termolecular contacts in this structure. The shortest contacts (3.36 Å) involve phenyl carbon atoms for which the sum of the van der Waals radii is 3.40 Å.[39]

As a check on the accuracy of this structure, it is gratifying to find that the averaged C–C bond length in the phenyl groups (1.378 ± 0.011 Å) is in good agreement with the values found for crystalline benzene (1.392 Å[40]) and other metal dibenzoylmethanates (cf. Table VIII). The phenyl groups are planar, with the average displacement of the 48 carbon atoms from the mean planes of the eight phenyl rings being 0.007 Å (maximum displacement 0.017 Å). However, the phenyl groups are twisted out of the plane of the C_3O_2 portion of the ligand by angles that vary from 17.3° to 41.9° (average 26.9°; cf. Table VIII).

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Registry No. Zr(bzbz)$_4$, 17455-33-3.

Supplementary Material Available: A listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Crystal Structure of Rubidium Fluoroxysulfate. Characterization of the Fluoroxysulfate Anion[1]

E. GEBERT, E. H. APPELMAN,* and A. H. REIS, JR.*

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The rubidium salt of the recently identified fluoroxysulfate anion, $FOSO_3^-$, has been characterized by single-crystal X-ray diffraction. $RbFOSO_3$ crystallizes in the centrosymmetric triclinic space group, $P\bar{1}$, with unit cell constants $a = 5.503$ (2) Å, $b = 5.623$ (1) Å, $c = 7.603$ (3) Å, $\alpha = 100.64$ (2)°, $\beta = 106.72$ (2)°, $\gamma = 93.22$ (2)°, and $Z = 2$. The X-ray data refine to an $R_F = 0.067$ for 664 reflections with $F^2 > \sigma F^2$. The fluoroxysulfate anion has distorted tetrahedral coordination with each central sulfur atom bound to four oxygens. The S–O bond distances are 1.435 (8), 1.426 (8), 1.441 (7), and 1.652 (9) Å. The O–F bond distance is 1.412 (10) Å, and the S–O–F bond angle is 107.8 (6)°. Each Rb^+ cation is coordinated to nine oxygen atoms and two fluorine atoms.

Introduction

Appelman et al.[2] have recently reported the preparation of rubidium and cesium fluoroxysulfates, $Rb^+FOSO_3^-$ and $Cs^+FOSO_3^-$. Both materials were shown to be powerful oxidizing and fluorinating agents. Infrared, Raman, and NMR spectra of these salts are consistent with the formulation of the anion as a fluoroxyion or hypofluorite, $FOSO_3^-$. Although other hypofluorites are known, they are all neutral molecules that are gases at room temperature. The fluoroxysulfates are the first saltlike hypofluorites to be isolated and as such are particularly amenable to detailed structure determination by X-ray diffraction. Preliminary X-ray powder diffraction photographs of the two salts indicated them to be isomorphous. Inasmuch as the rubidium salt was more readily obtainable in the crystalline form, the structure of this material has been completely determined in the present study.

Experimental Section

Preparation of Material. Rubidium fluoroxysulfate was prepared by passing fluorine (20 mol % in N_2) through a 1.3 M solution of rubidium sulfate at 0 °C.[2] The precipitate was separated by cen-

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Table I. Experimental Details for $Rb^+FOSO_3^-$

cell constants at $T = 20$ °C	$a = 5.503$ (2) Å, $b = 5.623$ (1) Å, $c = 7.603$ (3) Å, $\alpha = 100.64$ (2)°, $\beta = 106.72$ (2)°, $\gamma = 93.22$ (2)°
cell vol	219.9 (1) Å^3
mol wt	200.53
calcd dens	3.02 g cm^{-1}
Z	2
space group	$P\bar{1}$
radiation	Mo Kα, $\lambda = 0.710\ 69$ Å
max 2θ	50.0° ($+h,\pm k,\pm l$)
scan type	θ-2θ coupled
scan width	$[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
scan speed	variable, 1.96-29.30°/min
crystal	general orientation, volume = 0.237 × 10^{-5} cm^3 (0.01 × 0.01 × 0.02 cm), abs coef = 122.23 cm^{-1}, max transmission factor = 0.40, min transmission factor = 0.19, no. of reflctns collected = 788
R_F	0.067 for 664 with $F_o^2 > \sigma F_o^2$
R_{wF^2}	0.107
GOF	2.243

trifuging, washed with water, and dried under vacuum.[2] A satisfactory single crystal was chosen by microscopic examination of the dried sample.

X-ray Data Collection. A single crystal (0.01 × 0.01 × 0.02 cm) of $RbFOSO_3$ was sealed into a glass capillary and mounted on a Syntex $P2_1$ automatic diffractometer under dedicated control of a NOVA computer. The diffractometer, at a takeoff angle of 6°, was equipped with a molybdenum X-ray tube and a graphite monochromator ($\lambda = 0.7107$ Å, $d = 3.36$ Å (002)).

The crystal was optically centered in a random orientation. Cell orientation, unit cell parameters, and crystal quality were determined as previously described.[3] Three intense standard reflections were monitored every 97 reflections as a guide to the stability of the system and crystal. During data collection, which took ~24 h, the combined intensity of the standard reflections dropped 15%. The crystal became cloudy, indicating radiation damage. Intensity data were collected to a 2θ maximum of 50° over four octants; 788 reflections were collected. An examination of the data revealed no systematic absences, therefore confirming the space group as $P1$ or $P\bar{1}$. Experimental information is listed in Table I.

Solution and Structure Refinement. Absorption, Lorentz, and polarization corrections were applied to the data by the program DATALIB.[4] Because of the steady decrease in intensity of the check reflections, the data were normalized in DATALIB to the interpolated value of the sum of the net counts of the standard reflections. The rubidium ion was located from a three-dimensional Patterson map. Space group $P\bar{1}$ was initially chosen. A three-dimensional Fourier synthesis based on phasing from the Rb^+ provided a refined position for that ion and determined the positions of the $FOSO_3^-$ ions. Full-matrix least-squares refinement of a scale factor, atomic positions, and anisotropic thermal parameters gave a final $R_F = 0.067$ for the 664 reflections with $F_o^2 > \sigma F_o^2$. Seven reflections were removed from the least-squares analysis because of low transmission coefficients that resulted from overcorrection for absorption due to the irregularity of the crystal. Because of the quality of the refinement, space group $P\bar{1}$ was verifed. The quantity minimized during refinement is $\sum w|F_o^2 - F_c^2|^2$, where F_o and F_c are the observed and calculated structure factor amplitudes. Weights are assigned as $w = 1/(\sigma F_o^2)^2$, $\sigma(I) = [SC + \tau^2(B_1 + B_2) + P^2I^2]^{1/2}$. SC is the scan count, τ is the scan-to-background time ratio, B_1 and B_2 are the background counts on each side of a peak, I is the net intensity, and p is a systematic error factor set to 0.03, a value found to be appropriate in this laboratory. The agreement indices are

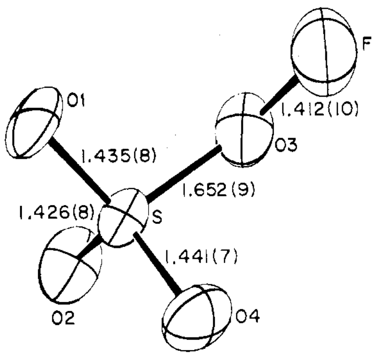

Figure 1. Interatomic distances in $FOSO_3^-$.

$$R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_{wF^2} = [\sum w|F_o^2 - F_c^2|^2 / \sum w(F_o^2)^2]^{1/2}$$

$$\mathrm{GOF} = [\sum w|F_o^2 - F_c^2|^2/(N_o - N_r)]^{1/2}$$

N_o is the number of independent reflections and N_r is the number of parameters varied. The programs S5FOUR[5] and S5XFLS[5] were used for Fourier and least-squares refinements. Bond distances, angles, and estimated standard deviations (esd's) were determined by the program S5FFE.[5] Molecular drawings were prepared by using ORTEP.[6] The atomic coordinates and the corresponding anisotropic temperature parameters are given in Table II. Scattering factors were taken from the compilation of Cromer and Waber[7] and were modified for the real and imaginary components of anomalous dispersion.[8] A listing of F_o and F_c is given as supplementary material.

Structure Description and Discussion

The structure of the fluoroxysulfate anion is shown in Figure 1, and its interatomic distances and angles are given in Table III. The ion has a distorted tetrahedral symmetry. The S–OF bond, which we may consider to be a sulfur–oxygen single bond, has a length of 1.652 (9) Å. The other sulfur–oxygen bonds, which may be regarded as double bonds, have an average length of 1.434 (8) Å. In the analogous ions $HOSO_3^-$ and $C_2H_5OSO_3^-$, the sulfur–oxygen single bond lengths are 1.57 (2) and 1.604 (4) Å, respectively, while the average sulfur–oxygen double bond lengths are about 1.46 Å.[9-11] Hence, the $FOSO_3^-$ ion appears to have a relatively long sulfur–oxygen single bond and relatively short sulfur–oxygen double bonds. We may rationalize these effects in terms of the high electronegativity of the fluorine atom, which draws electron density out of the S–OF bond, causing it to lengthen. At the same time, this also reduces the electron density on the sulfur, causing an increase in the double-bond character of the other sulfur–oxygen bonds and thereby shortening them.

The O–F bond length of 1.412 (10) Å is identical with that found in OF_2,[12] while the F–O–S angle of 107.8 (6)° is somewhat larger than the F–O–F angle of 103.2°.[12] This increase in angle may reflect a repulsion between the fluorine

Table II. Positional Atomic Coordinates and Anisotropic Thermal Parameters[a] of $Rb^+FOSO_3^-$ [b]

atoms	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	0.1099 (2)	0.3350 (2)	0.2388 (2)	0.032 (1)	0.041 (1)	0.037 (1)	−0.003 (0)	0.007 (0)	0.019 (1)
F	0.2084 (14)	−0.1385 (12)	0.5284 (11)	0.072 (5)	0.044 (4)	0.072 (5)	−0.008 (4)	0.015 (5)	0.009 (4)
S	0.3856 (5)	0.2224 (5)	0.7878 (4)	0.030 (2)	0.030 (2)	0.037 (2)	0.000 (1)	0.011 (1)	0.014 (1)
O1	0.3409 (14)	0.3717 (12)	0.6502 (11)	0.050 (5)	0.038 (5)	0.048 (5)	0.001 (4)	0.009 (4)	0.030 (4)
O2	0.6339 (14)	0.2689 (14)	0.9219 (11)	0.031 (4)	0.057 (5)	0.055 (6)	−0.005 (4)	−0.003 (4)	0.025 (5)
O3	0.4287 (15)	−0.0493 (14)	0.6827 (12)	0.048 (5)	0.039 (5)	0.056 (6)	−0.003 (4)	0.009 (5)	0.012 (4)
O4	0.1727 (14)	0.1811 (14)	0.8573 (11)	0.040 (5)	0.050 (5)	0.055 (5)	0.002 (4)	0.027 (4)	0.014 (4)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. [b] Estimated standard deviations are given in parentheses.

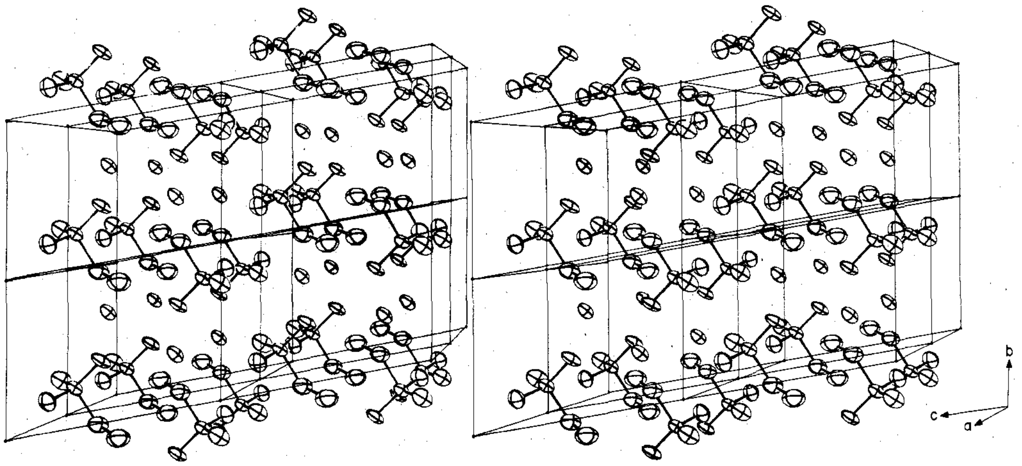

Figure 2. Stereoview of eight unit cells of $Rb^+FOSO_3^-$.

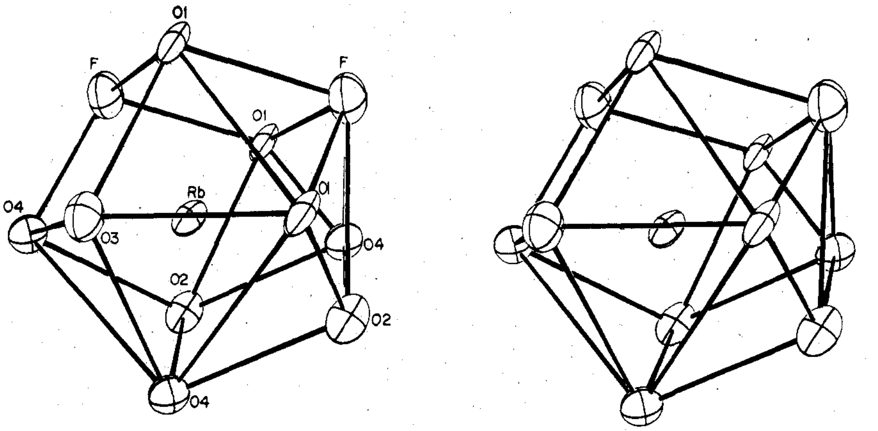

Figure 3. Stereoview of the distorted polyhedron formed by Rb^+ bonding in $Rb^+FOSO_3^-$.

Table III. Interatomic Distances (Å) and Angles (deg) of $Rb^+FOSO_3^-$ [a]

Rb-O(2)	2.955 (10)	F-O(3)	1.412 (10)
Rb-O(1)	2.981 (9)	S-O(2)	1.426 (8)
Rb-O(4)	2.994 (8)	S-O(1)	1.435 (8)
Rb-O(3)	3.053 (8)	S-O(4)	1.441 (7)
Rb-O(4)	3.071 (8)	S-O(3)	1.652 (9)
Rb-F	3.116 (9)	O(1)-O(2)	2.41 (1)
Rb-O(1)	3.166 (8)	O(1)-O(4)	2.42 (1)
Rb-O(2)	3.175 (9)	O(1)-O(3)	2.49 (1)
Rb-F	3.261 (10)	O(2)-O(3)	2.27 (1)
Rb-O(1)	3.277 (8)	O(2)-O(4)	2.44 (1)
Rb-O(4)	3.303 (8)	O(3)-O(4)	2.46 (1)

O(2)-S-O(1)	115.1 (5)	O(1)-S-O(3)	107.0 (5)
O(2)-S-O(4)	117.0 (5)	O(4)-S-O(3)	105.4 (5)
O(2)-S-O(3)	95.0 (5)	F-O(3)-S	107.8 (6)
O(1)-S-O(4)	114.3 (5)		

[a] Estimated standard deviations are given in parentheses.

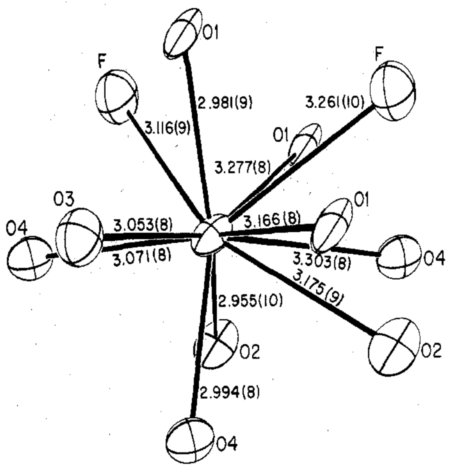

Figure 4. Elevenfold coordination around the Rb^+ ion in $Rb^+FOSO_3^-$, with interatomic distances shown.

atom and the oxygen atoms double bonded to the sulfur.

The distortion of the fluoroxysulfate anion is further reflected in the O–S–O angles of 95.0 (5)°, 105.4 (5)°, 107.0 (5)°, 114.3 (5)°, 115.1 (5)°, and 117.0 (5)°. The three O–S–O angles that involve the O–F unit are all smaller than the expected tetrahedral angle of 109.5°, while those angles that do not involve the O–F unit all exceed the tetrahedral value. This distortion is somewhat greater in $FOSO_3^-$ than in $HOSO_3^-$ and $C_2H_5OSO_3^-$, in which the average values of the O–S–O angles involving the OH or OC_2H_5 units are 105–106°, while the average values of the O–S–O angles that do not involve the OH or OC_2H_5 units are about 113°.[9-11] The corresponding average values for $FOSO_3^-$ are 102 and 115°, respectively. This distortion can be understood as a minimization of the repulsions among the three sulfur–oxygen double bonds. The distortion pushes the double-bonded oxygen atoms further apart but brings them closer to the single-bonded oxygen. The enhancement of this effect in $FOSO_3^-$ seems reasonable in view of the reduced electron density in the S–OF single bond and the resulting increase in the double-bond character of the other sulfur–oxygen bonds.

The differences among the chemically equivalent O–S–O angles in the $FOSO_3^-$ ion are probably due to the packing arrangement within the crystal, in which each Rb^+ ion is bound to several $FOSO_3^-$ ions. Similar effects are observed in the structure of $K^+C_2H_5OSO_3^-$.[11]

Figure 2 gives a stereoview of eight unit cells. The structure is centrosymmetric, consisting of discrete $FOSO_3^-$ and Rb^+

ions. There are two $Rb^+FOSO_3^-$ molecules in each unit cell. Each Rb^+ ion is coordinated to nine oxygen atoms and two fluorine atoms, forming the distorted polyhedron shown in Figures 3 and 4. The individual Rb–O and Rb–F distances are all unique and range from 2.955 (10) to 3.303 (8) Å. These distances are all within the range expected for normal 11-coordinated Rb–O and Rb–F bonds. There is no evidence of further interactions within the structure.

Registry No. $RbFOSO_3$, 70631-32-2.

Supplementary Material Available: A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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(1) This research has been conducted under the auspices of the Office of Basic Energy Sciences of the U.S. Department of Energy.

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(5) S5FOUR, S5XFLS, and S5FFE are Sigma 5 versions of the programs FOURIER by R. J. Dellaca and W. T. Robinson, ORXFLS3 by W. R. Busing and H. A. Levy, and ORFEE by W. R. Busing and H. A. Levy.

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Contribution from the Department of Chemistry,
Montana State University, Bozeman, Montana 59717

Mixed-Ligand Complexes of *O*-Phospho-DL-serine

M. S. MOHAN, D. BANCROFT, and E. H. ABBOTT*

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The formation of mixed-ligand complexes MHAL and MAL has been studied for A = histamine, 1,10-phenanthroline, or α,α'-bipyridyl, L = *O*-phospho-DL-serine, and M = Cu(II), Ni(II), Co(II), or Zn(II). Equilibrium data and ^{31}P NMR studies show that in the MAL complexes *O*-phosphoserine is tridentate with Ni(II), Co(II), and Zn(II) but bidentate with Cu(II). Due to the square-planar configuration of Cu(II), the phosphate moiety is not bound in the MAL complexes. The mixed-ligand complex $ZnAL^-$ (A = histamine) is exceptionally stable when compared to either binary precursors. This is probably the result of a change in coordination geometry from tetrahedral in the binary complexes to idealized octahedral in the mixed-ligand complexes. With the other mixed-ligand complexes of Ni(II), Co(II), and Zn(II) the formation constants are consistent with the addition of ligands to an essentially octahedral coordination sphere.

Introduction

The final step in the biosynthesis of serine is the hydrolysis of *O*-phosphoserine according to the equation

$$\text{phosphoserine} + H_2O \rightarrow \text{serine} + \text{orthophosphate}$$

This reaction is catalyzed by the enzyme phosphoserine phosphohydrolyase, and a mechanism involving the formation of an enzyme–substrate complex has been suggested.[1] The presence of divalent metal ions is required for the activation of this enzyme.[2] A number of other metal ion activated enzymatic reactions have been shown to proceed via higher order complexes and to occur within the coordination sphere of the metal ion.[3] For a better understanding of these higher order complexes, information regarding the extent and the nature of interaction between the metal ion, the enzyme, and the substrate would be invaluable. As phosphoserine is potentially tridentate (i.e., binding through the carboxylate, phosphate, and amino moieties), it is expected to bind metal ions strongly. Further the nature and the geometry of the metal ion would determine the extent to which these three sites bind, thus giving rise to a variety of complexes with differing stability and structures. In the activation of phosphoserine phosphohydrolyase it was found that while Mg(II), Co(II), Fe(II), Mn(II), Ni(II), and Zn(II) activate the enzyme, other bivalent metal ions like Cu(II), Cd(II), and Ca(II) do not.[2] This raises the interesting question of whether in the ternary complexes involving the enzyme, metal ion, and phosphoserine the binding sites are different for the above two sets of metal ions. It was therefore considered important to undertake a detailed study of the interaction of bivalent metal ions with phosphoserine and to study the formation of ternary complexes in solutions containing a nitrogen donor, a bivalent metal ion, and phosphoserine. These ternary complexes could serve as models for the enzyme–metal ion–substrate complexes. in a previous study we have reported on the stabilities and structures of the binary metal complexes of phosphoserine with a number of bivalent metal ions.[4] In the present study we have investigated by potentiometry and ^{31}P NMR the stabilities and structures of ternary complexes formed in solutions containing phosphoserine and phenanthroline, bipyridyl, or histamine with the bivalent metal ions Cu(II), Ni(II), Co(II), and Zn(II).

Experimental Section

Materials. The ligands *O*-phospho-DL-serine, 1,10-phenanthroline, α,α'-bipyridyl, and histamine dihydrochloride were obtained from Sigma Chemical Co. The purity of these ligands and their molecular weights were determined by potentiometric titration with standard carbonate-free sodium hydroxide. The phosphoserine was used in the triprotonated form while the amines were employed in the diprotonated form. Stock solutions of Cu(II), Ni(II), Co(II), and Zn(II) were prepared from analytical grade nitrates and standardized by titrating with the disodium salt of EDTA.[5] Carbonate-free sodium hydroxide was prepared and standardized by titrating with potassium hydrogen phthalate (BDH AnalaR, dried for 2 h at 120 °C). Double-distilled water was used for the preparation of all stock and experimental solutions.

Potentiometric Measurements. Dissociation constants for the free ligands were determined by potentiometric titration of the ligands with standard carbonate-free sodium hydroxide. The stability constants for the binary complexes were computed from titrations in which the metal:ligand ratio was 1:2, while the constants for the ternary complexes were computed from titrations in which the total concentrations of the metal ion, the amine, and phosphoserine were in a 1:1:1 molar ratio. The concentration of the metal ions was approximately 2.0×10^{-3} M. Multiple titrations were carried out for each system.

All potentiometric titrations were carried out at 25.0 ± 0.1 °C with the apparatus and procedure described previously.[4] A constant ionic strength of 0.15 was maintained by the addition of potassium nitrate.

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