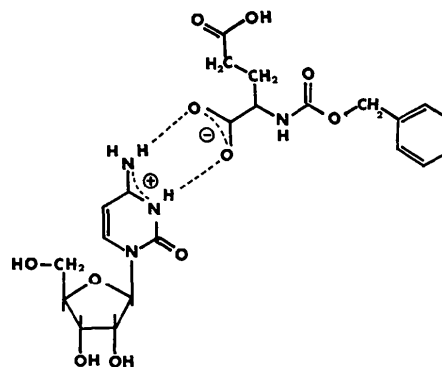


Table 2 (cont.)

C(2)—N(1)—C(6)	121.0 (14)	O(1A)—C(1)—O(1B)	125.0 (15)
C(2)—N(1)—C(1)	116.2 (14)	O(1A)—C(1)—C(2)	114.4 (14)
C(6)—N(1)—C(1)	122.6 (13)	O(1B)—C(1)—C(2)	120.5 (14)
N(1)—C(2)—O(2)	120.7 (15)	C(1)—C(2)—C(3)	107.4 (12)
N(1)—C(2)—N(3)	117.8 (15)	C(1)—C(2)—N(2)	110.7 (13)
C(4)—C(5)—C(6)	120.0 (16)	C(3)—C(2)—N(2)	110.5 (12)
C(5)—C(4)—N(4)	122.4 (15)	C(2)—C(3)—C(4)	110.8 (13)
N(3)—C(4)—N(4)	120.2 (15)	O(5A)—C(5)—O(5B)	121.3 (18)
N(3)—C(4)—C(5)	117.3 (14)	C(4)—C(5)—O(5B)	124.7 (18)
C(2)—N(3)—C(4)	123.4 (14)	C(4)—C(5)—O(5A)	113.8 (15)
N(3)—C(2)—O(2)	121.4 (15)	C(3)—C(4)—C(5)	113.2 (14)
N(1)—C(6)—C(5)	120.3 (15)	C(2)—N(2)—C(1')	118.9 (13)
N(1)—C(1)—C(2)	109.5 (12)	N(2)—C(1)—O(1')	124.8 (17)
N(1)—C(1)—O(1')	107.9 (13)	N(2)—C(1)—O(2')	111.8 (15)
C(2)—C(1)—O(1')	104.2 (12)	O(1)—C(1)—O(2')	123.4 (17)
C(1)—C(2)—C(3)	101.2 (12)	C(1)—O(2)—C(3')	117.2 (15)
C(1)—C(2)—O(2')	105.7 (11)	O(2)—C(3)—C(4')	101.7 (18)
C(4)—C(5)—O(5')	111.1 (12)	C(3)—C(4)—C(5')	116.7 (24)
C(5)—C(4)—O(1')	111.4 (12)	C(3)—C(4)—C(9')	123.6 (22)
C(3)—C(4)—O(1')	104.8 (11)	C(5)—C(4)—C(9')	119.2 (27)
C(3)—C(4)—C(5')	109.4 (12)	C(4)—C(5)—C(6')	112.5 (33)
C(4)—C(3)—O(3')	115.4 (12)	C(7)—C(8)—C(9')	123.0 (31)
C(2)—C(3)—O(3')	117.6 (13)	C(6)—C(7)—C(8')	110.7 (33)
C(2)—C(3)—C(4')	101.4 (11)	C(5)—C(6)—C(7')	128.9 (37)
C(3)—C(2)—O(2')	111.3 (12)	C(4)—C(9)—C(8')	123.5 (27)
C(1)—O(1)—C(4')	112.9 (11)		

Fig. 2. The molecular complex formed by the cytosinyl cation and the *N*-CBZ-glu anion.

within the range of hydrogen-bond distances: N(4)(c)···W(O1), 2.85 Å; O(1A)(g)···W(O1), 2.80 Å; O(2')(c)···W(O2), 2.92 Å; O(5B)(g)···W(O1), 2.99 Å; N(2)(g)···O(1')(g), 3.00 Å. But the number of interactions is greater than the number of protons available for hydrogen bonding. This may be due to a bifurcated hydrogen bond or van der Waals contacts.

The molecular packing is as follows: The sugar moiety in cytidine forms hydrogen bonds along the screw of the *b* axis, while the cytosine moiety binds the two carboxylic acid groups. Also water molecules are hydrogen bonded in the vacancies in the van der Waals packing. The most hydrophobic part of the complex is the carbobenzoxy group in *N*-CBZ-glu which is located along the other screw axis. Although *N*-CBZ-glu binds

with cytidine in two ways using the two-hydrogen-bond scheme, *i.e.*, through the α - and γ -carboxyl groups, the acidic nature of *N*-CBZ-glu is maintained by binding through the α position. This is analogous to the acid-base interaction between an organic acid and nucleotide base groups (Tamura, Yoshikawa, Sato & Hata, 1973). It is almost certain that even in solution, both components associate with each other. We feel that there is some biological significance in this type of binding between nucleotide and peptide systems.

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Copper(I) Tetracetonitrile Perchlorate

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Abstract. $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$, orthorhombic, $Pn2_1a$, $a = 24.25$ (2), $b = 20.75$ (2), $c = 8.42$ (1) Å, $Z = 12$, $D_x = 1.54$ g cm⁻³. The positional and thermal parameters

of the 54 nonhydrogen atoms of the asymmetric unit were refined *versus* the 1726 most significant reflexions to an *R* of 0.077. The copper(I) ions are tetrahedrally

coordinated by the nitrogens of the linear acetonitrile molecules with a mean Cu–N distance of 1.99 Å. The mean Cl–O distance in the ClO_4^- tetrahedra is 1.39 Å.

Introduction. The $\text{Cu}(\text{CH}_3\text{CN})_4^+$ ion has been suggested by Hemmerich & Sigwart (1963) as a model for the coordination of copper in some flavoenzymes. Gould & Ehrenberg (1968) have shown that irradiation of $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$ crystals, with γ radiation from a ^{60}Co source, produced distorted tetrahedrally coordinated Cu^{2+} centres stable at 77 K. They have also shown that the characteristics of the electron spin resonance and the light absorption spectra for these Cu^{2+} centres are similar to those of some oxidoreductases containing copper and suggest that the coordination around copper in these enzymes is an intermediate between planar quadratic and tetrahedral. Such a coordination in these enzymes would imply that the copper ions could be oxidized and reduced without any drastic changes of the enzyme conformation, and would in this way facilitate a fast electron transport in the enzymes. The present study was undertaken to obtain information on the coordination of the non-irradiated $\text{Cu}(\text{CH}_3\text{CN})_4^+$ ion. Colourless crystals of $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$ were prepared by dissolving Cu_2O and CH_3CN in 2M HClO_4 at 100°C (Hemmerich & Sigwart, 1963) and then allowing the solution to slowly evaporate at room temperature. Since the crystals are hygroscopic and easily oxidized, the crystals to be studied were kept in sealed thin-walled glass capillaries. The crystal selected for data collection had the dimensions 0.1 × 0.06 × 0.4 mm and was mounted along its elongation (the *c* axis). Single-crystal X-ray photographs were consistent with the space groups *Pnma* and *Pn2₁a*. The intensities of 2102 independent reflexions with $\theta \leq 63^\circ$ were measured at room temperature on a General Electric manual single-crystal diffractometer using Ni-filtered Cu *K* radiation and a scintillation detector with pulse-height discrimination. The X-ray intensity data were corrected for polarization, Lorentz and crystal absorption ($\mu = 41.4 \text{ cm}^{-1}$) effects. The absorption in the glass capillaries was neglected. In the subsequent calculations only the 1726 most significant reflexions [$I > 3\sigma(I)$], as judged by conventional counter statistics, were used.

Several attempts to solve the derived Patterson function for the copper and chlorine positions failed, mainly because of the large overlap in the Patterson space. Instead, direct methods applied in a somewhat unorthodox manner described below were used to yield the heavy-atom positional parameters. Since the statistics of the normalized structure factor values, $|E|$, indicated a centric distribution of most of the electron density it was decided to regard the structure as being centrosymmetric, space group *Pnma*, as a first approximation. Thus the 174 highest $|E|$ values (≥ 1.4) were used, and the 907 best triple-product sign relationships among them were generated ($P_+ \geq 0.975$). No unknown sign was needed to solve the relationships when apply-

ing the simple computerized symbolic addition procedure described by Norrestam (1971) and the calculated single *E* map gave reasonable values for the positional parameters of the six independent copper and chlorine atoms. However, it was apparent from packing considerations that *Pnma* could not be the correct space group although the heavy-atom positions could be approximately described in this space group. Thus, the symmetry of the heavy-atom positions was lowered to correspond to the noncentrosymmetric space group *Pn2₁a*. Full-matrix least-squares refinement of the heavy-atom parameters obtained, followed by difference electron density calculations, revealed the positions of the remaining 48 independent nonhydrogen atoms. It should be noted that no convergence in the preliminary least-squares refinements of the heavy-atom parameters was achieved when all the 1726 reflexions were used. This problem was overcome by using only those reflexions having $\sin \theta/\lambda$ values between 0.20 and 0.40.

The positional parameters finally obtained for all the 54 nonhydrogen atoms of the asymmetric unit were refined by full-matrix least-squares calculations to an *R* index of 0.077. In this last refinement the 18 copper, chlorine and oxygen atoms were allowed to vibrate anisotropically while isotropic temperature factors were used for the remaining 36 nonhydrogen atoms. No attempts were made to locate the 36 independent hydrogen atoms. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1964) with the dispersion corrections by Cromer (1965).*

Discussion. The final nonhydrogen atomic coordinates and the thermal parameters are listed in Tables 1, 2 and 3. Fig. 1 indicates the positions of the atoms of one asymmetric unit and shows the atomic labelling. For carbon, nitrogen and oxygen the first figure of the numbering scheme refers to the label of the associated copper or chlorine atom. A packing diagram of the unit cell projected on the *ab* plane is shown in Fig. 2.

Each copper atom is tetrahedrally coordinated by nitrogen from four almost linear acetonitrile molecules. The acetonitrile molecules are arranged around the copper atoms so that the whole copper(I) tetraacetonitrile complex can be described as having an almost ideal tetrahedral symmetry. The asymmetric unit is built up by three such copper(I) tetraacetonitrile groups and three perchlorate ions which alternate along the *c* axis in such a way that the three copper and the three chlorine positions respectively are approximately related by a threefold rotation axis. This threefold symmetry of the asymmetric unit is not obeyed, however, by the carbon, nitrogen and oxygen atoms. Thus

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30646 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates for the Cu, Cl and O atoms*

The estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0.2085 (1)	0.2500 (0)	0.8051 (2)
Cu(2)	0.4603 (1)	0.0727 (2)	0.7007 (3)
Cu(3)	0.4566 (1)	0.4159 (2)	0.7854 (3)
Cl(1)	0.5409 (1)	0.2485 (4)	0.2618 (9)
Cl(2)	0.2967 (2)	0.0853 (3)	0.2314 (8)
Cl(3)	0.2943 (2)	0.4135 (4)	0.2326 (8)
O(11)	0.4860 (5)	0.2445 (12)	0.2117 (21)
O(12)	0.5675 (9)	0.1905 (10)	0.2125 (36)
O(13)	0.5671 (8)	0.3015 (10)	0.1940 (23)
O(14)	0.5456 (10)	0.2533 (18)	0.4227 (21)
O(21)	0.2407 (9)	0.0870 (10)	0.2537 (38)
O(22)	0.3203 (7)	0.0243 (9)	0.2899 (24)
O(23)	0.3213 (9)	0.1383 (10)	0.2926 (34)
O(24)	0.3058 (22)	0.0859 (19)	0.0767 (30)
O(31)	0.2410 (6)	0.4099 (9)	0.2968 (20)
O(32)	0.3239 (7)	0.3565 (9)	0.2825 (30)
O(33)	0.3208 (7)	0.4682 (7)	0.2772 (21)
O(34)	0.2910 (8)	0.4126 (13)	0.0668 (20)

neither the three copper(I) tetraacetonitrile groups nor the three perchlorate ions have the same orientations.

In Table 4 the interatomic distances below 2.3 Å are listed. The average Cu-N distances around the three copper(I) ions, Cu(1), Cu(2), and Cu(3), are 1.98, 1.98 and 2.00 Å respectively. The average C-C and C-N bond distances in the acetonitrile molecules are 1.48 and 1.13 Å respectively. In the perchlorate ions the average Cl-O distance becomes 1.39 Å. These distances agree fairly well with those found in similar Cu(I) coordination compounds (*cf.* Blount, Freeman, Hemmerich & Sigwart, 1969). In bis(succinodinitrile)-copper(I) perchlorate (Blount *et al.*, 1969) the corresponding Cu-N, C-N, C-C and Cl-O distances are 1.99, 1.12, 1.48 and 1.40 Å respectively.

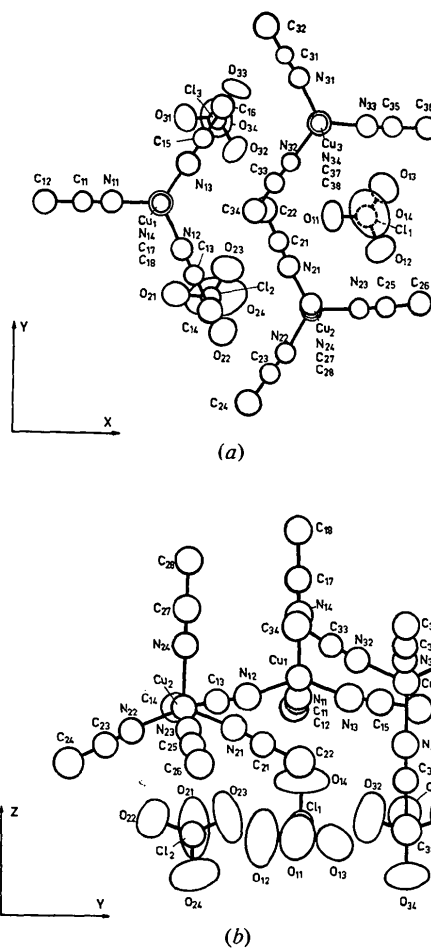


Fig. 1. Contents of the asymmetric unit, projected (a) on the *ab* plane and (b) on the *bc* plane.

Table 2. *Anisotropic thermal parameters ($\times 10^4$) for Cu, Cl and O atoms*

The estimated standard deviations are given in parentheses. The temperature factor expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + kh\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	17 (1)	31 (1)	186 (4)	1 (1)	-4 (2)	-8 (5)
Cu(2)	18 (1)	31 (1)	171 (5)	0 (1)	-4 (2)	-1 (4)
Cu(3)	18 (1)	30 (1)	167 (4)	-0 (1)	1 (2)	4 (4)
Cl(1)	18 (1)	29 (1)	191 (8)	-1 (2)	0 (3)	4 (5)
Cl(2)	16 (1)	28 (2)	175 (9)	3 (2)	-6 (4)	9 (6)
Cl(3)	17 (1)	31 (1)	169 (9)	7 (2)	6 (4)	24 (6)
O(12)	43 (5)	50 (7)	922 (10)	29 (10)	5 (35)	50 (4)
O(11)	23 (3)	64 (5)	561 (5)	-4 (9)	-33 (17)	4 (4)
O(13)	41 (5)	62 (7)	373 (4)	-20 (9)	-8 (20)	-6 (3)
O(14)	91 (9)	149 (16)	191 (3)	-48 (27)	-1 (22)	-1 (4)
O(22)	40 (5)	54 (6)	408 (4)	9 (8)	-53 (22)	3 (3)
O(21)	40 (5)	41 (5)	1069 (12)	-2 (8)	40 (35)	-3 (4)
O(23)	54 (6)	44 (6)	727 (8)	-5 (9)	-144 (34)	-13 (4)
O(24)	198 (25)	118 (18)	296 (6)	67 (31)	102 (59)	9 (5)
O(34)	51 (5)	96 (9)	184 (3)	-17 (11)	-3 (18)	2 (3)
O(31)	28 (3)	50 (4)	389 (4)	-8 (7)	81 (17)	2 (2)
O(33)	40 (4)	23 (4)	400 (4)	-25 (6)	-1 (20)	-4 (2)
O(32)	26 (4)	48 (6)	712 (8)	22 (7)	-14 (24)	8 (3)

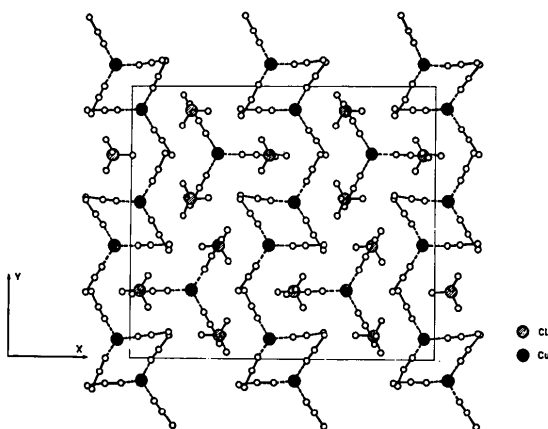


Fig. 2. Packing diagram of the unit cell projected on the *ab* plane.

Table 3. Fractional atomic coordinates and isotropic temperature factors for N and C atoms

The estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
N(14)	0.2084 (5)	0.2507 (9)	1.0405 (15)	5.4 (2) Å ²
C(17)	0.2089 (6)	0.2502 (11)	1.1721 (18)	5.1 (3)
C(18)	0.2092 (6)	0.2514 (11)	1.3503 (19)	5.9 (3)
N(12)	0.2466 (6)	0.1700 (7)	0.7388 (17)	5.0 (3)
C(13)	0.2688 (7)	0.1234 (8)	0.7225 (21)	4.7 (3)
C(14)	0.2980 (8)	0.0607 (11)	0.7019 (26)	6.5 (4)
N(11)	0.1297 (4)	0.2486 (8)	0.7370 (14)	5.2 (2)
C(11)	0.0834 (6)	0.2463 (9)	0.7184 (15)	4.6 (2)
C(12)	0.0237 (7)	0.2424 (10)	0.6975 (18)	6.1 (4)
N(13)	0.2488 (6)	0.3272 (8)	0.7314 (20)	6.3 (3)
C(15)	0.2709 (7)	0.3752 (9)	0.7135 (23)	5.1 (3)
C(16)	0.3009 (8)	0.4348 (10)	0.6866 (27)	6.9 (5)
N(21)	0.4202 (5)	0.1491 (7)	0.6223 (17)	5.1 (3)
C(21)	0.4016 (6)	0.1935 (7)	0.5617 (19)	4.4 (3)
C(22)	0.3756 (7)	0.2498 (14)	0.4940 (23)	7.0 (4)
C(23)	0.5373 (5)	0.0798 (6)	0.6186 (16)	5.0 (3)
C(25)	0.5804 (6)	0.0858 (7)	0.5613 (18)	4.6 (3)
N(26)	0.6353 (8)	0.0961 (11)	0.4915 (25)	6.4 (5)
N(22)	0.4230 (15)	-0.0070 (6)	0.6168 (16)	4.7 (3)
C(23)	0.3993 (6)	-0.0472 (7)	0.5660 (19)	4.5 (3)
C(24)	0.3672 (8)	-0.1020 (11)	0.5011 (26)	6.7 (5)
N(24)	0.4583 (5)	0.0768 (6)	0.9333 (17)	4.8 (3)
C(27)	0.4586 (7)	0.0792 (9)	1.0687 (22)	5.5 (4)
C(28)	0.4595 (7)	0.0835 (9)	1.2458 (21)	5.1 (4)
N(34)	0.4555 (5)	0.4132 (8)	0.5534 (17)	5.6 (3)
C(37)	0.4554 (6)	0.4135 (9)	0.4204 (20)	4.7 (3)
C(38)	0.4573 (8)	0.4146 (12)	0.2389 (24)	6.6 (4)
N(33)	0.5346 (5)	0.4133 (6)	0.8700 (15)	4.9 (2)
C(35)	0.5753 (6)	0.4146 (8)	0.9233 (18)	4.6 (3)
C(36)	0.6318 (7)	0.4162 (11)	0.9959 (23)	5.7 (4)
N(32)	0.4145 (5)	0.3400 (6)	0.8714 (16)	4.3 (2)
C(33)	0.3903 (6)	0.2995 (7)	0.9265 (18)	4.3 (3)
C(34)	0.3605 (5)	0.2473 (12)	0.9998 (21)	6.2 (3)
N(31)	0.4197 (5)	0.4945 (7)	0.8751 (17)	5.1 (3)
C(31)	0.3954 (6)	0.5332 (7)	0.9376 (18)	4.2 (3)
C(32)	0.3634 (10)	0.5852 (14)	1.0173 (31)	7.8 (5)

Table 4. Intramolecular bond distances, less than 2.3 Å, between nonhydrogen atoms

Estimated standard deviations are given in parentheses.

Cu(1)-N(11)	1.99 (1) Å	Cu(1)-N(13)	1.97 (2) Å
N(11)-C(11)	1.14 (2)	N(13)-C(15)	1.14 (2)
C(11)-C(12)	1.46 (2)	C(15)-C(16)	1.45 (3)
Cu(1)-N(12)	1.98 (2)	Cu(1)-N(14)	1.98 (1)
N(12)-C(13)	1.12 (2)	N(14)-C(17)	1.11 (2)
C(13)-C(14)	1.49 (3)	C(17)-C(18)	1.50 (2)
Cu(2)-N(21)	1.97 (1)	Cu(2)-N(23)	2.00 (1)
N(21)-C(21)	1.14 (2)	N(23)-C(25)	1.16 (2)
C(21)-C(22)	1.44 (3)	C(25)-C(26)	1.47 (3)
Cu(2)-N(22)	2.01 (1)	Cu(2)-N(24)	1.96 (1)
N(22)-C(23)	1.10 (2)	N(24)-C(27)	1.14 (2)
C(23)-C(24)	1.48 (3)	C(27)-C(28)	1.49 (3)
Cu(3)-N(31)	2.01 (1)	Cu(3)-N(33)	2.02 (1)
N(31)-C(31)	1.13 (2)	N(33)-C(35)	1.09 (2)
C(31)-C(32)	1.49 (3)	C(35)-C(36)	1.50 (2)
Cu(3)-N(32)	2.01 (1)	Cu(3)-N(34)	1.95 (1)
N(32)-C(33)	1.12 (2)	N(34)-C(37)	1.12 (2)
C(33)-C(34)	1.44 (3)	C(37)-C(38)	1.53 (3)
Cl(1)-O(11)	1.40 (1)	Cl(2)-O(21)	1.37 (2)
Cl(1)-O(12)	1.43 (2)	Cl(2)-O(22)	1.47 (2)
Cl(1)-O(13)	1.39 (2)	Cl(2)-O(23)	1.35 (2)
Cl(1)-O(14)	1.36 (2)	Cl(2)-O(24)	1.32 (3)
Cl(3)-O(31)	1.40 (1)	Cl(3)-O(33)	1.35 (1)
Cl(3)-O(32)	1.45 (2)	Cl(3)-O(34)	1.40 (2)

The N-Cu-N and O-Cl-O angles, having values in the ranges 106–113° and 106–114°, respectively, agree fairly well with the tetrahedral value 109.5°. As mentioned earlier the acetonitrile molecules are almost linear which is indicated by the N-C-C bond angles which range from 176 to 180° with an average of 178°. The copper(I) tetraacetonitrile complex has an almost ideal tetrahedral symmetry as mentioned above. Thus, the approximately linear acetonitrile molecules point straight towards the copper ions as is shown by the Cu-N-C angles which range from 169 to 179° with an average of 174°.

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