ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 4, pp. 360–365. © Pleiades Publishing, Ltd., 2013.
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Synthesis, Structure, and Absorption Spectra of Complex Neptunium(V) Chromate with the Guanidinium Cation, $[C(NH_2)_3]_3[NpO_2(CrO_4)_2] \cdot (H_2O)$

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Received September 6, 2012

Abstract—A new complex of Np(V) with the chromate ion and an organic outer-sphere guanidinium cation is isolated from an aqueous solution. Its composition and structure are determined by X-ray diffraction analysis. The structure of $[C(NH_2)_3]_3[NpO_2(CrO_4)_2](H_2O)$ (**I**) is based on anionic chains $[NpO_2(CrO_4)_2]_n^{3n-}$ between which guanidinium cations and crystallization water molecules are localized. Coordination polyhedra of the Np atoms (pentagonal bipyramids) in the anionic chains are joined in pairs through common equatorial edges. Singularities of the electronic and IR absorption spectra of compound **I** are discussed.

DOI: 10.1134/S1070328413040027

INTRODUCTION

Chromate complexes form a not numerous group among structurally characterized compounds of pentavalent neptunium with tetrahedral anions of the XO_4^{2-} type (X = S, Se, Cr, Mo). This is primarily because of difficulties in preparing crystals useful for X-ray diffraction analysis. The character of complex formation in the NpO_2^+–CrO_4^{2-}–H_2O system impedes the isolation of single-phase products [1]. Simple neptunium(V) chromate has not been isolated yet as a single crystal, and assumptions on its composition and structure are based on the chemical, spectral, and thermal analyses data.

Complex Np(V) chromates are presented by the compounds with outer-sphere cations K^+, NH_4^+, Na^+, and Cs^+, as well as $[Co(NH_3)_6]^{3+}$ [1–5]. The compositions of these complexes are variable and correspond to the $NpO_2 : CrO_4$ molar ratio equal to 1 : 2, 1 : 1.5, or 1 : 1. However, there is no unambiguous relationship between the nature of the outer-sphere cation and the $NpO_2 : CrO_4$ ratio. On the one hand, the 1 : 2 composition is possible for both $[Co(NH_3)_6][NpO_2(CrO_4)_2](H_2O)_2$ and $[Co(NH_3)_6][NpO_2(CrO_4)_2(H_2O)](H_2O)_2$ and complex $Na_3[NpO_2(CrO_4)_2](H_2O)_5$. On the other hand, these compounds differ structurally: the coordination polyhedra of the Np atoms are isolated in the former two compounds, whereas the coordination polyhedra are joined in pairs through the common equatorial edges in the anionic $[NpO_2(CrO_4)_2]_n^{3n-}$ chains in the third complex. In anions of the same composition observed in the structure of the anhydrous $K_3[NpO_2(CrO_4)_2]$ complex, the coordination polyhedra are joined into infinite chains.

In this work, the results of studying the first complex of Np(V) chromate with the organic guanidinium cation are presented and supplement the available concepts on the Np(V) compounds with tetrahedral anions of *d* elements.

EXPERIMENTAL

Synthesis. Solutions of ^{237}Np were purified prior to use according to a standard procedure: by the anion-exchange method followed by the precipitation of neptunium(IV) oxalate with reflux in nitric acid (~12 mol/L). To prepare neptunium(V) chromate, its hydroxide was dissolved in 0.2 M chromic acid obtained by the dissolution of commercial CrO_3 in water. Guanidinium chromate was obtained by mixing solutions of equimolar amounts of 0.2 M chromic acid and 1 M guanidinium carbonate. The isothermal evaporation at ambient temperature of a mixture containing neptunoyl chromate (0.02–0.05 mol/L) and guanidinium chromate in a molar ratio of ~1 : 3 within several hours gave dark prismatic crystals of compound $[C(NH_2)_3]_3[NpO_2(CrO_4)_2](H_2O)$, whose fracture is colored in red-brown.

The IR and visible spectra of the crystalline sample were measured in a fused NaCl matrix on Specord M80 (Germany) and Shimadzu UV-3100 (Japan) spectrophotometers, respectively, at ambient temperature. A Radelkis pH meter (Hungary) was used for measuring pH of solutions.

X-ray diffraction analysis was carried out at the Center of Collective Use of Physical Investigation Methods (Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences) on a Bruker KAPPA APEX II automated four-circle diffractometer with a two-dimensional detector (MoK_α radiation, graphite monochromator) [6]. Unit cell parameters were refined over the whole data array [7]. Absorption corrections were applied using the SADABS program [8]. The structure was solved by a direct method (SHELXS-97) [9] and refined by the full-matrix least-squares method (SHELXL-97) [9] for F^2 over all data in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms of the guanidinium cations were placed in geometrically calculated positions with the isotropic temperature factors equal to 1.2 U_{eq}(N). The hydrogen atoms of the water molecule were localized from the difference Fourier synthesis and refined by imposing conditions of tending the O–H distances to 0.85(2) Å and H–H distances to 1.35(2) Å and with the isotropic temperature factors equal to 1.5 U_{eq}(O).

Selected crystallographic data and characteristics of X-ray diffraction experiments are given in Table 1. The bond lengths and bond angles in the environment of the Np and Cr atoms are listed in Table 2. The coordinates of atoms were deposited at the Cambridge Crystallographic Data Centre (no. 889136; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data and details of the X-ray diffraction experiment and refinement for structure **I**

Parameter	Value
Molecular formula	$C_3H_{20}N_9O_{11}Cr_2Np$
Formula weight	699.28
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal sizes, mm	0.18 × 0.08 × 0.04
Unit cell parameters:	
a, Å	9.9543(3)
b, Å	19.4414(6)
c, Å	10.1313(3)
β, deg	114.573(1)
V, Å^3; Z	1783.09(9); 4
ρ_{calcd}, g/cm^3	2.605
$\mu(MoK_\alpha)$, mm^{-1}	4.95
θ_{max}, deg	30
Number of measured reflections	16037/5158
Number of independent reflections with $I > 2\sigma(I)$	3985
Number of refined parameters	241
T_{max}, T_{min}	0.766, 0.569
$R_1(F)$, $wR_2(F^2)$ ($I > 2\sigma(I)$)	0.0335, 0.0625
$R_1(F)$, $wR_2(F^2)$ (all data)	0.0533, 0.0683
Goodness-of-fit	0.977
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.673, –0.860

RESULTS AND DISCUSSION

Structure **I** is based on infinite anionic chains $[NpO_2(CrO_4)_2]_n^{3n-}$ (Fig. 1) extended along the [100] direction. Similar anionic chains have earlier been observed in the structure of $Na_3[NpO_2(CrO_4)_2](H_2O)_5$ [5].

In the equatorial plane, the neptunoyldioxo cations are surrounded by five O atoms of four chromate ions: two bidentate chelate-bridging $Cr(1)O_4^{2-}$ and two bidentate-bridging $Cr(2)O_4^{2-}$ anions. The coordination polyhedra of the Np atoms are joined in pairs through the common equatorial edges due to the bridging function of the O(11) atoms. The dioxo cations somewhat differ from linear and symmetric ones: their Np–O distances are 1.813(3) and 1.854(3) Å, and the ONpO angle is 177.50(16)°. The Np–O distances in the equatorial plane vary from 2.383(4) to 2.581(4) Å. The maximum deviation of the O atoms of the equato-

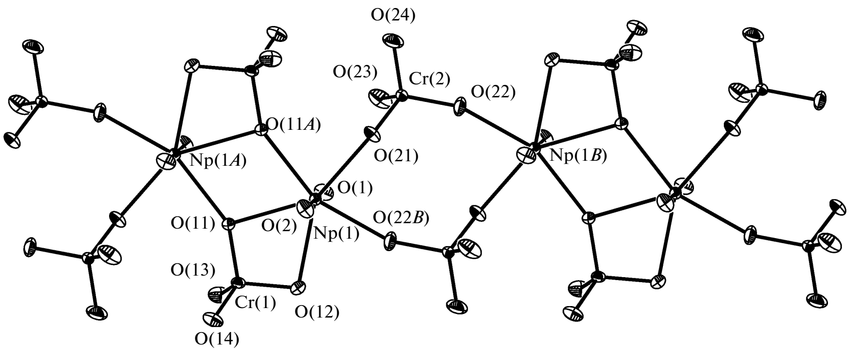

Fig. 1. Anionic chain $[NpO_2(CrO_4)_2]_n^{3n-}$ in structure **I**. Thermal vibrational ellipsoids are shown with the 50% probability.

Table 2. Interatomic distances (d, Å) and bond angles (ω, deg) in structure **I***

Bond	d, Å	Angle	ω, deg
Np(1)–O(1)	1.813(3)	O(1)Np(1)O(2)	177.50(16)
Np(1)–O(2)	1.854(3)	O(11)Np(1)O(12)	62.08(11)
Np(1)–O(11)	2.513(3)	O(11)Np(1)O(11)^{i}	68.34(13)
Np(1)–O(12)	2.581(4)	O(11A)Np(1)O(21)	79.18(12)
Np(1)–O(21)	2.420(3)	O(21)Np(1)O(22)^{ii}	77.49(14)
Np(1)–O(11)^{i}	2.440(3)	O(22)^{ii} Np(1)O(12)	73.79(15)
Np(1)–O(22)^{ii}	2.383(4)	O(11)Cr(1)O(12)	102.86(17)
Cr(1)–O(11)	1.702(3)	O(11)Cr(1)O(13)	112.10(19)
Cr(1)–O(12)	1.659(4)	O(11)Cr(1)O(14)	112.47(19)
Cr(1)–O(13)	1.628(4)	O(12)Cr(1)O(13)	111.2(2)
Cr(1)–O(14)	1.614(4)	O(12)Cr(1)O(14)	109.6(2)
Cr(2)–O(21)	1.673(3)	O(13)Cr(1)O(14)	108.6(2)
Cr(2)–O(22)	1.635(4)	O(21)Cr(2)O(22)	111.5(2)
Cr(2)–O(23)	1.616(4)	O(21)Cr(2)O(23)	109.37(19)
Cr(2)–O(24)	1.625(4)	O(21)Cr(2)O(24)	109.3(2)
		O(22)Cr(2)O(23)	109.6(3)
		O(22)Cr(2)O(24)	108.9(2)
		O(23)Cr(2)O(24)	108.1(2)

* Symmetry transforms: ^{i} $1 - x, 1 - y, 1 - z$, ^{ii} $-x, 1 - y, 1 - z$.

rial environment of the dioxo cation from the root-mean-square plane is 0.182(3) Å for the O(12) atom.

There is the coordination modes of the chromate ions depend on the distances and angles in them. The maximum Cr–O distances are observed for the coordinated O atoms. The OCrO angle for two coordinated O atoms is minimum in the bidentate chelate-bridging Cr(1)O_4^{2-} anion, whereas the corresponding angle is maximum in the bidentate-bridging Cr(2)O_4^{2-} anion (Table 2).

The layers parallel to the (010) plane formed by the anionic chains and the guanidinium cations and crystallization water molecules localized between them can be distinguished in the crystalline packing (Fig. 2). The structure contains many hydrogen bonds, which are mainly weak (Table 3), connecting the cations and anionic chains in the layer and between the layers and water molecules within the same layer. Note that the difference in the Np–O(1) and Np–O(2) distances in the dioxo cation cannot be explained by the participation of its O atoms in the hydrogen bonds.

The fragment of the electronic absorption spectrum of complex **I** is shown in Fig. 3. A noticeably broadened absorption band, whose shape can be considered as an envelope of many poorly resolved *f–f* transitions, is observed at 900–1060 nm in the spectrum. Unlike the Np(V) compounds with the tetrahedral anions of *p* elements, such as SO_4^{2-} and SeO_4^{2-}, pentavalent neptunium chromates have a special character of the absorption spectra in the visible and near-IR regions. Broad absorption bands, whose imaginary maxima are shifted to the long-wavelength region by 40–60 nm over the spectrum of the hydrated neptunoyl ion, are observed in the spectra of all studied chromates instead of the narrow intense bands of the 5*f*–5*f* electronic transitions from the ground state $^3H_4 \rightarrow {}^3F_4$ characteristic of the NpO_2^+ ion with the electronic configuration $5f^2$.

An anomalously large long-wavelength shift of the *f–f* bands was observed in the spectra of the Np(V) compounds with the anions of *d* elements: pertechnetate, vanadate, and molybdate ions [10]. The strong interaction of these ions with the central Np(V) atom decreases the distances between the energy levels of the latter. However, the shape of the bands of *f–f* electronic transitions differed in the spectra of the mentioned compounds: the bands had a distinct edging at the short-wavelength side, a high intensity, and a small half-width.

It is difficult to estimate the intensity and half-width of absorption bands for Np(V) chromates. The spectra of all earlier studied compounds exhibited smoothened shapes of the bands, and the center of gravity of the bands found graphically was taken as the main maximum. In the spectrum of compound **I**, the broad total band has a weak structure possibly caused by many hydrogen bonds provided by the presence of the guanidinium cation. In the spectral range from 1015 to 1050 nm, the shape of this band is satisfactorily approximated by 12 Lorentzian components (Fig. 3), the most intense of which has a maximum at 1034.2 nm.

A comparison of the spectra of compound **I** and earlier studied Np(V) chromates (Table 4) shows that the position of the main absorption bands depends implicitly on the composition and structure of the complexes. The highest long-wavelength shift of the absorption band of the NpO_2^+ ion is observed in the anhydrous complexes, where the coordination polyhedra of neptunium are linked to form four-unit chains. The absolute value of the bathochromic shift decreases if the chromate structure includes water molecules. As can be seen from the data presented in Table 4, all structures of Np(V) chromates are characterized by short interatomic Np···Cr distances, which confirms the mechanism of the intramolecular redox process Np(V)/Cr(VI) ↔ Np(VI)/Cr(V) proposed [1] that leads to a considerable broadening and shift of the bands of *f–f* electronic transitions in the spectra. Recent studies performed by the modern physical methods give some quantitative characteristics of similar processes. The electron transfer with the formation of Bipy–Mn(IV)–(μ-O)–Mn(IV) and Cr(V), where the charge separation retained within several

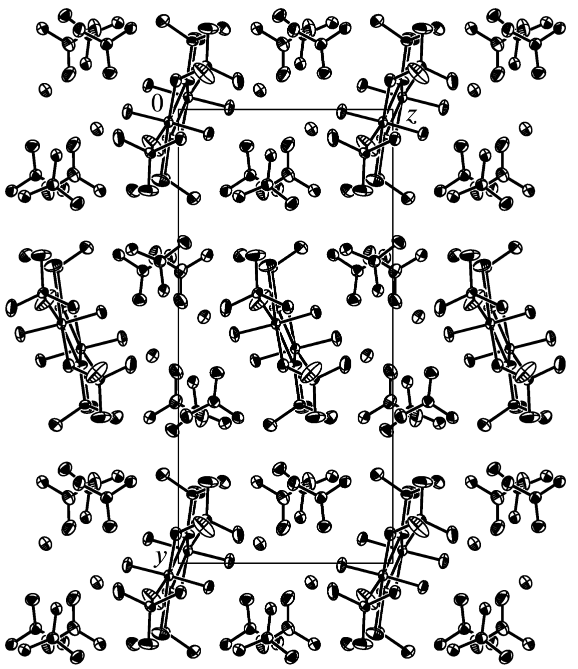

Fig. 2. Crystalline packing of structure **I**. Hydrogen atoms and hydrogen bonds are omitted.

min, was observed [11] in the Bipy–Mn(III)–(μ-O)–Mn(IV) system in the presence of Cr(VI). Evidently, such a long time of reversible electronic transitions should result in a considerable broadening of the spectral bands.

The IR spectrum of compound **I** (Fig. 4) contains in the high-frequency range (4000–3000 cm^{-1}) relatively narrow intense bands corresponding to stretching vibrations ν(OH) of the crystallization water molecules and ν(NH) of the guanidinium cation in the composition of the compound. Although these bands are partially overlapped, their maxima are easily identified (Table 5).

The bands of stretching vibrationsν_{as}(CN) of the guanidinium cation with maxima near 1680 cm^{-1} are the most intense bands in the range from 1700 to 500 cm^{-1}. The partial π character of the C–N bonds in the structure of the guanidinium ion determines the high intensity of these vibrations [12]. A range of 540–520 cm^{-1} is characteristic of bending vibrations δ(NCN) of this group.

The stretching vibrations of the chromate ions appear as very intense bands but at lower frequencies than, for example, those in simple chromate Na_2CrO_4 [1] or in $Na_3[NpO_2(CrO_4)_2](H_2O)_5$ [5], i.e., these vibrations are sensitive to the structure of the complex. A good resolution in the spectrum of compound **I** makes it possible to identify the bending planar and nonplanar vibrations of the chromate ion near 400 cm^{-1}. Antisymmetric vibrations of the neptunoyl group $\nu_{as}(NpO_2)$ appear as a medium-intensity band at 796 cm^{-1}.

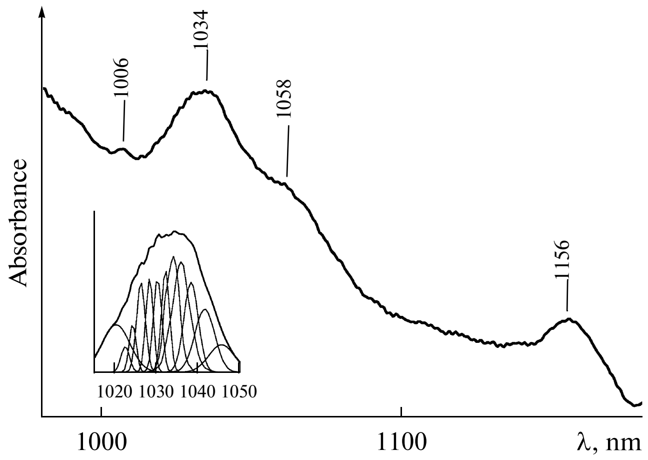

Fig. 3. Electronic absorption spectrum of compound **I** (3.2 mg in 220 mg of the matrix).

Thus, the synthesized and studied new neptunium complex has structural and spectral characteristics typical of the already known series of Np(V) chromates. The replacement of the outer-sphere inorganic cation by the guanidinium cation exerts a slight effect on the structure of the compound formed. As mentioned above, the main structural motif of compound **I** is presented by the infinite anionic chains $[NpO_2(CrO_4)_2]_n^{3n-}$, extended along the [100] direction, which is the same as in the structure of $Na_3[NpO_2(CrO_4)_2](H_2O)_5$ [5]. The character of the electronic spectrum of compound **I** shows a certain uniqueness of the NpO_2^+–CrO_4^{2-}, system in which the electron transfer observed. Such process is unknown, for example, for Np(VI) chromates with the electronic configuration $5f^1$.

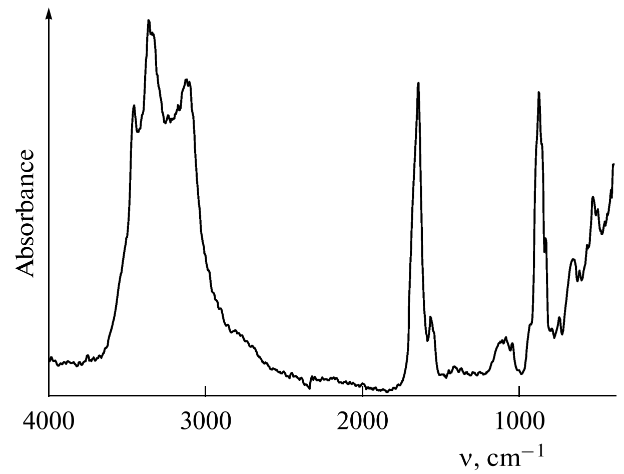

Fig. 4. IR spectrum of crystalline compound **I** (1.4 mg in 220 mg of the matrix).

Table 3. Geometric parameters of hydrogen bonds in structure **I**

Contact D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for atom A
	D–H	H···A	D···A		
O(1*w*)–H(1*C*)···O(23)	0.858(19)	2.23(3)	3.012(6)	152(5)	
O(1*w*)–H(1*D*)···N(9)	0.842(19)	2.29(4)	2.924(6)	133(5)	$x, y, z - 1$
N(1)–H(1*A*)···O(13)	0.86	2.30	2.951(6)	133	$x, -y + 3/2, z + 1/2$
N(1)–H(1*B*)···O(12)	0.86	2.35	3.209(7)	176	
N(2)–H(2*A*)···O(2)	0.86	2.20	3.022(6)	159	$x, -y + 3/2, z - 1/2$
N(2)–H(2*B*)···O(2)	0.86	2.17	3.001(6)	163	$-x + 1, y + 1/2, -z + 3/2$
N(3)–H(3*A*)···O(12)	0.86	2.35	3.075(6)	143	$x, -y + 3/2, z - 1/2$
N(3)–H(3*B*)···O(13)	0.86	2.42	2.999(6)	125	
N(4)–H(4*A*)···O(24)	0.86	2.37	3.208(7)	164	$-x, -y + 1, -z$
N(4)–H(4*B*)···O(24)	0.86	2.30	3.008(7)	140	$-x, y + 1/2, -z + 1/2$
N(5)–H(5*A*)···O(1)	0.86	2.28	3.001(6)	142	
N(5)–H(5*B*)···O(24)	0.86	2.12	2.878(6)	146	$-x, y + 1/2, -z + 1/2$
N(6)–H(6*A*)···O(1)	0.86	2.03	2.827(5)	153	
N(6)–H(6*B*)···O(23)	0.86	1.93	2.773(6)	168	$-x, -y + 1, -z$
N(7)–H(7*A*)···O(1W)	0.86	2.35	3.077(6)	143	$x, y, z + 1$
N(7)–H(7*B*)···O(13)	0.86	2.28	3.074(6)	154	$-x + 1, y - 1/2, -z + 3/2$
N(8)–H(8*A*)···O(21)	0.86	2.20	2.968(6)	149	
N(8)–H(8*B*)···O(14)	0.86	2.06	2.916(6)	171	$-x + 1, y - 1/2, -z + 3/2$
N(9)–H(9*A*)···O(21)	0.86	2.29	3.044(6)	146	
N(9)–H(9*B*)···O(1W)	0.86	2.14	2.924(6)	152	$x, y, z+1$

Table 4. Electronic absorption spectra of the known Np(V) chromate complexes

Compound	Position of main maximum, nm	Interatomic distance Np···Cr, Å
$K_3[NpO_2(CrO_4)_2]$	1040	3.202, 3.952, 3.941, 3.971
$(NH_4)_4[(NpO_2)_2(CrO_4)_3]$*	1042	3.222, 3.770, 3.850, 3.990 3.219, 3.917, 3.973, 4.058
$Cs[(NpO_2)(CrO_4)](H_2O)$	1038	3.214, 3.791, 3.919, 4.018
$Cs[(NpO_2)(CrO_4)(H_2O)](H_2O)$	1036	3.204, 3.956, 3.994
$Na_3[NpO_2(CrO_4)_2](H_2O)_5$	1029	3.228, 3.854, 3.931, 3.955
$[C(NH_2)_3]_3[NpO_2(CrO_4)_2](H_2O)$	1034	3.2298(8), 3.7882(7), 3.9868(8), 3.9619(8)

* Two independent Np atoms.

Table 5. Positions of absorption band maxima corresponding to the characteristic vibrations in the IR spectrum of compound **I**

Assignment	ν, cm^{-1}
ν(OH), ν(NH)	3460, 3456, 3332, 3240, 3128
ν_{as}(CN), δ(HOH)	1652, 1640, 1628, 1568
$\nu_{as}(CrO_4)$	912, 896
ν_s(CN)	1120, 1084
$\nu_s(CrO_4)$	932, 880, 864, 836, 820 sh
$\nu_{as}(NpO_2)$	796
$\rho(H_2O)$	752
δ(NCN)	538, 500
δ(OCrO)	436, 424

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 11-03-01231a and 12-03-01075a).

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