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Synthesis and characterisation of the first examples of four-membered ring ruthenalactam complexes

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ABSTRACT

Reaction of the complexes $[RuCl_2(PPh_3)L]$ (L = η^6-*p*-cymene or η^6-hexamethylbenzene) with *N*-cyanoacetylurethane $[NCCH_2C(O)NHCO_2Et]$ and tertiary amine base in refluxing methanol gives the first examples of mononuclear complexes containing the four-membered ruthenalactam ring, Ru–C–C(O)–N. The complexes were characterised by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and ESI mass spectrometry. A single-crystal X-ray diffraction study on the *p*-cymene complex showed the four-membered ruthenalactam ring to be planar.

The four-membered metallalactam ring system **1** is well-known for metal centres such as platinum(II) and palladium(II) [1–5] together with gold(III) [6]. We have developed facile synthetic routes to such complexes, involving the reaction of a metal dichloride complex with a suitable ligand precursor, which are reacted in the presence of base, either a tertiary amine in methanol, or silver(I) oxide in dichloromethane. *N*-Cyanoacetylurethane, $NCCH_2C(O)NHCO_2Et$, is one such precursor that has been used to synthesise metallalactam complexes of platinum(II) [1] and palladium(II) [2], giving the substituted ring system **2**. The presence of relatively acidic C–H and N–H protons in *N*-cyanoacetylurethane allows synthesis of such metallalactam complexes under mild reaction conditions, with the platinum complex being formed through an intermediate monodentate *N*-bonded ligand, as shown by the isolation and characterisation of the complex *cis*-$[PtCl\{N(CO_2Et)C(O)CH_2CN\}(PPh_3)_2]$ **3** [7]. In the case of gold(III) derivatives of *N*-cyanoacetylurethane, the initial four-membered auralactam $AuCH(CN)C(O)N(CO_2Et)$ ring was found to undergo an interesting dimerisation process, giving an eight-membered $Au\{CH(CN)C(O)N(CO_2Et)\}_2Au$ ring in complex **4** [6]. We therefore wished to investigate the coordination chemistry of *N*-cyanoacetylurethane towards other transition metal centres. However, simple four-membered metallalactam ring systems formed by the other platinum group metals (Rh, Ir, Ru, Os) have not been isolated to date, though the related diruthenium complex **5** has been structurally characterised [8], and some ruthenalactam species have been proposed as intermediates in some ruthenium-catalysed cycloaddition reactions of isocyanates [9,10]. In this paper the first isolated examples of ruthenalactam complexes, containing π-arene ancillary ligands, are reported; this metal–ligand system has been previously used to synthesise a range of ruthenacyclic complexes [11].

Reaction of $[RuCl_2(PPh_3)(\eta^6\text{-}C_6Me_6)]$ [12] with *N*-cyanoacetylurethane in refluxing methanol with triethylamine base, followed by precipitation of the product by addition of water gave a yellow precipitate of the ruthenalactam complex $[Ru\{CH(CN)C(O)N(CO_2Et)\}(PPh_3)(\eta^6\text{-}C_6Me_6)]$ **6**,[13] which was found to be spectroscopically pure and gave satisfactory microanalytical data. However, reaction of the related complex $[RuCl_2(PPh_3)(\eta^6\text{-}p\text{-cymene})]$ [14] (*p*-cymene = $p\text{-}MeC_6H_4Pr^i$) with *N*-cyanoacetylurethane was less straightforward, despite several attempts using different reaction conditions. Refluxing of the reaction mixture resulted in a green colour; recovery of the product by precipitation with water, followed by recrystallisation from dichloromethane and petroleum spirits gave a small number of yellow crystals of **7** together with some dark green material [15].

Complexes **6** and **7** give strong $[M + H]^+$ ions in their positive ion ESI mass spectra using gentle ionisation conditions (capillary exit voltage of 100 V) giving ions for **6** at *m/z* 681.291 (calculated 681.183) and for **7** at *m/z* 653.039 (calculated *m/z* 653.151). The $[M + Na]^+$ ions were also observed, but were weak. The fragmentation behaviour of **6** was also investigated; at increased voltages (160 V), fragmentation by loss of PPh_3 occurred giving ions such as $[M + Na\text{-}PPh_3]^+$ (*m/z* 441.150, calculated 441.073). The ions showed the expected isotope patterns that arise due to the presence of polyisotopic Ru. $^{31}P\{^1H\}$ NMR spectra of the complexes showed a single peak at similar chemical shifts (**6** δ 49.2, **7** δ 49.8) that are shifted relative to the starting complex $[RuCl_2(PPh_3)(\eta^6\text{-}p\text{-cymene})]$ (δ 24.2). The IR spectrum of **6** showed the expected bands, with a C≡N stretch at 2350 cm^{-1} and two CO stretches at 1701 and 1644 cm^{-1}.

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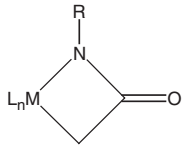
The ^{1}H NMR spectrum of the hexamethylbenzene complex **6** was relatively straightforward, showing a triplet and quartet from the cyanoacetyl ethyl group, a singlet from the C_6Me_6 ligand (δ 1.89), a set of multiplets for the PPh_3 protons, together with a doublet at δ 2.12 for the ruthenalactam CH proton, showing coupling to phosphorus [^{3}J(PH) 8.7 Hz]. This resonance is significantly shifted upfield,



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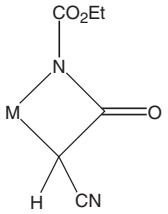
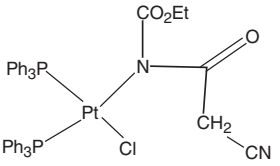


2, M=Pt, Pd



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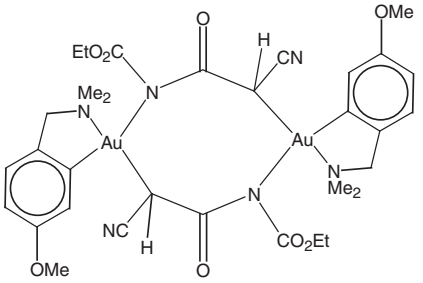

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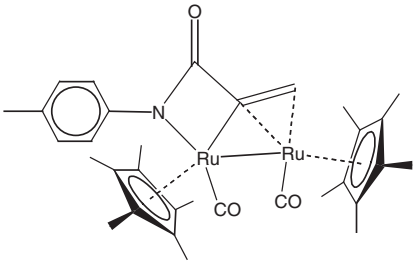

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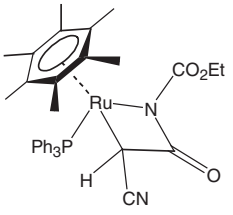

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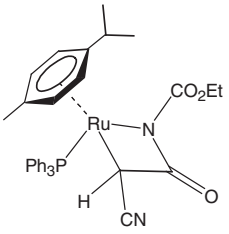

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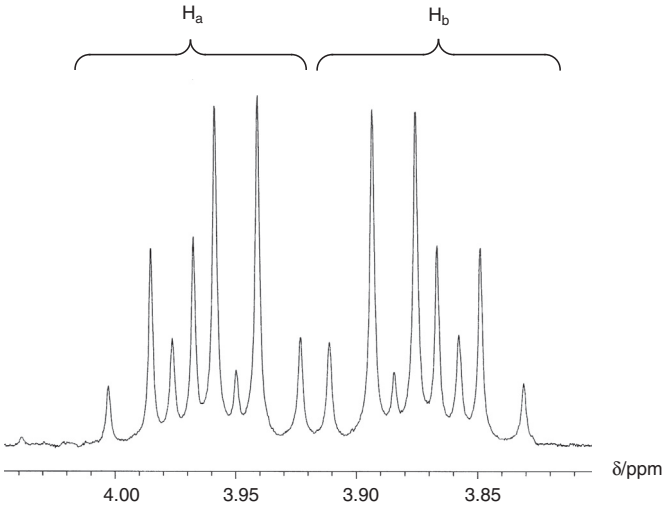

Fig. 1. Part of the ^{1}H NMR spectrum ($CDCl_3$ solution) of [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] **7**, showing the presence of two doublets of quartets for the inequivalent CH_2 protons H_a and H_b of the ethyl ester substituent.

relative to the CH_2 protons in *N*-cyanoacetylurethane, which appear at δ 4.06.

The ^{1}H NMR spectrum of **7** was more complex. All four aromatic CH protons from the *p*-cymene ligand are inequivalent. Each appears as a doublet due to ^{3}J(HH) coupling, with three of the signals showing additional resolved long-range coupling, presumably cross-ring ^{4}J 'W'-coupling [16]. Two of the protons clearly form an AB type pattern, with more intense inner lines. The methyl groups of the cymene *iso*-propyl substituent are inequivalent and appear as two doublets at δ 1.08 and 1.23, with coupling to the *iso*-propyl CH proton. The protons of the ethyl group also show a more complex pattern in **7** compared to **6**. The CH_3 protons appear as a triplet, but the CH_2 protons (Fig. 1) are diastereotopic and each appears as a resonance approximating to a doublet of quartets due to ^{2}J(HH) geminal coupling, together with ^{3}J(HH) coupling to the CH_3 protons in an ABX_3 spin system. The ruthenalactam proton appears at δ 2.2 as a doublet due to phosphorus coupling [^{3}J(PH) 8.6 Hz], while the **CH**$(CH_3)_2$ proton from the *p*-cymene ligand gives a quintet at δ 2.63.

In order to unequivocally characterise the ruthenalactam ring system, an X-ray structure determination was carried out on the *p*-cymene complex **7**, which gave a small number of crystals suitable for study [17]. The molecular structure is shown in Fig. 2 together with selected bond lengths and angles. The complex contains the typical 'piano-stool' arrangement of an η^6 *p*-cymene ligand, the chelating *N*,*C*-bonded ligand (confirming the formation of the ruthenalactam ring), and a triphenylphosphine. The ruthenalactam ring system pays a strong resemblance to the corresponding platinalactam ring in [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] [1], (cod = cyclo-octa-1,5-diene) which is the only other structurally characterised four-membered ring metallalactam derived from *N*-cyanoacetylurethane.

The Ru–C–C–N ring is highly planar, with a fold angle between the N(1)–Ru(1)–C(1) and C(1)–C(2)–N(1) planes of only 1.84°. The torsion angles Ru(1)–C(1)–C(2)–O(1) and Ru(1)–N(1)–C(2)–O(1) [both 178.8(2)°] corroborate this planarity. The N(1)–Ru(1)–C(1) bite angle of the metallacyclic ligand is 64.49(7)°, which is comparable to the angle of 67.0(3)° in the platinum complex [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] [1]. The CO_2 group of the ester substituent is also reasonably coplanar

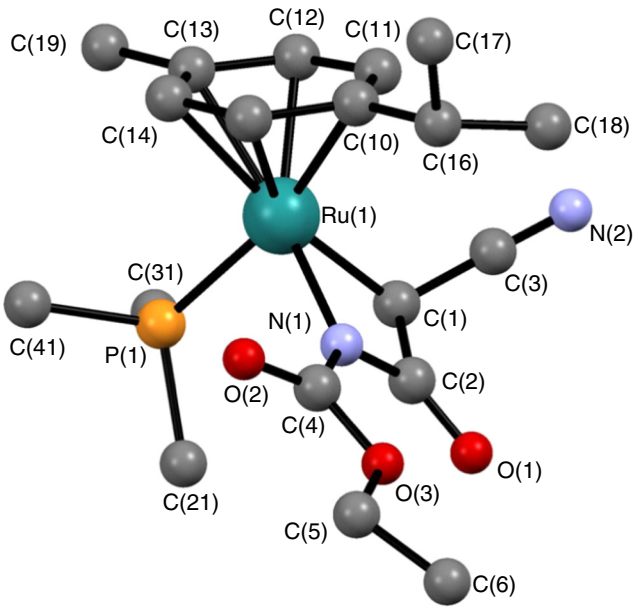

Fig. 2. Molecular structure of the complex [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] **7**. Only the *ipso* carbons of the triphenylphosphine ligand are shown for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1) 2.3259(5), Ru(1)–N(1) 2.0948(17), Ru(1)–C(1) 2.1654(19), N(1)–C(2) 1.377(3), C(1)–C(2) 1.539(3), C(2)–O(1) 1.209(3), C(1)–C(3) 1.451(3), C(3)–N(2) 1.150(3), N(1)–C(4) 1.367(3), Ru–C(cymene) range 2.217(2) to 2.277(2), mean 2.244(2), C(1)–Ru(1)–N(1) 64.49(7), Ru(1)–N(1)–C(2) 100.62(12), N(1)–C(2)–C(1) 102.36(16), Ru(1)–C(1)–C(2) 92.50(12), C(1)–C(3)–N(2) 177.5(2), P(1)–Ru(1)–N(1) 89.02(5), P(1)–Ru(1)–C(1) 85.65(6).

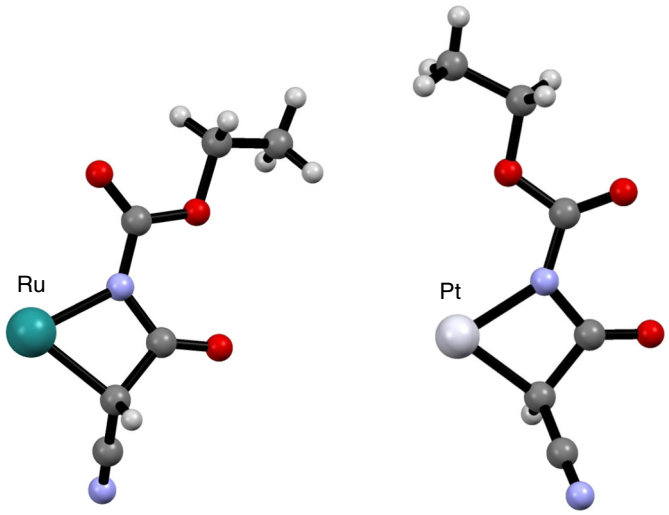

Fig. 3. A comparison of the metallalactam rings of [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] **7** (left) and [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] (right, cod = cyclo-octa-1,5-diene), showing the different arrangements of the CO_2Et substituent with respect to the metallalactam ring.

with the ruthenalactam ring, with C(2)–N(1)–C(4)–O(2) and Ru(1)–N(1)–C(4)–O(3) torsion angles of 169.6(2) and 172.1(1)° respectively. The Ru–N and Ru–CH(CN) bond distances of **7** are in the expected range, for example the Ru–C(1) bond distance of 2.1654(19) Å is identical to that of 2.169(4) Å in the cyanoalkyl complex [Ru{CH(CN)SO_2Ph}(η^5-C_5H_5)(CO)(PPh_3)] [18]. The Ru–C and Ru–N bonds of **7** are larger by 0.0788 and 0.0964 Å respectively, when compared to [Pt{CH(CN)C(O)N(CO_2Et)}(cod)], consistent with the 0.1 Å greater covalent radius of ruthenium. The C═O bond distances of **7** [C(2)–O(1) 1.209(3) and C(4)–O(2) 1.222(3) Å] are also comparable to the corresponding distances in [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] [1.196(9) and 1.215(9) Å]. The cyano group, C(3)–N(2), is directed towards the *p*-cymene ring, and the ruthenalactam hydrogen points H(1) towards the PPh_3 ligand [with a H(1)···H(22) non-bonded distance of 2.4537(1) Å]. This arrangement presumably arises in order to minimise steric interactions between the CN group and the PPh_3 ligand.

The most significant difference between [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] and [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] involves the orientation of the ester substituent. In [Pt{CH(CN)C(O)N(CO_2Et)}(cod)] the OEt group is *proximal* to the platinum atom, whereas in [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] it is *distal*, as shown in the comparison in Fig. 3. This is presumably due to the greater steric bulk of the *p*-cymene and PPh_3 ligands in the Ru complex. The *p*-cymene ligand bonds slightly asymmetrically to the ruthenium, as a result of the steric effects involving the PPh_3 ligand; the Ru(1)–C(13) and Ru(1)–C(14) bonds – those closest to the PPh_3 ligand – are the two longest Ru–C(cymene) bond lengths.

This study indicates that metallalactam complexes of another platinum group metal can be readily synthesised by a simple one-pot procedure; investigations into metallalactam complexes of other metals are in progress.

Acknowledgments

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Appendix A. Supplementary material

CCDC 976610 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.04.002.

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[13] Synthesis of [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-C_6Me_6)] **6**: [$RuCl_2$(PPh_3)(η^6-C_6Me_6)] (50 mg, 0.084 mmol) and *N*-cyanoacetylurethane (33 mg, 0.211 mmol, Aldrich Chemical Co.) in methanol (15 mL) was heated to reflux. After 5 min. excess Et_3N was added and the mixture refluxed for an additional 25 min. giving a yellow solution. Addition of water (80 mL) gave a yellow precipitate that was allowed to stand overnight before being filtered, washed with water (25 mL) and petroleum spirits (20 mL) and dried under vacuum to give **6** (25 mg, 44%). Found: C 62.7; H 5.9; N 3.9. $C_{36}H_{39}N_2O_3PRu$ requires C 63.6; H 5.8; N 4.1%. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 49.2 (s). ^1H NMR ($CDCl_3$), δ 7.4–7.6 (m, 15H, PPh_3), 4.14 [q, 2H, C**H**$_2$CH$_3$, ^{3}J(HH) 7.1], 2.12 [d, 1H, C**H**CN, ^{3}J(PH) 8.7], 1.88 (s, 18H, C_6Me_6), 1.25 [t, CH_2C**H**$_3$, ^{3}J(HH) 7.1]. ESI MS (MeOH), *m/z* 441.150 [M + Na-PPh_3]$^+$, 681.295 [M + H]$^+$, 703.277 [M + Na]$^+$. IR (KBr disk): ν(CN) 2350 cm^{-1}, ν(CO) 1701, 1644 cm^{-1}.
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[15] Synthesis of [Ru{CH(CN)C(O)N(CO_2Et)}(PPh_3)(η^6-*p*-cymene)] **7**: [$RuCl_2$(PPh_3)(η^6-*p*-cymene)] (61 mg, 0.106 mmol) and *N*-cyanoacetylurethane (81 mg, 0.519 mmol) were mixed in methanol (22 mL) and the mixture warmed to reflux. After 5 min. aqueous trimethylamine solution (1 mL) was added and the mixture refluxed for ca. 1 hour. Water (100 mL) was added, giving a murky green solution. The mixture was evaporated to dryness on a rotary evaporator. The solid was redissolved in dichloromethane (3 mL) and petroleum spirits (30 mL) added. Slow evaporation of the solution gave a mixture of green solid on the bottom of the vessel, and a small number of yellow crystals on the side. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 49.8 (s). ^1H NMR ($CDCl_3$), δ 7.55–7.40 (m, 15H, PPh_3), 5.90 [dd, 1H, CH of *p*-cymene, ^{3}J(HH) 6.3, ^{4}J(HH) 1.4], 5.48 [dd, 1H, CH of *p*-cymene, ^{3}J(HH) 5.8, ^{4}J(HH) 1.0], 5.38 [dd, 1H, CH of *p*-cymene, ^{3}J(HH) 5.8, ^{4}J(HH) 1.1], 4.51 [d, 1H, CH of *p*-cymene, ^{3}J(HH) 6.2], 3.96 [dq, 1H, CH_2 ^{2}J(HH) 10.7, ^{3}J(HH) 7.1], 3.87 [dq, 1H, CH_2, ^{2}J(HH) 10.6, ^{3}J(HH) 7.1], 2.62 [quintet, 1H, C**H**(CH_3), ^{3}J(HH) 6.9], 2.20 [d, 1H, C**H**CN, ^{3}J(PH) 8.6], 1.70 (s, 3H, C_6H_4C**H**$_3$), 1.22 [d, 3H, CH(C**H**$_3$) of *p*-cymene, ^{3}J(HH) 7.0], 1.17 [t, 3H, CH_2C**H**$_3$, ^{3}J(HH) 7.1] and 1.07 [d, 3H, CH(C**H**$_3$) of *p*-cymene, ^{3}J(HH) 6.8]. ESI MS (MeOH), *m/z* 653.265 [M + H]$^+$.
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[17] Crystal data for **6**: $C_{34}H_{35}N_2O_3PRu$; M_r = 651.68; Monoclinic; space group C2/c; *a* =36.0940(11) Å; *b* = 10.1847(3) Å; *c* = 16.3123(5) Å; β = 100.033(2)°; V = 5904.8(3) Å^3; Z = 8; T = 89(2) K; λ(Mo-K_α) = 0.71073 Å; μ(Mo-K_α) = 0.623 mm^{-1}; d_{calc} = 1.466 g cm^{-3}; 104731 reflections collected; 7086 unique (R_{int} = 0.0455); giving R_1 = 0.0352, wR_2 = 0.0906 for data with [$I > 2\sigma(I)$] and R_1 = 0.0380, wR_2 = 0.0924 for all data. Residual electron density (e$^-$Å^{-3}) max/min: 2.893/−0.605. An arbitrary sphere of data were collected on a dark yellow block-like crystal, having approximate dimensions of 0.38 × 0.34 × 0.24 mm, on a Bruker APEX II CCD diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarisation effects [SADABS; R. H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33] and analysed for space group determination. The structure was solved by direct methods and developed routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in calculated positions. On completion of refinement there were two significant residual peaks. One (2.7 e Å^{-3}) appeared to arise from orientational disorder of the *iso*-propyl group but was not modelled. The other (2.9 e Å^{-3}) was adjacent to the mid-point of the Ru–P vector, and cannot be assigned to any chemically-sensible feature, so must be an artifact of unknown origin. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others) [G. M. Sheldrick, Acta Crystallogr. A64 (2008) 112].
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