

(3.2 to 3.5 Å) summarized by Srinivasan & Chacko (1967).

The dimer-like units are linked into a three-dimensional network by a strong N-H...N hydrogen bond. The N...N distance of  $2.961 \pm 0.003$  Å is shorter than the majority of the -NH<sub>2</sub>...ring-N distances reported by Fuller (1959), which average  $3.06 \pm 0.08$  Å.

The second hydrogen atom, H(25), on the nitrogen atom N(2) forms no intermolecular hydrogen bonds, which may be a result of steric hindrance. Since the molecule is approximately planar and H(25) is oriented toward the pyridine ring, the approach of an acceptor atom is severely restricted. The H(25)...N(2) distance of 2.26 Å, which is less than a van der Waals contact, suggests a possible intramolecular hydrogen bond. However, both the N-H...N angle of 104.2° and the H-N...N angle of 57.1° argue against a hydrogen bond, leaving the question unresolved.

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## The Crystal and Molecular Structure of Dichloro-DL-methioninepalladium(II)

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Methionine and its metallic complexes have biological as well as chemical interest, because of their suspected antiviral and carcinostatic properties. The present palladium complex has been found to be a bidentate, and to form dimers in the crystalline state. It crystallizes in the monoclinic space-group  $P2_1/n$  with four molecules per unit cell. Its cell parameters are  $a=6.920$ ,  $b=13.788$ ,  $c=10.531$  Å,  $\beta=94.69^\circ$ . Refinement of the structure was hampered by radiation damage and terminated at  $R=0.12$ . Bond distances in the methionine portion of the molecule compare satisfactorily with those in the free methionine molecule.

### Introduction

The structure of dichloro-DL-methioninepalladium(II), PdCl<sub>2</sub>(MtH), was originally investigated to discover the configuration of the ligand, in particular whether it was a bidentate or a tridentate. The sulphur and nitrogen atoms were expected to be bonded to the palladium atom, but the bonding of the oxygen atom was in doubt. Subsequent infrared studies by McAuliffe (1967) focused attention on the hydrogen bonding of the oxygen atoms and a preliminary report on this aspect has been published (Stephenson, McConnell & Warren, 1967).

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There is general biological interest in this compound, since it is suspected that methionine, and its metal complexes to a greater extent, possess antiviral and carcinostatic properties. A comparison is made later between the structure of PdCl<sub>2</sub>(MtH) and the free methionine molecule (Mathieson, 1952).

### Experimental

The crystals of PdCl<sub>2</sub>(MtH) were grown from aqueous solution in the form of fine needles, which were often twinned. The crystals broke easily on handling, so those chosen for X-ray study were mounted in Linde-

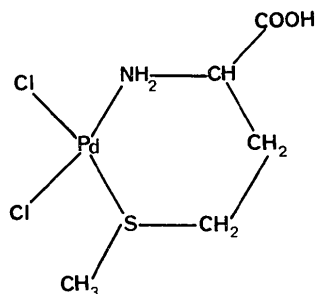
mann glass tubes, with a small amount of silicone grease as adhesive.

#### Crystal data

Name: dichloro-DL-methioninepalladium(II)

Formula:  $\text{PdCl}_2\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$

Structural formula



Condensed formula:  $\text{PdCl}_2(\text{MtH})$

F.W. 326.21 ( $^{12}\text{C} = 12$ )

Habit: long prismatic, a.

Colour: bright orange.

Cell parameters at 20°C. Monoclinic, *b* axis unique.

$$a = 6.920 \pm 0.003 \text{ \AA}$$

$$b = 13.788 \pm 0.003$$

$$c = 10.531 \pm 0.004$$

$$\beta = 94.69 \pm 0.02^\circ$$

Errors quoted are  $3 \times$  the standard deviations.

Cell volume  $1001.4 \pm 1.2 \text{ \AA}^3$

$D_m = 2.0 \text{ g.cm}^{-3}$  (floatation)

$Z = 4$  molecules per unit cell

$D_x = 2.10 \text{ g.cm}^{-3}$

Radiation: Ni-filtered Cu radiation

$$\lambda (\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$$

$$\lambda (\text{Cu } K\alpha_2) = 1.54433$$

Linear absorption coefficient,  $\mu = 206 \text{ cm}^{-1}$

1800 reflexions were available for measurement representing about 85% of the Cu sphere.

Systematic absences  $h0l, h+l=2n+1$

$$0k0, k=2n+1$$

Space group  $P2_1/n$

Solubility: moderately soluble in water, slightly soluble in acetone.

Accurate unit-cell dimensions were obtained from  $h0l$  and  $0kl$  Weissenberg photographs, using crystals sprinkled with silicon powder as a calibrating substance. The cell parameters and their standard deviations were calculated by a least-squares program written by Kastalsky (1967), which used as data the  $\theta$  values of one hundred and three spots measured in relation to the 533 and 444 powder lines of silicon.

The intensity data were collected with Cu  $K\alpha$  radiation by the multiple film (3 film packs, 3 films per pack), equi-inclination Weissenberg technique. It was originally intended to use the same crystal to obtain

both the data around the *a* axis, in levels 0 to 5, and cross-correlation data about the *c* axis, in levels 0 to 7. However, it was discovered after levels  $0kl$  to  $4kl$  had been collected, that the crystal had suffered radiation damage, which appeared to involve both chemical breakdown and structural derangement.

A subsequent investigation in which a crystal was irradiated for 180 hours, and Weissenberg photographs taken at intervals during the irradiation showed that the damage was progressive, roughly proportional to the amount of irradiation. The spots became increasingly more diffuse, and weaker ones tended to disappear. Although quite noticeable in the  $4kl$  photographs, the effects of the damage did not preclude measurement, and these data above were used for the early stages of the structure determination. For the  $5kl$  and *c* axis data, it was decided to use a different crystal for each layer, at that time intending to repeat  $1kl$  through  $4kl$  with new crystals. It was finally decided that the original data were better than at first thought, and that little would be gained by repeating the *a* axis data, or by taking further *c* axis levels. One could not expect data of better than moderate accuracy without taking time and trouble out of all proportion to the needs of the problem.

The data were corrected for absorption before scaling, using a modification of a program (*CDRABS*) written by G. Cox of the Australian Atomic Energy Commission. The number of different crystals, together with the small size (about 0.1 mm) necessitated by the high linear absorption coefficient, complicated the absorption correction procedure and further detracted from the accuracy of the data.

The inter-layer scale factors were calculated by a program written by G. Paul, University of Sydney, based on the method of Rae (1965). The weighting scheme, for both this scaling program and the least-squares structure factor program, was determined empirically as follows. The scaling program was run with weights  $1/\sigma^2$ , assuming constant fractional errors. From the differences in scaled observations of common reflexions, estimates of the absolute error were obtained for each reflexion. These estimates were averaged, in ranges of structure factor, giving the average  $|\Delta F|$  as a function of  $|F|$ . Weights proportional to  $1/|\Delta F|^2$  were then used in the program, and the process recycled until consistent input and output schemes were achieved. The 'goodness of fit' of the structure program, defined by  $\sum w|\Delta F|^2/(m-s)$  where *m* is the number of observations and *s* the number of parameters, was 0.96, indicating that a fair amount of internal self-consistency had been achieved. The final scheme adopted was

$$w = 0.5 \text{ for } |F_{\text{obs}}| \leq 25$$

$$w = \frac{5}{|F| - 15} \text{ for } |F_{\text{obs}}| > 25,$$

which is similar to many commonly used schemes.

When the refinement was well advanced, at  $R=14\%$ , corrections to  $F_{\text{obs}}$  were calculated for the anomalous dispersion due to the Pd atom, ( $\Delta f' = -0.5$  electrons,  $\Delta f'' = 4$  electrons), using the method of Patterson (1963). The largest corrections were of the order of only 1%, so the dispersion effects were ignored.

### Solution of the structure

The initial stages of the solution were undertaken on UTECOM, an English Electric DEUCE machine, which was being phased out of service, so it was decided to commence the solution with data from  $0kl$  to  $4kl$ . A Patterson synthesis computed from these data contained strong peaks corresponding to the Pd-Pd vectors. A difference map, from structure factors calculated using the Pd atom only, confirmed the Pd position and indicated the position of three of the larger atoms bonded to the Pd, *viz.* Cl(1), Cl(2) and S. Successive difference maps, interpreted with the help of chemical considerations, fixed the positions of all atoms. The remaining data were collected at this point, and prepared for refinement.

### Refinement

The refinement was carried out on an IBM 360/50 machine, using a modification, by D. C. Craig of the University of New South Wales, of the program *ORFLS* (Busing, Martin & Levy, 1962). This is a full-matrix least-squares refinement program in which the function minimized is  $\sum w|\Delta F|^2$ . At first, only intensities from  $0kl$  to  $5kl$ , internally scaled, and isotropic temperature factors were used and the  $R$  value was

reduced to 16.6% in 8 cycles. At this stage the full  $a$  and  $c$  axis data, scaled as above, were used and anisotropic temperature factors introduced. The refinement terminated at  $R=12.0\%$  after a further 6 cycles. At this stage, parameter shifts were less than 20% of the standard deviations. A difference map computed from the final atomic positions gave no indication of any irregularity in the final atomic arrangement.

About 300 of the total of 1800 reflexions available for measurement were unobserved. These were not included in the refinement because it was felt that many would have been observed but for the broadening of spots due to radiation damage. Uncorrected dispersion effects could also be significant for very weak reflexions.

The final positional and thermal parameters are given in Table 1, and Table 2 shows the observed and calculated structure factors on 10 times the absolute scale.

Table 1. Atomic parameters

(a) Positional parameters ( $\times 10^4$ )

Figures in parentheses are standard deviations  $\times 10^4$

	$x/a$	$y/b$	$z/c$
Pd	3041 (01)	4324 (01)	0419 (01)
Cl(1)	2352 (07)	5945 (02)	0811 (04)
Cl(2)	3941 (08)	4014 (03)	2475 (04)
S	3642 (07)	2729 (02)	0128 (03)
O(1)	2307 (26)	4187 (10)	-4369 (11)
O(2)	0311 (23)	5059 (11)	-3604 (11)
N	2158 (21)	4646 (09)	-1393 (13)
C(1)	1639 (27)	4499 (12)	-3628 (16)
C(2)	2732 (28)	4087 (11)	-2456 (14)
C(3)	2198 (28)	3028 (11)	-2363 (17)
C(4)	3585 (26)	2462 (11)	-1521 (14)
C(5)	1465 (38)	2121 (16)	0505 (20)

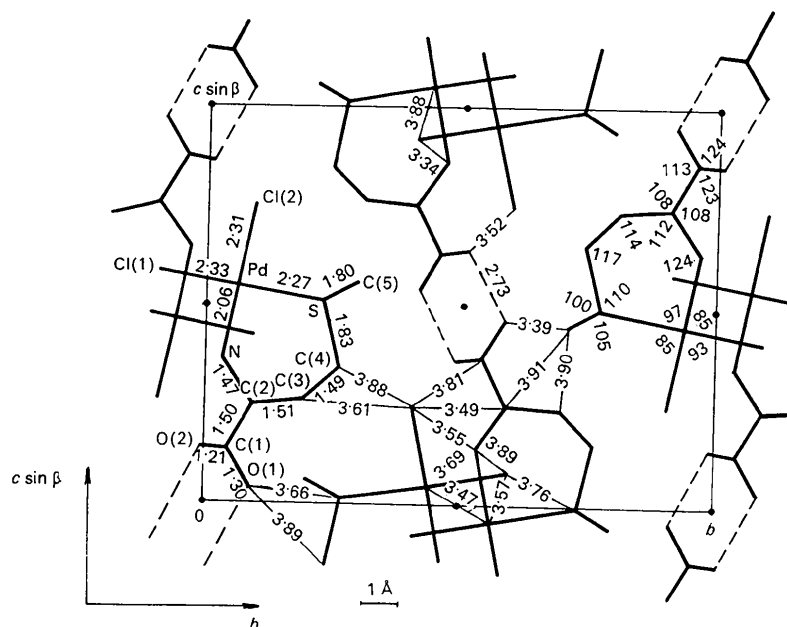


Fig. 1. Projection down the  $a$  axis showing bond distances, ( $\text{\AA}$ ) bond angles (degrees), and intermolecular contact distances ( $\text{\AA}$ ) less than 4  $\text{\AA}$ . The dimers are clearly shown, joined by hydrogen bonds (dashed lines).

Table 1 (cont.)

(b) Thermal parameters ( $\times 10^4$ )

The  $B_{ij}$  are coefficients in the expression:

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)].$$

(Individual standard deviations for  $B_{ij}$  are not shown, but average about 10%.)

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Pd	131	44	57	3	-14	0
Cl(1)	156	45	104	7	3	-16
Cl(2)	249	64	61	8	-23	1
S	197	41	61	10	-21	6
O(1)	357	88	45	47	-23	13
O(2)	361	98	63	71	-49	7
N	132	39	78	-11	-17	-4
C(1)	96	62	81	12	-9	7
C(2)	176	47	56	-2	-48	9
C(3)	233	46	84	4	-45	-2
C(4)	185	46	62	10	-40	-9
C(5)	400	71	105	-76	50	22

Discussion of the structure

Figs. 1 and 2 are projections of the unit cell down the  $a$  and  $b$  axes respectively. Fig. 2 shows the layer-like packing parallel to  $(10\bar{1})$ , in accord with the observed cleavage behaviour. Fig. 1 also shows bond distances and angles, and intermolecular contacts less than 4 Å.

These projections show that the methionine molecule acts as a bidentate, and coordinates to the palladium atom through the sulphur and nitrogen atoms. A six-membered ring is therefore formed which is approximately planar. The four atoms, Cl(1), Cl(2), S and N, form an approximately square-planar configuration around the Pd atom, the calculated distances from the best least-squares plane through these five atoms being for Pd, 0.024; Cl(1), -0.013; Cl(2), 0.001; S, -0.013 and N, 0.001 Å.

The coordinating nitrogen atom is tetrahedrally surrounded by a palladium, a carbon and two hydrogen atoms: these latter do not participate in intermolecular hydrogen bonding. The methionine molecule therefore, does not have the zwitterion structure that it possesses in the free state, *viz.*  $\text{CH}_3\text{NH}_3^+\text{COO}^-$  (Mathieson, 1952). The un-ionized carboxyl group is hydrogen-bonded to the carboxyl group of an adjacent molecule (Fig. 1). This hydrogen-bonding scheme is the only intermolecular hydrogen-bonding system and is associated with a centre of symmetry between carboxyl groups. The molecules are therefore associated as dimers and other intermolecular forces are of the van der Waals type, as shown by the intermolecular distances given in Fig. 1.

In this respect there is a considerable difference between the intermolecular forces occurring in a crystal

Table 2. Observed and calculated structure factors

Reflexions marked with an asterisk (\*) were omitted from the refinement. Unobserved reflexions were not calculated for reasons given in the text. The columns are the index  $l$ ,  $10F_{\text{obs}}$  and  $10F_{\text{calc}}$ .

$hkl$	$10F_{\text{obs}}$	$10F_{\text{calc}}$
000	1000	1000
100	100	100
200	100	100
300	100	100
400	100	100
500	100	100
600	100	100
700	100	100
800	100	100
900	100	100
1000	100	100
1100	100	100
1200	100	100
1300	100	100
1400	100	100
1500	100	100
1600	100	100
1700	100	100
1800	100	100
1900	100	100
2000	100	100
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2200	100	100
2300	100	100
2400	100	100
2500	100	100
2600	100	100
2700	100	100
2800	100	100
2900	100	100
3000	100	100
3100	100	100
3200	100	100
3300	100	100
3400	100	100
3500	100	100
3600	100	100
3700	100	100
3800	100	100
3900	100	100
4000	100	100
4100	100	100
4200	100	100
4300	100	100
4400	100	100
4500	100	100
4600	100	100
4700	100	100
4800	100	100
4900	100	100
5000	100	100
5100	100	100
5200	100	100
5300	100	100
5400	100	100
5500	100	100
5600	100	100
5700	100	100
5800	100	100
5900	100	100
6000	100	100
6100	100	100
6200	100	100
6300	100	100
6400	100	100
6500	100	100
6600	100	100
6700	100	100
6800	100	100
6900	100	100
7000	100	100
7100	100	100
7200	100	100
7300	100	100
7400	100	100
7500	100	100
7600	100	100
7700	100	100
7800	100	100
7900	100	100
8000	100	100
8100	100	100
8200	100	100
8300	100	100
8400	100	100
8500	100	100
8600	100	100
8700	100	100
8800	100	100
8900	100	100
9000	100	100
9100	100	100
9200	100	100
9300	100	100
9400	100	100
9500	100	100
9600	100	100
9700	100	100
9800	100	100
9900	100	100
10000	100	100

Table 2 (cont.)

Table 2 (cont.) contains a large amount of data, including bond lengths, bond angles, and standard deviations for the structure of dichloro-DL-methioninepalladium(II). The data is organized into several columns, with the first column listing the bond type and the subsequent columns providing numerical values and standard deviations in parentheses. The data is presented in a dense, vertical format.

of  $\text{PdCl}_2(\text{MtH})$  and in a crystal of DL-methionine. In the latter structure, an extensive hydrogen-bonding scheme exists in which each nitrogen atom of a methionine molecule is hydrogen-bonded to three other oxygen atoms of neighbouring molecules, and the oxygen atoms of each carboxyl group are asymmetrically hydrogen-bonded to three nitrogen atoms from neighbouring molecules.

A comparison of interatomic distances and bond angles of  $\text{PdCl}_2(\text{MtH})$  and those of the two forms of methionine is given in Tables 3 and 4. Mathieson (1952) reported that the C-C distances in  $\alpha$  and  $\beta$  methionine showed rather marked variation from the normal single-bond value of 1.54 Å, and that the alternation of bond lengths along the chain, including the C-S bonds in both cases, was similar to that observed in L-threonine. It was suggested that these were associated with the modification of the configuration of the carboxyl group by the asymmetric hydrogen bonding. In the present instance the hydrogen bonding is perfectly symmetric, and a similar alternation of calculated bond lengths is observed, although the C-C bond lengths show no anomalies. If this alternation is real, Mathieson's explanation would seem to be in error. However, in view of the standard deviations for  $\text{PdCl}_2(\text{MtH})$  given in Table 3, and those which might be expected for the methionine molecule, it is very doubtful if any significance can be attributed to any

of the differences observed. Since the methionine molecule forms part of the ring in  $\text{PdCl}_2(\text{MtH})$ , some bond angles are not comparable between the two structures.

Table 3. Bond distances in  $\text{PdCl}_2(\text{MtH})$  and methionine  
Standard deviations in the  $\text{PdCl}_2(\text{MtH})$  values are in parentheses

	$\text{PdCl}_2(\text{MtH})$	$\alpha$ -Methionine	$\beta$ -Methionine
Pd—Cl(1)	2.332 (04) Å		
Pd—Cl(2)	2.308 (04)		
Pd—S	2.265 (04)		
Pd—N	2.061 (14)		
S—C(5)	1.800 (21)	1.77 Å	1.78 Å
S—C(4)	1.827 (16)	1.79	1.80
C(3)—C(4)	1.493 (22)	1.51	1.54
C(2)—C(3)	1.506 (23)	1.55	1.58
C(2)—N	1.472 (23)	1.52	1.50
C(1)—C(2)	1.536 (22)	1.47	1.52
C(1)—O(1)	1.295 (23)	1.28	1.28
C(1)—O(2)	1.205 (21)	1.21	1.21
O—O	2.727 (18)		
(Hydrogen bond)			

The  $\text{CH}_2\text{COO}^-$  groups, in both uncoordinated and coordinated methionine molecules, are planar. In the former situation the adjacent nitrogen atom lies 0.70 Å out of the plane, whereas in the coordinated state this nitrogen atom lies in the plane, its calculated deviation distance being only 0.01 Å.

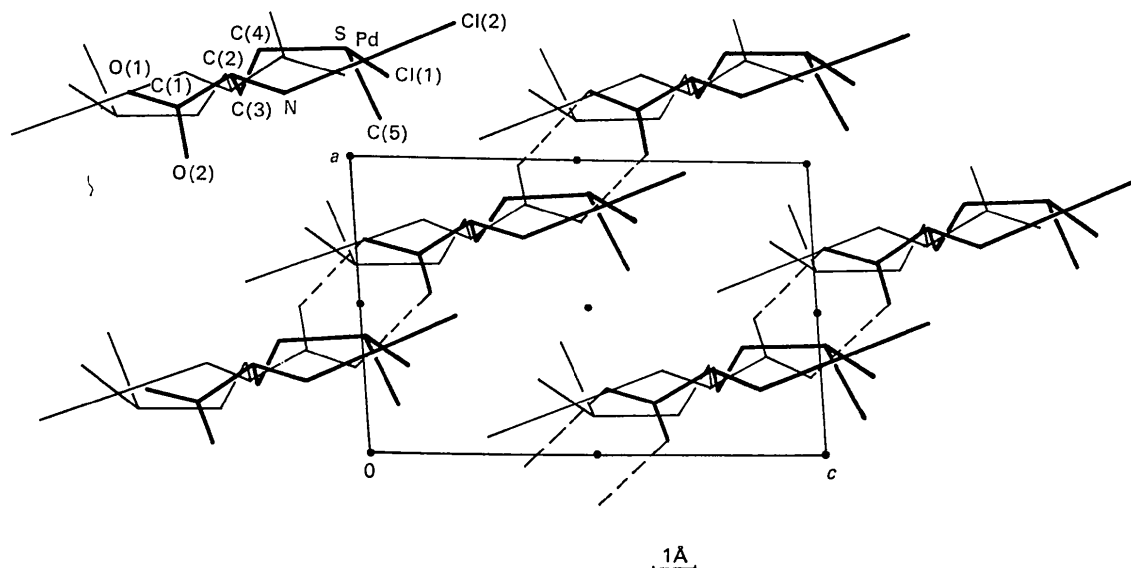


Fig. 2. Projection down the  $b$  axis. Dashed lines represent hydrogen bonds.

Table 4. Bond angles in  $\text{PdCl}_2(\text{MtH})$  and methionine

Standard deviations in the  $\text{PdCl}_2(\text{MtH})$  values are in parentheses.

	$\text{PdCl}_2(\text{MtH})$	$\alpha$ -Methionine	$\beta$ -Methionine
Cl(1)-Pd-Cl(2)	92.54 (0.18)°		
Cl(1)-Pd-N	85.30 (0.38)		
Cl(2)-Pd-S	85.25 (0.16)		
S-Pd-N	96.88 (0.37)		
Pd-S-C(5)	104.55 (0.85)		
Pd-S-C(4)	110.20 (0.53)		
C(5)-S-C(4)	100.14 (0.94)	100°	100°
S-C(4)-C(3)	117.04 (1.25)	111	109
C(4)-C(3)-C(3)	113.68 (1.38)	111	113
C(3)-C(2)-N	111.94 (1.48)	110	109
C(2)-N-Pd	123.86 (0.98)		
C(3)-C(2)-C(1)	107.89 (1.30)	111	108
N-C(2)-C(1)	107.96 (1.35)	112	110
O(1)-C(1)-O(2)	123.77 (1.69)	121	122
O(2)-C(1)-C(3)	113.22 (1.52)	119	120
O(1)-C(1)-C(3)	123.00 (1.74)	120	118

All distance and angle calculations were carried out using *ORFFE* (Busing, Martin & Levy, 1964) modified by D. C. Craig.

### Conclusion

Accuracy in the atomic and thermal parameters for this crystal has been hampered by radiation damage, but the parameters for the lighter atoms are probably limited to an equal extent by the presence of the heavy atom, (Cruickshank, 1960). However, it has been possible to establish definitely the main structural features of the crystal, namely that the molecule is a bidentate, and that molecules are associated as dimers, rather than forming a polymeric structure as suggested by McAuliffe (1967).

It is a pleasure to thank Professor S. E. Livingstone of the Chemistry Department, University of New

South Wales, for the supply of crystals of  $\text{PdCl}_2(\text{MtH})$ , and for many helpful discussions.

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