Acta Cryst. (1957). **10**, 173

The Crystal Structure of Ammonium Silver Dithiocyanate

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(*Received* 8 *October* 1956)

The crystal structure of $NH_4Ag(SCN)_2$ has been determined from three-dimensional X-ray data. The structure is built up by AgSCN molecules, NH_4^+ ions and SCN^- ions. The nature of the chemical bonds is discussed and comparisons are made with other complex thiocyanates.

1. Introduction

It has generally been assumed that compounds such as $NH_4Ag(SCN)_2$ contain $Ag(SCN)_2^-$ ions, and this study was started in order to determine the structure of that $Ag(SCN)_2^-$ ion. We had a particular interest in finding out whether the non-linearity of the silver coordination, found in AgSCN (Lindqvist, 1957), would be confirmed.

2. Preparation of crystals

$NH_4Ag(SCN)_2$ was first prepared by Gössman (1856). Our method of preparation is somewhat different and follows from a phase diagram given by Occleshaw (1932). At 25° C. NH_4SCN, H_2O and freshly precipitated AgSCN were taken in such proportions as to give a point in the solution region but just above the curve of $NH_4Ag(SCN)_2$ in the diagram. After all AgSCN and NH_4SCN had dissolved the solution was filtered free from small amounts of silver and was placed over sulphuric acid to lose water. Needle-shaped crystals of $NH_4Ag(SCN)_2$ formed (they could not be washed with water, for this results in the formation of AgSCN). The substance is stable in dry air (X-ray exposures during winter time) but eight months later a check showed that the single crystal used had decomposed. A crystal of the dimensions $0{\cdot}24 \times 0{\cdot}03 \times 0{\cdot}03$ mm. was used for the X-ray work.

3. Crystal data

The lattice constants were determined from powder photographs with an internal standard of NaCl, using Cu $K\alpha$ and Cr $K\alpha$ radiation in a Guinier-type camera. For the dimensions of the monoclinic unit cell the following average values were obtained:

$$a = 4{\cdot}02,\ b = 23{\cdot}86,\ c = 7{\cdot}23\ \text{Å},\ \beta = 96{\cdot}08^\circ$$

(we are indebted to Mr Yngve Hermodsson for the determination of these data). There are four molecules in the unit cell. $D_{\text{obs.}} = 2{\cdot}28$ g.cm.$^{-3}$; $D_{\text{calc.}} = 2{\cdot}33$ g.cm.$^{-3}$. Reflexions $h0l$ present only when $h+l = 2n$; $0k0$ only when $k = 2n$. Space group $P2_1/n$ (No. 14).

The single crystal was rotated around the a axis, and Weissenberg photographs were taken using Cu K radiation. Three zones (h = 0–2) were recorded. A precession photograph was taken of the layer $hk0$.

The intensities were estimated visually using the multiple-film technique. The ratio of the strongest to the weakest measured intensity in any layer was about 200:1.

The relative $|F|^2$ values were obtained after corrections using the charts of Lu (1943) and Waser (1951).

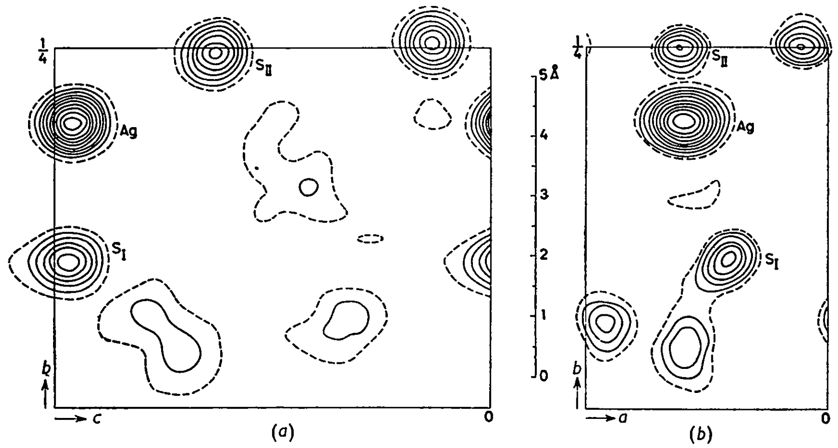
4. The determination of the atomic positions

The general position in $P2_1/n$ is $4(e)$: $\pm(x, y, z)$, $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. The silver position could thus be determined from the Patterson functions $P(\frac{1}{2}, y, \frac{1}{2})$ and $P(x, \frac{1}{2}, z)$. (These and following Fourier calculations were made partly on the Hägg–Laurent (1946) machine, partly with Robertson strips.) The function $P(\frac{1}{2}, y, \frac{1}{2})$ has a high maximum in $y = 0{\cdot}104$, giving $y_{\text{Ag}} = \pm 0{\cdot}198$ or $0{\cdot}698$. The function $P(x, \frac{1}{2}, z)$ has the highest maximum in $x = 0{\cdot}68$ and $z = 0{\cdot}04$, giving $(x_{\text{Ag}}, z_{\text{Ag}})$: $\pm(0{\cdot}42, 0{\cdot}04)$ or $(0{\cdot}92,\ 0{\cdot}04)$ or $(0{\cdot}42,\ 0{\cdot}54)$ or $(0{\cdot}92, 0{\cdot}54)$. The silver parameters arbitrarily chosen were $x_{\text{Ag}} = 0{\cdot}42$, $y_{\text{Ag}} = 0{\cdot}198$, $z_{\text{Ag}} = 0{\cdot}04$.

These parameters were used for a preliminary determination of the signs of $F(0kl)$ and $F(hk0)$, and the electron-density projections $\varrho(y, z)$ and $\varrho(x, y)$ were calculated. The silver positions were confirmed and the next highest maxima were considered to be sulphur atoms. The final projections, obtained when the sulphur atoms were included in the structure-factor calculations, are shown in Fig. 1(*a*) and (*b*). Our later results have shown that some of the lower maxima in these projections can be explained as nitrogen and carbon atoms. These atomic positions were, however, derived from the three-dimensional data.

Signs could be given to almost all $F(0kl)$, $F(1kl)$ and $F(2kl)$ with the knowledge of the silver and sulphur positions, and these signs were used for a three-dimensional electron-density computation (only two signs were later changed owing to the contributions from the light atoms). The following atomic positions were obtained:

$$\begin{array}{llll} \text{Ag:} & x = 0{\cdot}410, & y = 0{\cdot}199, & z = 0{\cdot}043; \\ \text{S}_{\text{I}}: & x = 0{\cdot}630, & y = 0{\cdot}102, & z = 0{\cdot}024; \\ \text{S}_{\text{II}}: & x = 0{\cdot}404, & y = 0{\cdot}247, & z = 0{\cdot}367. \end{array}$$



(a) (b)

Fig. 1. Electron-density projection (a) along the a axis, (b) along the c axis. Contours are drawn at intervals of 7 e.Å^{-2} for the silver atom and of 3·5 e.Å^{-2} for the other atoms. The dashed lines indicate the lowest contours.

The ratios between the magnitudes of these maxima are 23:8:9, in satisfactory agreement with the calculated ratios 23·5:8:8.

There are six other maxima of approximately the same magnitude, slightly smaller than a half sulphur maximum. Four of these could easily be interpreted as the carbon and nitrogen atoms of the thiocyanate groups:

C$_{\rm I}$: x = 0·49, y = 0·06, z = 0·20;
N$_{\rm I}$: x = 0·38, y = 0·04, z = 0·31;
C$_{\rm II}$: x = 0·53, y = 0·19, z = 0·49;
N$_{\rm II}$: x = 0·60, y = 0·15, z = 0·56.

Using these atomic positions, the structure factors $F(0kl)$ were calculated with a temperature factor 4·6 Å^2. A differential electron-density projection along the a axis (Fig. 2) (subtracting Ag, S$_{\rm I}$ and S$_{\rm II}$) clearly showed that one of the remaining two maxima was due to series-termination errors. The parameters for the nitrogen atom in the NH_4^+ group are (from $\varrho(x, y, z)$):

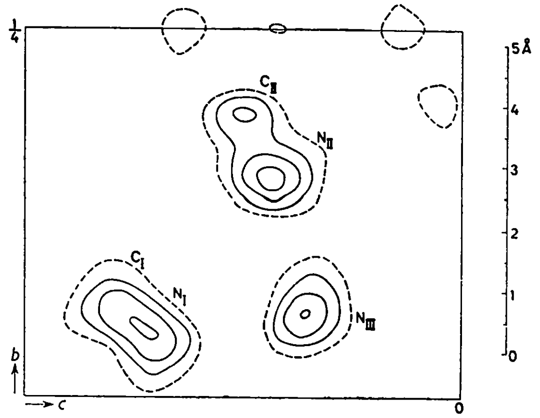


Fig. 2. Differential electron-density projection along the a axis (Ag, S$_{\rm I}$ and S$_{\rm II}$ are subtracted). Contours are drawn at intervals of 1·75 e.Å^{-2}. The dashed lines indicate the lowest contours.

N$_{\rm III}$: x = 0·08, y = 0·06, z = 0·66.

The structure factors $F(0kl)$, $F(1kl)$ and $F(2kl)$ were then calculated, and empirical temperature factors including absorption effects were determined for each h layer: 4·4, 3·7 and 1·8 (absorption effects were also included in the scaling factors between the layers and explain the trend in the values obtained). The reliability indexes are $R(0kl)$ = 0·115, $R(1kl)$ = 0·166 and $R(2kl)$ = 0·240.

5. Refinement and assessment of accuracies

A three-dimensional back-shift correction was carried out giving the following final atomic positions:

Ag: x = 0·411, y = 0·1987, z = 0·040;
S$_{\rm I}$: x = 0·630, y = 0·1022, z = 0·021;
C$_{\rm I}$: x = 0·508, y = 0·0650, z = 0·185;
N$_{\rm I}$: x = 0·378, y = 0·0383, z = 0·306;
S$_{\rm II}$: x = 0·397, y = 0·2473, z = 0·369;
C$_{\rm II}$: x = 0·517, y = 0·1915, z = 0·508;
N$_{\rm II}$: x = 0·577, y = 0·1505, z = 0·571;
N$_{\rm III}$: x = 0·062, y = 0·0615, z = 0·662.

The R values were not significantly changed by the correction: 0·109, 0·151 and 0·238. The negative results obtained in the case of AgSCN (Lindqvist, 1957) suggest that the positions of the light atoms are rather uncertain. The thorough re-investigation of AgSCN might give a better knowledge about the possibilities of further improvements. In the following discussions the atomic positions obtained after one back-shift correction have been used (a copy of the observed and calculated F values can be obtained on request).

To obtain a rough measure of the standard deviations in the atomic coordinates, Cruickshank's method (1949) was used. The standard deviations obtained are:

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Ag:	0·007	0·003	0·004
S_I:	0·016	0·008	0·011
C_I:	0·097	0·027	0·050
N_I:	0·105	0·029	0·042
S_{II}:	0·016	0·007	0·009
C_{II}:	0·065	0·027	0·065
N_{II}:	0·059	0·025	0·035
N_{III}:	0·049	0·024	0·035

These values are of the same order of magnitude as those obtained for AgSCN (Lindqvist, 1957), but slightly higher. The highest values are obtained for $\sigma(x)$ owing to the unsatisfactory reflexion statistics in h. The standard deviations for C_I and N_I are larger than for the other light atoms because they are not quite well resolved.

6. Description and discussion of the structure

The crystal structure is well demonstrated in the projection along the a axis (Fig. 3). It does not contain $Ag(SCN)_2^-$ ions but is built up by AgSCN molecules, SCN^- ions and NH_4^+ ions. Here the word 'molecule' is used to describe an uncharged discrete group of atoms held together by obviously covalent bonds.

The view-point that the structure contains an AgSCN molecule is justified because one of the Ag–S distances is significantly shorter than the others, and is of the same order of magnitude as a calculated covalent bond length. The following Ag–S distances exist: 2·474±0·020 Å within the AgSCN molecule, 2·654±0·019 Å, 2·630±0·027 Å and 2·742±0·029 Å from one AgSCN molecule to three surrounding SCN^- ions (dashed lines in Fig. 3). A comparison may be made with AgSCN (Lindqvist, 1957): 2·428±0·011 Å within one chain AgSCN, 2·886±0·012 Å and 2·997±0·011 Å between different chains.

The silver atom coordinates the four sulphur atoms in a very distorted tetrahedron and has no other coordination.

The dimensions within the thiocyanate groups are S_I–C_I = 1·599±0·110 Å and C_I–N_I = 1·241±0·197 Å in the AgSCN molecule, S_{II}–C_{II} = 1·707±0·086 Å and C_{II}–N_{II} = 1·095±0·107 Å in the SCN^- ion. The differences cannot be considered as significant, and no bond orders can be deduced from the S–C or C–N bonds. Both groups show deviations from linearity but the perpendicular distances from the carbon atoms to the lines from sulphur to nitrogen are smaller than the standard deviations in the atomic coordinates of the carbon atom (cf. the more detailed discussion in the paper on AgSCN). The angle at the sulphur atom in the AgSCN molecule is 110° (cf. 104° in AgSCN), the value being rather uncertain because a carbon position with large standard deviations is included in the angle.

The principles of the packing can be studied in Fig. 3.

The NH_4^+ ion is surrounded by five nitrogen atoms at distances of 3·039±0·157 Å, 3·268±0·144 Å 2·990±0·145 Å (to N_I atoms), 3·085±0·129 Å, 2·911±0·117 Å (to N_{II} atoms) and by two sulphur atoms S_I at 3·414±0·085 Å and 3·412±0·079 Å. In NH_4SCN (Zhdanov & Zvonkova, 1953) NH_4^+ is surrounded by two nitrogen atoms (2·99 Å and 3·02 Å) and two sulphur atoms (3·34 Å and 3·43 Å). The calculated sums of the ionic radius of NH_4^+ and the van der Waals radii of N and S are 2·95 Å and 3·30 Å, in reasonable agreement with the distances found in these two structures. The NH_4^+–N distance has been explained by Zhdanov & Zvonkova as a hydrogen bond, but this does not necessarily follow from the experimental results.

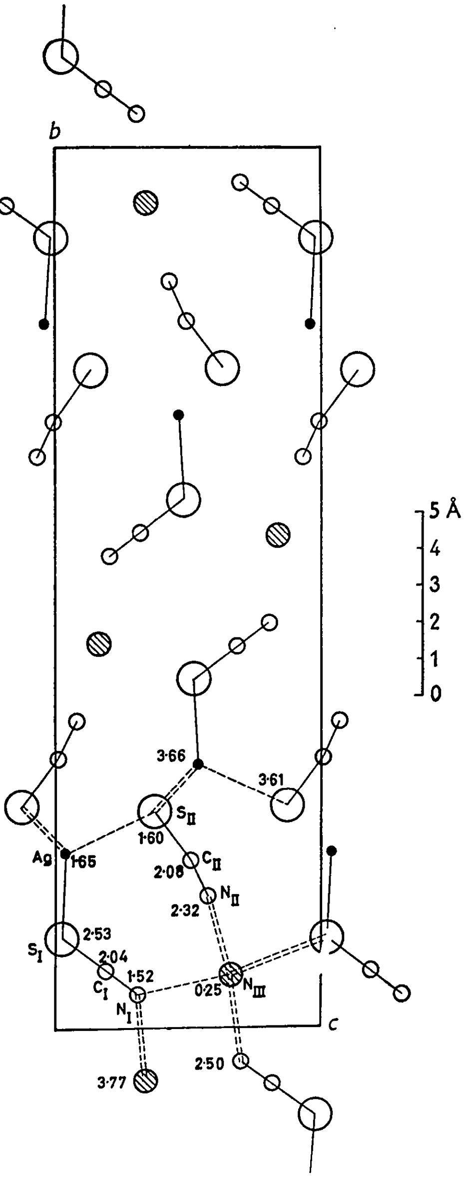


Fig. 3. Projection of the crystal structure along the a axis. The figures give the x values in Ångström units. Full lines indicate covalent bonds, dashed lines ionic interaction.

The coordination around the S_I atom is a distorted tetrahedron of two NH_4^+, one Ag and one C_I, while the coordination around S_{II} is a distorted flat trigonal pyramid of three Ag and one C_{II}.

The packing distances, within the limits of experimental error, are never shorter than the calculated van der Waals contact distances. The parallel packing of the AgSCN molecules at the centres of symmetry is loosened by the inserted NH_4^+ ions and is appreciably larger than the calculated van der Waals contact distances.

The part of the crystal structure which corresponds to the net composition $Ag(SCN)_2^-$ is built like a layer lattice with distorted tetrahedral coordination around the silver atoms, the tetrahedron sharing corners in two directions (one such layer extended in the direction of the *a* and *c* axis is situated between the planes $y = 0$ and $y = \frac{1}{2}$ in Fig. 3).

7. Comparison with AgSCN and NH_4SCN

The non-existence of discrete $Ag(SCN)_2^-$ ions is an unpredicted feature of the structure and will give rise to some questions. The basic problem is why $NH_4Ag(SCN)_2$ is energetically favoured before $NH_4SCN+AgSCN$. It is difficult to calculate the complete lattice energies for these structures, but some comparisons can be made with the structures of AgSCN and NH_4SCN. For this purpose AgSCN can be described as AgSCN molecules joined by two covalent Ag–N bonds and two 'long' Ag–S bonds to other AgSCN molecules. In $NH_4Ag(SCN)_2$ the AgSCN molecules are joined by three 'long' Ag–S bonds to SCN^- ions (actually shorter bonds than in AgSCN) and by five ionic bonds to NH_4^+. In NH_4SCN the SCN^- ions are surrounded by four NH_4^+ ions and the NH_4^+ ions by two sulphur and two nitrogen ends of SCN^- ions. In $NH_4Ag(SCN)_2$ the SCN^- ions form three 'long' S–Ag bonds (shorter than in AgSCN) and two ionic bonds to NH_4^+, while the coordination around NH_4^+ has increased to five nitrogen and two sulphur atoms. There is thus an increase in total ionic interaction, and even if the van der Waals contacts may be more favourable in AgSCN and NH_4SCN (S–S contacts) the stability of $NH_4Ag(SCN)_2$ is quite reasonably explained by the structure.

8. Comparison with other complex thiocyanates

The metal–thiocyanate bonding in complex thiocyanates formed by different elements shows some interesting features.

In the first long row of the periodic system the crystal structures of the complex thiocyanates of Cr, Co and Zn are known. Examples of compounds studied are $NH_4[Cr(SCN)_4(NH_3)_2].H_2O$ (Saito, Takeuchi & Pepinsky, 1955), $K_2Co(SCN)_4.4H_2O$ and $K_2Zn(SCN)_4.4H_2O$ (Zhdanov & Zvonkova, 1953). In all these cases the metal ions coordinate the nitrogen ends of the thiocyanate groups. The interatomic distances can be interpreted as covalent or ionic bond lengths (the values do not differ much).

In the second and third long rows of the periodic system the coordination is known for complex thiocyanates of Rh, Ag, Cd, Pt and Hg. In addition to $NH_4Ag(SCN)_2$, examples of compounds studied are $K_3Rh(SCN)_6$, $K_2Cd(SCN)_4H_2O$, $K_2Pt(SCN)_4$ and $K_2Hg(SCN)_4$ (Zhdanov & Zvonkova, 1953). In all cases the metal ions coordinate the sulphur ends of the thiocyanate groups, and the interatomic distances indicate that at least some of the metal–sulphur bonds are covalent. The cadmium atoms coordinate nitrogen as well.

This difference is further demonstrated in the structure of $CoHg(SCN)_4$ (Jeffery, 1947) where the nitrogen ends form bonds with cobalt and the sulphur ends with mercury.

It would be of great interest to study complex thiocyanate of elements like nickel, copper, molybdenum, palladium, ruthenium and gold in order to investigate further this difference in chemical bond formation.

9. The nature of the chemical bonds in $NH_4Ag(SCN)_2$

The most interesting feature of this structure is that silver forms only one obviously covalent bond, giving rise to the formation of AgSCN molecules in the structure. The *sp* hybridization still prevalent in AgSCN(N–Ag–S) has thus been lost by the addition of NH_4SCN.

The existence of the AgSCN molecule in $NH_4Ag(SCN)_2$ has its analogue in the compound $KHg(SCN)_3$ (Zhdanov & Zvonkova, 1953), which is built up by distorted $Hg(SCN)_2$ molecules, NH_4^+ ions and SCN^- ions as manifested in the two types of Hg–S distances (2·45–2·51 Å and 2·78 Å). The bond angle at Hg is 155°. (The structure has not been discussed in these terms by the authors.)

This comparison thus gives the rather natural result that Ag forms *one* covalent bond and Hg *two* covalent bonds in these compounds. If any further suggestion should be made in this connection it would be that silver does not so easily form diagonal bonds with sulphur atoms as with nitrogen atoms (cf. $Ag(NH_3)_2^+$). More silver–sulphur complexes should, however, be studied before any definite conclusions can be drawn. Such investigations will be started in this Institute.

It must also be remembered that in $K_2Hg(SCN)_4$ (Zhdanov & Zvonkova, 1953) the $Hg(SCN)_2$ molecule has disappeared and four covalent Hg–S bonds are formed, corresponding to sp^3 hybridization. This raises the question about the chemical bonds in $K_2Ag(SCN)_3$ (Foote, 1903) and $Na_3Ag(SCN)_4$ (Cernatescu, 1921; Occleshaw, 1932). It still remains to discuss the nature of the 'long' Ag–S bonds of 2·63, 2·65 and 2·74 Å. They can best be compared with the AgCl distance

2·77 Å in AgCl, which would correspond to 2·65 Å for a coordination number four. The ionic bond distance Ag–S is difficult to estimate but the lowest value (Goldschmidt) calculated after correction for the coordination is 2·71–2·76 Å. These bonds can therefore best be described as ionic bonds Ag^+–SCN^- with a reduced bond length due to polarization. The discussion as to the exact nature of the chemical bond will offer the same problems as arise for AgCl.

The larger values obtained in AgSCN (2·89 and 3·00 Å) are due to the packing of the chains in that structure.

10. Ionic conditions in solution

A very careful study of the ionic conditions in solution has been made by Leden & Nilsson (1955). They have found that in a solution which is saturated with $NaAg(SCN)_2.(H_2O)_2$ the complex ions can be described by the formula $Ag_m(SCN)_{2m+2}^{-(m+2)}$, where small values of m dominate but a series of m values are represented. These results make it easier to understand that no discrete $Ag(SCN)_2^-$ ions are formed in the solid state. On the other hand it is difficult to give a structural interpretation of the formula obtained by Leden. The first two members of the series are evidently related according to the equation

$$2Ag(SCN)_4^{3-} \rightleftharpoons Ag_2(SCN)_6^{4-} + 2SCN^- .$$

This suggests that two SCN groups are shared between two silver atoms, forming a double sulphur bridge. $NH_4Ag(SCN)_2$ contains, however, only simple sulphur bridges. Other structural suggestions can be made, but first it would be important to know whether the bonding in the solid state is very similar to that in the concentrated aqueous solution. A study of the infra-red spectra of the solid compound as well as the saturated solution has therefore been started in Uppsala.

Finally we wish to thank Prof. Hägg for all the facilities placed at our disposal.

The work has been supported financially by the Swedish Natural Science Research Council, whose support is gratefully acknowledged.

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Acta Cryst. (1957). **10**, 177

The Fraction of Structure Factors Determined in Sign by a Selected Atom or Group of Atoms in a Molecule

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(*Received* 30 *October* 1956)

The number of structure factors whose signs are determined by the presence in a molecule of a selected atom, or group of atoms, is calculated in terms of the ratio of the root-mean-square contribution to the structure factors of the atom or atoms to that of the remainder of the molecule, and is expressed as a fraction of the total number of structure factors.

1. Introduction

Since a crystal-structure analysis depending on the presence in a molecule of an atom or atoms, of higher atomic number than the remaining atoms, can lead to a determination of the molecular structure independently of any chemical information, the heavy-atom technique is of very considerable importance; in the future, with the growing availability of improved computing techniques, it may become for the chemist of even more importance as a rival to conventional chemical methods of determining molecular structure. Among recent examples of the use of this method may be mentioned the analyses of *iso*-cryptopleurine methiodide (Fridrichsons & Mathieson, 1954), and of lanostenyl iodoacetate (Curtis, Fridrichsons &

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