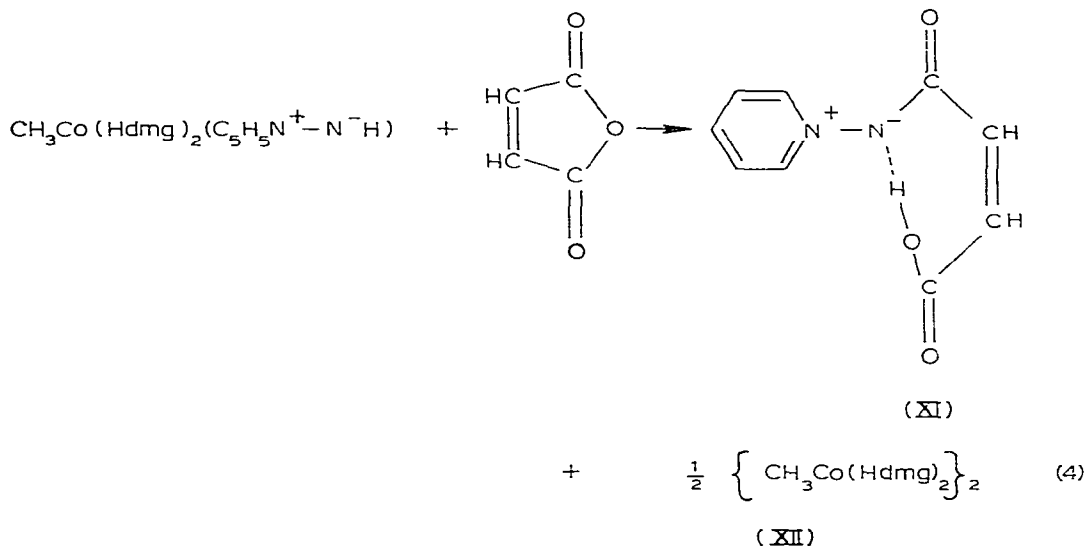
δ = 17.6 ppm suggesting the possible presence of a hydrogen bond between the N$^-$ atom and carboxylic proton. This is conceivable since all the atoms of the N-acryloylimine part of XI should be coplanar if the imine nitrogen has sp^2 character and a structural model indicates that the bond distance between N and H is reasonable. It is likely that the N$^-$ of the pyridine N-imine ligand attacked the carbonyl carbon of maleic anhydride to form (pyridine N-acryloylimine)carboxylic acid which could not be coordinated to cobalt due to the hydrogen bond and/or steric effects.

Pyridine N-imine is a 1,3-dipole and undergoes 1,3-dipolar cycloaddition with a dipolarophile [13,14]. It is reported that free pyridine N-imine, which is formed *in situ*, reacts with acetylenedicarboxylic acid dimethyl ester, followed by dehydrogenation, to give pyrazolo[1,5-a]pyridine-2,3-dicarboxylic acid dimethyl ester (XIV) [13]. Complex I also reacted with acetylenedicarboxylic acid dimethyl ester in chloroform at room temperature and formed XII and XIV, (eq. 5).

When this reaction was monitored in an NMR tube, the spectral pattern changed from that of I to that of XII multiplet signals in the region δ = 4.8—6.3 ppm, and a yellow complex precipitated, which was shown to be XII. The complex signals (δ = 4.8—6.3 ppm) resemble the spectrum of dihydropyrazolo[1,5-a]-pyridine derivatives [15]. The pyridine N-imine ligand in I probably reacted

$$CH_3Co(Hdmg)_2(C_5H_5N^+-N^-H) + CH_3OOC-C\equiv C-COOCH_3 \longrightarrow$$

$$\frac{1}{2}\left\{CH_3Co(Hdmg)_2\right\}_2 +$$

(XII)

(XIII)

$$\downarrow -H$$

(5)

(XIV)

with acetylenedicarboxylic acid dimethyl ester in a 1,3-dipolar cycloaddition fashion and the intermediate product XIII was dehydrogenated to form XIV. However, we could not identify the hydrogen acceptor. Probably because of steric reasons, XIV did not coordinate to methylcobaloxime.

An X-ray structure determination of I has shown that the imino nitrogen has sp^2 character having N=N double bond contribution and that it coordinates to cobalt using a formal lone pair on the imino nitrogen [8]. In view of the above results, it seems reasonable that the coordinated pyridine N-imine in the complex I has similar reactivity towards acid anhydrides and an acetylene derivative to that of free pyridine N-imine which is a 1,3-dipole represented as follows.

It should be possible to use the present complexes as stable precursors of pyridine N-imines for some synthetic purposes.

Experimental

N-substituted pyridine N-imines were synthesized according to literature methods [7,16]. ^{1}H NMR and IR spectra were recorded with a Hitachi R-24B spectrometer and a Hitachi 260 spectrometer, respectively.

Preparation of I

An ethanol solution of $CH_3Co(Hdmg)_2S(CH_3)_2$ [17] (15.0 g; 0.04 mol) was added dropwise to an ethanol solution of pyridine N-imine which was generated by treating pyridine (24 ml; 0.30 mol) with hydroxylamine-O-sulfonic acid (11.3 g; 0.10 mol) and K_2CO_3 (13.4 g; 0.10 mol) under N_2 and the mixture was stirred for 24 h at room temperature. The solution was evaporated and CH_2Cl_2 (100 ml) was added to the residue and filtered. Hexane (200 ml) was added to the filtrate to precipitate crude crystals which were recrystallized from CH_2Cl_2-hexane to give yellow-brown needle crystals. Yield 12.0 g (73.6% based on Co).

Preparation of complexes II—V

The preparations of II—V were similar to that of I except for some minor differences. In the case of IV, $CH_3Co(Hdmg)_2(4\text{-}CH_3C_5H_4N)$ (20.7%) precipitated prior to the formation of the complex IV. In the case of V, a small amount of $\{CH_3Co(Hdmg)_2\}_2$ was also obtained. The color of these complexes were dark-red (II), yellow-brown (III), red-orange (IV) and dark-red (V). Yields: 80.4 (II), 48.3% (III), 17.5% (IV), 55.3% (V).

Preparation of IX

$CH_3Co(Hdmg)_2S(CH_3)_2$ (1.5 g; 4.20 mmol) was added to a THF (40 ml) solution of pyridine N-carboethoxyimine (0.7 g, 4.30 mmol) and the solution was stirred for 24 h at room temperature under N_2. The solution was evaporated and the residue recrystallized from CH_2Cl_2-ether to give red-brown crystals. Yield 1.5 g (75.0%).

Reactions of I with acid anhydrides; formation of the complexes VI—VIII

To a chloroform (30 ml) solution of I (1.0 g; 2.5 mmol) was added benzoic anhydride (570 mg; 2.5 mmol) and the resulting solution was refluxed for 3 h under N_2 and stirred overnight at room temperature. The solvent was evaporated, the residue was extracted with CH_2Cl_2 (20 ml) and hexane (40 ml) was added to the extract to separate oily material which was removed by filtration. The filtrate was evaporated and the residue was washed with ether (40 ml). The crude product was recrystallized from CH_2Cl_2-ether to give fine red-brown crystals which were washed with ether (20 ml) and hexane (20 ml) and dried. Yield 420 mg (33.4%). From the solution which was obtained by washing the residue with ether, benzoic acid (109 mg; 35.6%) was isolated by sublimation.

The reactions of I with acetic anhydride and propionic anhydride formed VII (45.1%) and VIII (53.0%), respectively.

Reactions of I with maleic anhydride

Maleic anhydride (256 mg; 2.51 mmol) was added to a chloroform (30 ml) solution of I (1.00 g; 2.51 mmol) and the solution was refluxed for 4 h under N_2 and stirred overnight at room temperature. Ether (20 ml) was added to the solution, and filtered. Ethanol (15 ml) was added to the residue and filtered. The residue was recrystallized from ethanol to form white crystals of XI. Yield 278 mg (57.7%). Anal. Found: C, 56.03; H, 4.08; N, 14.43. Calcd. for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N. 14.58%. ^1H NMR ($CDCl_3$, δ, ppm): 6.08 (d,

2 H, J = 12 Hz), 6.50 (d, 2 H, J = 12 Hz), 7.8—8.3 (m, 3 H), 8.65 (m, 2 H), 17.6 (s, 1 H). IR: ν(CO), 1694 cm^{-1}. M.p. 183—184°C (dec).

Reaction of I with acetylenedicarboxylic acid dimethyl ester

Acetylenecarboxylic acid dimethyl ester (0.184 ml; 1.50 mmol) was added to a chloroform (3.5 ml) solution of I (298 mg; 0.75 mmol) and the solution was stirred for 3 h at room temperature. Hexane (25 ml) was added to the solution to form a yellow precipitate, which was recrystallized from ethanol-hexane to give XII as dark-red crystals. Yield 76 mg (33.4%). The washing filtrates were evaporated and the residue was dissolved in CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was chromatographed on a silica gel column (CHCl$_3$ eluent) and XIV was obtained as white crystals. Yield 39 mg (22.2%). Anal. Found: C, 56.56; H, 4.39; N, 12.09. Calcd. for C$_{11}$H$_{10}$N$_2$O$_4$: C, 56.41; H, 4.31; N, 11.96%. M.p. 69.3—69.8°C (lit. [13] 70—71°C). ^{1}H NMR (CDCl$_3$, δ, ppm): 3.84 (s, 3 H), 3.94 (s, 3 H), 6.92 (t, 1 H), 7.42 (t, 1 H), 8.03 (d, 1 H), 8.25 (d, 1 H). IR: ν(CO) 1740, 1706, 1693 cm^{-1}.

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