



NO_2^- and SCN^- -intercalated layered double hydroxides: structure and orientation of anions in the interlayer gallery

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MS received 13 October 2016; accepted 11 July 2017; published online 5 February 2018

Abstract. NO_2^- and SCN^- are two common small inorganic anions. The former is a common industrial pollutant. The latter is linear and is a good mimic for the toxic CN^- ion. The structures of these two anions are refined within the gallery of the [Zn–Al]-layered double hydroxide (LDH). Both LDHs crystallize as mixed anion phases. The nitrite is found to co-exist with the nitrate ion. The nitrite ion is intercalated with its molecular plane inclined to the metal hydroxide layer. In the case of the SCN^- intercalated LDH, no other anion was detected by ion chromatography, suggesting that the SCN^- deficiency is compensated by intercalated hydroxyl ions. In this case, the SCN^- ion is found to be intercalated with its molecular axis inclined to the metal hydroxide layer.

Keywords. Nitrite ion; thiocyanate ion; layered double hydroxide; structure refinement.

1. Introduction

The layered double hydroxides (LDHs) comprise two structural units: (i) ionocovalently bonded metal hydroxide layer of the composition $[\text{M}(\text{II})_{1-x}\text{M}'(\text{III})_x(\text{OH})_2]^{x+}$ ($\text{M} = \text{Zn}$, $\text{M}' = \text{Al}$; in this work), and (ii) the interlayer comprising the charge compensating anion and its hydration sphere having the composition $[(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}]$. There is a general understanding that the hydroxyl ions occupy positions described by a hexagonal packing of atoms with the two cations occupying alternative layers of octahedral sites. The vacant layers of octahedral sites constitute the interlayer gallery into which the charge compensating anions are intercalated along with water molecules. While the metal hydroxide layer derives its structure from that of $\text{Mg}(\text{OH})_2$ and is adequately described [1,2], there is no corresponding model to describe the packing of atoms in the interlayer gallery.

The structure of the interlayer has to be determined by diffraction studies of laboratory-synthesized powder samples [3,4] or single crystalline mineral samples [1,5–7]. Given the high affinity of the metal hydroxide layer for ambient CO_2 , a majority of the LDHs intercalate carbonate ions. The first attempt to describe the structure of the interlayer was made by Taylor [1], who proposed that the carbonate ion (molecular symmetry, D_{3h}) is intercalated with its molecular plane parallel to metal hydroxide layer in trigonal prismatic sites (local site symmetry, D_{3h}) defined by the hydroxyl ions lining the gallery. In Taylor's [1] model, the 2-D arrays of hydroxyl ions on either side of the interlayer gallery are in an eclipsed

configuration. The matching of the molecular symmetry of the CO_3^{2-} ion and the local symmetry of the interlayer site, in Taylor's [1] opinion maximizes the hydrogen bonding interaction between the metal hydroxide layers and the intercalated carbonates. For similar reasons, Taylor [1] proposed that the O-atom of the intercalated water molecule shares the same site as the O-atoms of the intercalated CO_3^{2-} ion. This proposal is now widely accepted and adequately accounts for the observed diffraction data from both single crystalline [1,5–7] and powder diffraction studies [3,4]. The same structure model is now extended to Cl^- -intercalated LDHs [8], wherein the Cl^- ion is shown to occupy the same site as that of the O-atom of carbonate ion.

However, a number of difficulties arise in describing the structure of LDHs comprising other anions having a different charge and/or molecular symmetry from that of the CO_3^{2-} ion. The major of these difficulties lies in the description of NO_3^- -intercalated LDHs and this problem is adequately dealt elsewhere [9]. Briefly, the nitrate ion intercalates with its molecular plane parallel to the metal hydroxide layer at low layer charge ($x \leq 0.25$) and with its molecular plane inclined at an angle $\sim 70^\circ$ to the metal hydroxide layer at high layer charge ($x = 0.33$).

Another commonly found anion in laboratory-synthesized and mineral LDHs is SO_4^{2-} . The free ion has a tetrahedral molecular symmetry, which is retained when the SO_4^{2-} ion is loosely intercalated in the LDH interlayer. The resulting LDH phase is turbostratically disordered. When the SO_4^{2-} ion is strongly bound, the anisotropic crystal field

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12034-017-1530-x>) contains supplementary material, which is available to authorized users.

of the LDH crystal brings down the symmetry of the intercalated SO_4^{2-} ion to C_{3v} or D_{2d} [10] keeping with Halford's [11] rule. In addition, the intercalated SO_4^{2-} undergoes different degrees of hydration giving a range of polytypes with basal spacings in the range of 8–11 Å and these phases are fully reviewed elsewhere [10,12,13]. These observations led to the concept of anion-mediated polytypism in LDHs [3,14].

It is generally observed that the incorporation of large anions leads to a loss of registry between the metal hydroxide layers leading to turbostratic disorder [15]. Under such condition, it is practically impossible to evolve structure models to describe the packing of atoms in the interlayer by diffraction studies.

In the field of environmental remediation, one of the applications of LDHs is sorption/uptake of toxic anions from industrial and natural water bodies [16]. Among the toxic industrial anionic wastes are the nitrites and cyanides. NO_2^- ion has C_{2v} symmetry and the linear SCN^- ion was chosen as a model for CN^- . In this work, we synthesize NO_2^- and SCN^- -intercalated LDHs of Zn and Al and attempt to describe the structure of the interlayer.

2. Experimental

2.1 Synthesis of LDHs

All the chemicals used for the synthesis were procured from Merck, India, and used without further purification. All the stock metal salt solutions were standardized before using in the synthesis.

The [Zn–Al– NO_2] and [Zn–Al–SCN] LDHs were synthesized by coprecipitation at constant pH = 8 and temperature of 60°C. In a typical co-precipitation, a mixed metal nitrate solution (50 ml, total metal concentration 1 M) was added slowly (addition rate is 2 ml min⁻¹) to a reaction vessel containing a solution (100 ml) of $\text{NaNO}_2/\text{NaSCN}$ 10 times excess of the stoichiometric requirement. The pH of the reaction mixture was maintained by simultaneous addition of NaOH (0.25 M) using a Metrohm 718 STAT Titrino operating in the pH stat mode. To avoid carbonate contamination, N_2 gas was continuously purged through the reaction mixture during precipitation and ageing (18 h, 60°C). The obtained precipitates were washed with hot deionized and decarbonated water and dried in an oven at 65°C (18 h).

2.2 Materials characterization

The samples were characterized by powder X-ray diffraction (PXRD) with a Bruker D8 Advance powder diffractometer (source $\text{CuK}\alpha$ radiation, Ni filter, $\lambda = 1.5418$ Å) operating in reflection geometry. For structure refinement, data were collected at a scan rate of 0.12° 2 θ min⁻¹ (step size 0.02°, step time 10 s per step, 5°–100° 2 θ). IR spectra of the samples were recorded with a Bruker Model Alpha-P IR spectrometer (Diamond ATR cell, 4 cm⁻¹ resolution, 400–4000 cm⁻¹).

The anion content of the LDHs was estimated by ion chromatography using a Metrohm Model 861 Advanced Compact ion chromatograph fitted with a Metrosep SUP5 150 column. The pre-weighed samples were dissolved in sulphuric acid and injected into the chromatograph. The chromatograph response was calibrated using the standard stock solutions of the corresponding sodium salts ($\text{NaNO}_2/\text{NaSCN}$). Thermo-gravimetric analysis (TGA) was performed with a Mettler Toledo Model 851^e TG-sDTA system driven by Star^e software. A three segment heating programme was employed consisting of two ramps (30–100°C and 100–800°C) and a stay at 100°C (1 h).

2.3 Structure refinement

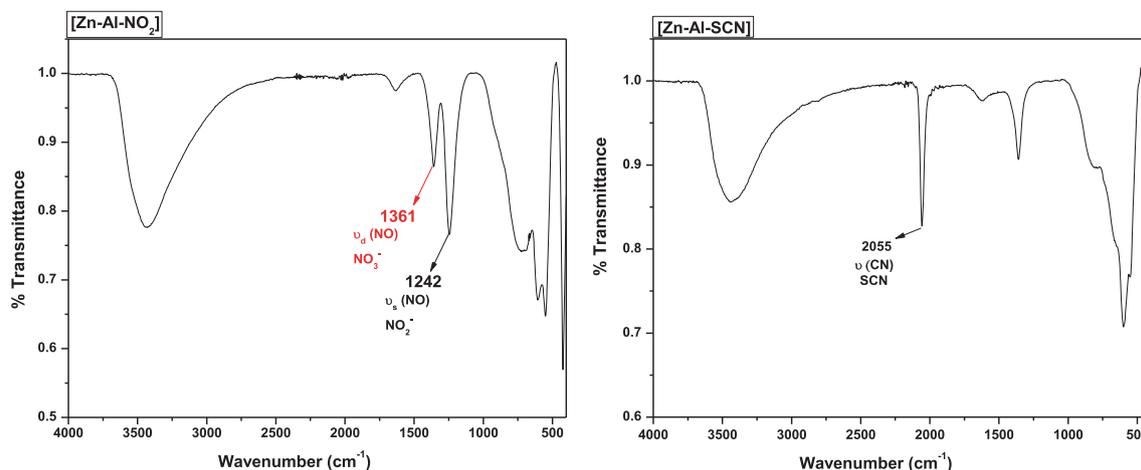
The PXRD patterns of the samples were indexed to a cell of rhombohedral symmetry and the cell parameters refined using code PROSZKI (APPLEMAN). The resultant Dewolff's Mn values (supplementary table S1) are satisfactory. For structure refinement, the partial structure model comprising the metal hydroxide layer was taken from the published structure of the [Zn–Al– NO_3] LDH (CCDC no. 917173) [9] and input into code FOX [17,18]. The anion position and orientation was obtained from code FOX by an optimization procedure described elsewhere [9]. The optimized structure was taken into the structure refinement program GSAS [19] to continue the least squares refinement in the conventional way in the reciprocal space. The positions of water molecules were obtained by the difference Fourier method embedded in code GSAS.

3. Results and discussion

There are two difficulties encountered in delineating the structure of the interlayer of LDHs. The first difficulty is associated with the synthesis of ordered samples. The second difficulty is to obtain a single anion LDH. Navrotsky and co-workers [20,21] have shown that the enthalpy of formation of a LDH is sum of the enthalpies of formation of the divalent hydroxide, the trivalent hydroxide and the salt of the divalent metal. Application of this mechanical mixture model to the LDH under our consideration would result in $\text{Zn}_4\text{Al}_2(\text{OH})_{12}\text{X}_2 \cdot y\text{H}_2\text{O} = 3\text{Zn}(\text{OH})_2 + 2\text{Al}(\text{OH})_3 + \text{ZnX}_2 + y\text{H}_2\text{O}$, wherein each term corresponds to the ΔH_f of the corresponding phase. Relative stabilities of LDHs with different anions ($\text{X} = \text{Cl}, \text{NO}_3, \text{NO}_2, \text{SCN}, 1/2\text{CO}_3$) depend upon the ΔH_f of the salt ZnX_2 . If the entropy contribution is ignored, then the thermodynamic stability of the LDH is greatly decreased with the increase in solubility of the divalent metal salt. As salts of Zn with most univalent anions have very high solubility, the corresponding LDHs have poor thermodynamic stability. Consequently, all attempts to synthesize [Zn–Al–X] ($\text{X} = \text{NO}_2^-, \text{SCN}^-$) ions led to the formation of mixed anion LDHs. In the case of the NO_2^- -LDH, as opposed to the expected 0.33 mol per empirical formula unit of the LDH, only 0.16

Table 1. Results of chemical analysis and the approximate formula.

LDH	Anion content obtained from IC	Approximate formula
[Zn–Al–NO ₂]	NO ₂ ⁻ = 0.48; NO ₃ ⁻ = 0.33	Zn ₂ Al(OH) ₆ (NO ₂) _{0.48} (NO ₃) _{0.33} (OH) _{0.19} · 0.46H ₂ O
[Zn–Al–SCN]	SCN ⁻ = 0.65	Zn ₂ Al(OH) ₆ (SCN) _{0.65} (OH) _{0.35} · 0.17H ₂ O

**Figure 1.** IR spectra of [Zn–Al–NO₂] and [Zn–Al–SCN] LDHs.

mol of NO₂⁻ was observed. Ion chromatography revealed the incorporation of 0.11 mol NO₃⁻ per empirical formula unit. The nitrate was obtained from the precursor salt used for coprecipitation. In the case of the SCN⁻-LDH, only 0.22 mol of SCN⁻ was observed as opposed to the expected 0.33 mol per empirical formula unit of the LDH. In this case, although, the LDH was prepared using nitrate precursors, nitrate ions were below detection limits in the ion chromatographic (IC) analysis. In both LDHs, the shortfall in the charge compensating anion was made by the incorporation of OH⁻ (see table 1 for the results of chemical analysis and the approximate formula). The source of the hydroxyl ions is mildly alkaline pH used for precipitation (pH = 8). The incorporation of OH⁻ ions, likely strengthens the hydrogen bonding between the metal hydroxide layer and the interlayer and imparts some degree of stability and structural order to the LDH crystal. The intercalated water content was estimated by TGA studies after drying the sample at 100°C in the balance.

The mixed anion nature of the NO₂⁻-LDH is evident in the IR spectrum (figure 1), which reveals distinct absorptions due to both the nitrite (1242 cm⁻¹) and nitrate (1361 cm⁻¹) ions. The SCN⁻-LDH exhibits a sharp absorption due to the CN stretching mode (2055 cm⁻¹).

The PXRD patterns (figure 2) show prominent axial reflections (00*l*) in the low angle region (2θ < 25°). The first reflection corresponds to the basal spacing, which is sensitive to the size of the intercalated anion. The ionic radius of the NO₂⁻ ion (1.92 Å) is smaller than that of the SCN⁻ ion

(2.13 Å), but the difference is too small to be observed in a laboratory powder diffractometer. In fact, the observed difference in the basal spacing is well within the limits of experimental error. At higher angles (2θ > 25°) prominent 0*kl* reflections (k + l = 3*n*) (supplementary table S1) are observed, which show that the structure of the LDHs is that of the 3R₁ polytype, wherein the metal hydroxide layers are stacked AC CB BA AC, so on. Polytype identification helps to obtain a structure model for the metal hydroxide layers. The metal hydroxide layer was extracted from the structure of the [Zn–Al–NO₃] LDH (CCDC-917173) [9], and used as a starting point for the refinement process. The main challenge is to obtain the exact orientation of the charge compensating anion in the interlayer gallery. This was done by using code FOX [17,18]. Within the FOX formalism, the anion is introduced into the interlayer region as a molecule. The bond lengths and bond angles are kept fixed at values corresponding to that of the free ion. The intercalated anion is allowed to randomly translate within the interlayer space. After each move, the PXRD pattern is evaluated and compared with the observed pattern. A Monte Carlo procedure is employed to either accept or reject the new configuration using R_{wp} and R_p as cost functions.

In the case of NO₂⁻-LDH, both NO₃⁻ and NO₂⁻ ions were introduced into the interlayer region in relative proportions that matched the observed composition of the LDH. For the SCN⁻-LDH, one SCN⁻ ion was introduced into the interlayer. During the optimization procedure, the structures were

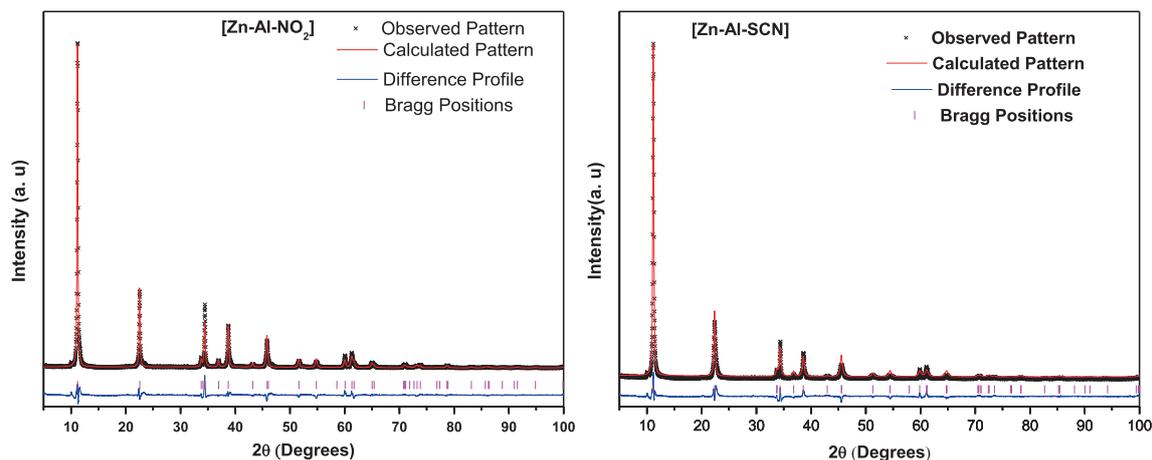


Figure 2. A Rietveld fit of the PXRD pattern of the [Zn–Al–NO₂] and [Zn–Al–SCN] LDHs.

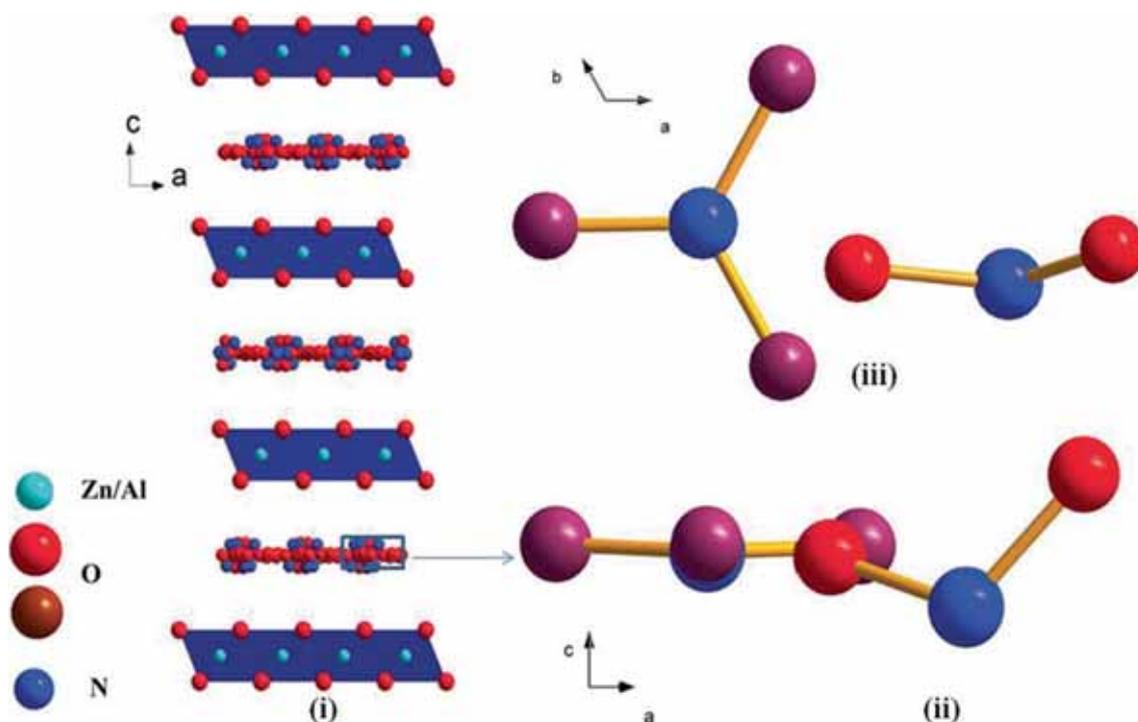


Figure 3. (i) The refined structure of [Zn–Al–NO₂/NO₃] LDH, the orientation of nitrate and nitrite anions in the interlayer viewed (ii) along *b*-direction and (iii) down *c*-direction.

visually monitored by making plots of the structure in real time to make note of any unphysical deviation of the computed structure. The converged structures reveal that the NO₂[−] ion is oriented with its molecular plane tilted at 73° to the metal hydroxide layer. The plane of the nitrate ion is parallel to the metal hydroxide layer. In the SCN[−]-LDH, the axis of SCN[−] ion is inclined at an angle of 23° to the metal hydroxide layer. These structure models were input into the code GSAS to complete the refinement process in the conventional manner in reciprocal space. Difference Fourier maps were evaluated

to find the positions of the intercalated water molecules. At the end of the refinement process (figure 2), the orientations of the anions did not significantly alter from the model proposed by code FOX (figures 3, 4, table 2, supplementary tables S2 and S3).

In the NO₂[−]-LDH, there is considerable positional disorder and all the interlayer atoms occupy the 36*i* (*x*, *y*, *z*) general positions. In the SCN[−]-LDH, despite the fact that the SCN[−] ion occupies general position, difference Fourier plots predict special positions (18*h*, 6*c*) for the intercalated

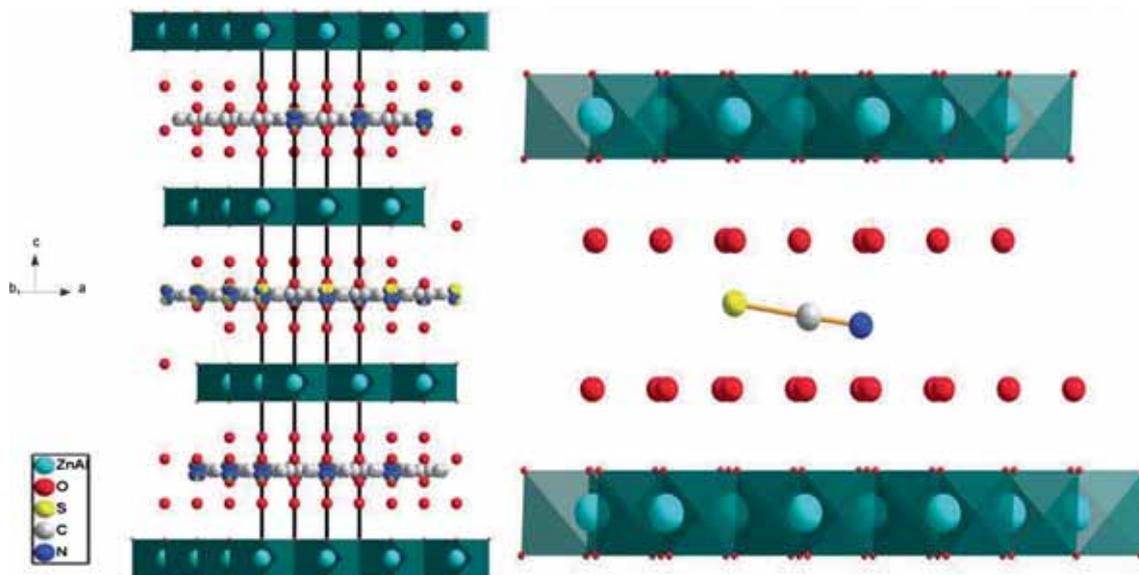


Figure 4. The refined structure of the $[\text{Zn-Al-SCN}]_{0.22}$ LDH showing the orientation of the thiocyanate anion in the interlayer.

Table 2. Results of Rietveld refinement of the structure of the $[\text{Zn-Al-NO}_2/\text{NO}_3]$ and $[\text{Zn-Al-SCN}]$ LDHs.

LDHs	$[\text{Zn-Al-NO}_2/\text{NO}_3]$	$[\text{Zn-Al-SCN}]$
Crystal system	Rhombohedral	Rhombohedral
Space group	$R\bar{3}m$	$R\bar{3}m$
Cell parameters/Å	$a = 3.0803(1)$ $c = 23.6446(8)$	$a = 3.0898(20)$ $c = 23.8680(13)$
Volume /Å ³	194.28(1)	197.35(2)
Parameters refined	50	38
R_{wp}	0.1413	0.1901
R_{p}	0.1060	0.1454
$R(F^2)$	0.1237	0.1541
χ^2	4.651	5.888

water molecules imparting confidence in the reliability of the computed structure model. The bond lengths and bond angles are in the expected range.

4. Conclusions

The powder diffraction technique in its application to LDHs suffers from two serious limitations. Only a limited number of Bragg reflections are observed. Even these are considerably broadened due to the incidence of planar faults making structure refinements difficult. This explains the paucity of structure data, especially in systems with anions of light atoms. This work makes an attempt to propose structure models, however approximate, where none exist. The key to improve these models is the synthesis of ordered samples.

Acknowledgements

We thank the Department of Science and Technology (DST), Government of India (GOI) for financial support. PVK is a recipient of the Ramanna Fellowship of the DST.

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