Crystal and Molecular Structure of Di-μ-carbonyl-(carbonyl-π-norbornadienecobaltio)carbonyl-π-cyclopentadienyliron

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The crystal structure of the title compound was determined by *X*-ray diffraction methods by the heavy-atom method from counter data, and refined by least-squares techniques to *R* 0·063 for 3936 unique reflections. The monoclinic unit cell, space group $P2_1/c$, has dimensions a = 18·013 ± 0·027, b = 6·553 ± 0·017, c = 13·031 ± 0·037 Å, β = 103·2 ± 0·1°, for Z = 4. The dimer molecule has the expected non-planar $Fe(CO)_2Co$ bridging system, the angle between the two Fe(CO)Co planes being 160·6°. The two π-bonded ligands are in a *cis*-configuration and the molecule as a whole has approximately *m* (C_s) symmetry. The metal to bridge-carbon distances are equivalent (mean 1·909 Å). The environment of the cobalt is square-based pyramidal, and that of the iron octahedral; Fe ··· Co is 2·520(1) Å.

INFRARED spectroscopic studies of compounds of the type [(π-dienyl)$FeCo(CO)_4$(π-diene)] have shown them to exist in solution as equilibrium mixtures of *cis*- and *trans*-isomers, in which the *cis*-forms are expected to have a near-planar $Fe(CO)_2Co$ bridging system.[1] However, the isomer predominant, in both solution and the solid state, is dependent on the identity of the diene. When

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[1] A. R. Manning, *J.C.S. Dalton*, 1972, 821.

this is 2,3-dimethylbuta-1,3-diene the *trans*-isomer predominates and this has been confirmed in the solid state by a structure analysis.[2] When it is norbornadiene the *cis*-isomer is dominant, and the *X*-ray crystal analysis of this compound was undertaken to determine its molecular structure, to establish the relationship between the π-bonded ligands, and to examine the $Fe(CO)_2Co$ bridging system.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{13}CoFeO_4$, $M = 384\cdot0$, Monoclinic, $a = 18\cdot013 \pm 0\cdot027$, $b = 6\cdot553 \pm 0\cdot017$, $c = 13\cdot031 \pm 0\cdot037$ Å, $\beta = 103\cdot2 \pm 0\cdot1°$, $U = 1497\cdot5$ Å^3, $D_m = 1\cdot68$ (by flotation), $Z = 4$, $D_c = 1\cdot703$, $F(000) = 776$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å, μ(Mo-K_α) = 21·6 cm^{-1} for cell parameters and intensity measurements. Space group $P2_1/c$ (C^5_{2h}, No. 14).

The complex crystallises as purple-brown plates lying on the (100) face with pinacoids {010} and {001}. Unit-cell parameters were determined from single-crystal precession photographs by the use of Mo-K_α radiation. The intensities were collected on a Philips PAILRED diffractometer by the use of monochromatic Mo-K_α radiation. Each reflection in the *h*0—11*l* layers for sin θ < 0·62 was recorded. 3972 Reflections gave counts for which $\sigma(I)/I < 0\cdot5$ (ref. 3) and these were used for the structure analysis. The intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied. Scattering-factor curves for all atoms were taken from ref. 4, the values for the cobalt and iron atoms being corrected for the effects of anomalous dispersion. All calculations were carried out on a PDP 10 computer at the University of Essex using programmes written by F. S. S.

Structure Determination.—The three-dimensional Patterson synthesis yielded the positions of the two metal atoms. A Fourier synthesis phased by these atoms gave the positions for all non-hydrogen atoms. Refinement of the structure was carried out by a least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight for each reflection, *w*, was initially unity and in the final refinement given by $w = (4\cdot0 - 0\cdot1\ |F_o| + 0\cdot00333|F_o|^2)^{-1}$, so that mean values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflections, having $|F_c| < \frac{1}{3}|F_o|$ were omitted from the least-squares analysis.

Initial refinement used a full-matrix procedure in which positional and individual isotropic thermal parameters for each atom were refined. A difference-Fourier synthesis, calculated when the maximum shift in a parameter was of the order of its σ, showed no unusual features, and gave the positions of all the hydrogen atoms. These were included in subsequent calculations with a thermal parameter of *B* 5·0 Å^2.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Owing to the large number of parameters (239) being refined it was necessary to refine them in block matrices. The four matrices contained (1) the overall scale and thermal parameter, (2) the metal atoms and those of the carbonyl groups, and atoms of (3) the cyclopentadienyl and (4) the norbornadienyl ligand. After several cycles the positional parameters of the hydrogen atoms were included in appropriate matrices. Refinement was terminated when the maximum shift in a parameter was $< 0\cdot1\sigma$. 3936 Reflections were included in the final cycle of refinement. The final value for *R*, based on 3972 reflections, was 0·063, and for R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ was 0·075.

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms}/Å
Fe	0·15985(3)	0·07743(10)	0·18106(5)	0·0006
Co	0·30379(3)	0·05940(8)	0·21919(4)	0·0005
O(B1)	0·2337(2)	0·3215(8)	0·0466(3)	0·004
O(B2)	0·2323(2)	−0·2646(6)	0·3103(3)	0·004
O(T1)	0·1196(3)	−0·2046(9)	0·0054(4)	0·006
O(T2)	0·3517(3)	−0·2292(7)	0·0760(3)	0·005
C(B1)	0·2317(2)	0·2029(8)	0·1143(3)	0·005
C(B2)	0·2299(3)	−0·1168(7)	0·2586(4)	0·005
C(T1)	0·1369(3)	−0·0942(10)	0·0750(5)	0·006
C(T2)	0·3326(3)	−0·1175(7)	0·1319(4)	0·005
C(1)	0·0519(4)	0·0749(12)	0·2143(8)	0·008
C(2)	0·1061(4)	0·1073(12)	0·3092(6)	0·008
C(3)	0·1454(3)	0·2881(10)	0·2993(5)	0·006
C(4)	0·1141(3)	0·3704(10)	0·2012(5)	0·006
C(5)	0·0586(3)	0·2433(13)	0·1469(6)	0·007
C(6)	0·3507(3)	0·0913(9)	0·3889(3)	0·005
C(7)	0·3996(3)	−0·0157(8)	0·3439(4)	0·005
C(8)	0·3488(3)	0·3586(7)	0·2688(4)	0·005
C(9)	0·3983(3)	0·2539(8)	0·2224(4)	0·005
C(10)	0·4535(3)	0·1420(9)	0·3122(4)	0·005
C(11)	0·3725(3)	0·3144(9)	0·3864(4)	0·005
C(12)	0·4595(3)	0·2993(11)	0·4021(5)	0·006
H(1)	0·020(5)	−0·017(13)	0·210(7)	0·09
H(2)	0·115(5)	0·006(14)	0·365(7)	0·09
H(3)	0·190(5)	0·329(13)	0·357(6)	0·08
H(4)	0·133(5)	0·525(13)	0·177(6)	0·08
H(5)	0·034(5)	0·266(14)	0·091(7)	0·09
H(6)	0·321(5)	0·001(13)	0·428(7)	0·08
H(7)	0·409(5)	−0·155(13)	0·343(7)	0·09
H(8)	0·315(5)	0·460(13)	0·235(7)	0·09
H(9)	0·403(5)	0·296(13)	0·167(7)	0·09
H(10)	0·498(5)	0·086(13)	0·304(6)	0·08
H(11)	0·350(5)	0·395(13)	0·439(7)	0·08
H(121)	0·490(5)	0·237(13)	0·470(7)	0·09
H(122)	0·484(5)	0·435(13)	0·390(7)	0·09

TABLE 2

Thermal parameters (× 10^4),* with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	16·0(2)	184·9(14)	42·1(3)	−5·2(4)	4·8(2)	0·5(6)
Co	16·5(1)	147·2(10)	30·2(2)	0·8(4)	5·6(1)	−3·7(5)
O(B1)	36(1)	384(14)	51(2)	4(4)	10(2)	68(5)
O(B2)	38(2)	182(8)	84(3)	−7(3)	15(2)	39(4)
O(T1)	56(2)	434(18)	88(4)	−19(5)	−8(2)	−91(7)
O(T2)	52(2)	282(12)	75(3)	7(4)	26(2)	−59(5)
C(B1)	20(1)	228(11)	35(2)	−4(3)	5(1)	6(4)
C(B2)	25(1)	160(9)	49(3)	−5(3)	11(2)	2(4)
C(T1)	27(2)	300(16)	65(4)	−17(4)	−6(2)	−23(6)
C(T2)	25(1)	199(10)	40(2)	−1(3)	9(1)	−9(4)
C(1)	25(2)	356(21)	160(9)	−34(5)	40(3)	−51(11)
C(2)	48(3)	347(20)	91(5)	29(6)	45(3)	44(9)
C(3)	32(2)	296(16)	64(4)	22(5)	16(2)	−27(6)
C(4)	30(2)	239(14)	87(5)	17(4)	13(2)	5(7)
C(5)	21(2)	434(24)	80(5)	29(5)	0(2)	−7(9)
C(6)	32(2)	260(13)	30(2)	−9(4)	6(2)	2(5)
C(7)	28(2)	213(11)	49(3)	15(3)	−1(2)	6(5)
C(8)	28(2)	144(9)	53(3)	−2(3)	6(2)	0(4)
C(9)	25(1)	232(12)	43(3)	−23(3)	11(2)	−13(5)
C(10)	16(1)	266(13)	64(3)	7(3)	2(2)	−33(6)
C(11)	29(2)	237(12)	48(3)	1(4)	8(2)	−39(5)
C(12)	29(2)	309(17)	60(4)	−9(5)	−3(2)	−45(7)

For all hydrogen atoms *B* 5·0 Å^2.

* Anisotropic thermal parameter is in the form: $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

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[2] I. L. C. Campbell and F. S. Stephens, *J.C.S. Dalton*, 1974, 923.

[3] M. Mack, *Norelco Reporter*, 1965, **12**, 40.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

Final atomic co-ordinates and thermal parameters are given, together with their estimated standard deviations, in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21165 (23 pp., 1 microfiche).*

DISCUSSION

Figure 1 shows a perspective drawing of the molecule and the labelling of the atoms,[5] and Figure 2 the packing of the molecules in the crystal. The molecules are held in the crystal by van der Waals forces. The closest approach of two oxygen atoms is 3·60 Å [O(B1) ··· O(T2) at x, $1 + y$, z] and of an oxygen and carbon atom is 3·30 Å [O(B2) ··· C(4) at x, $1 - y$, z]. All carbon–carbon contacts are >3·65 Å. Bond distances and angles, together with their estimated standard deviations derived directly from the least-squares inverse matrices, are given in Table 3. In general the C–H distances are appreciably shorter than accepted values,[6] but this is realistic since the hydrogen positions obtained are those of electron-density maxima rather than nuclei.

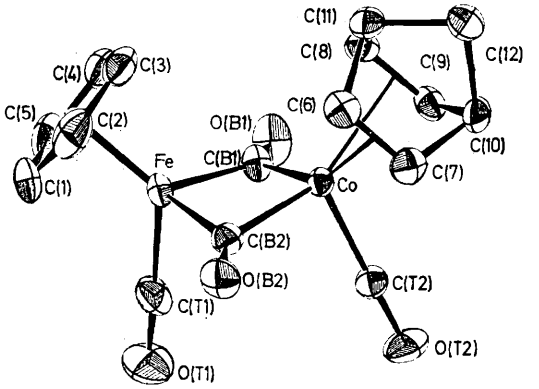

FIGURE 1 A perspective view of the molecule and the labelling of the atoms. The thermal ellipsoids are scaled to include 35% probability

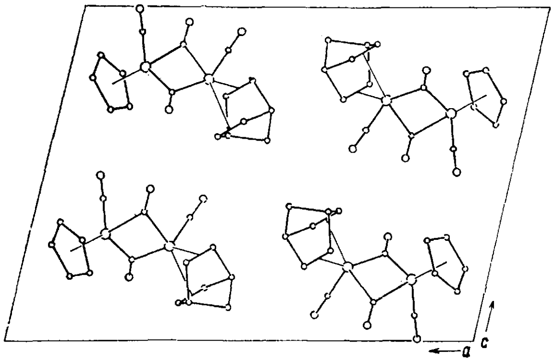

FIGURE 2 The unit-cell contents viewed along the *b* axis

The molecule consists of the iron and cobalt atoms bridged by two carbonyl groups with the cyclopentadienyl ligand π-bonded to the iron atom and the norbornadiene ligand π-bonded to the cobalt atom. The arrangement of the π-bonded fragments is such as to produce a *cis*-arrangement, similar to that found in *cis*-[$\{(C_5H_5)Fe(CO)_2\}_2$] (ref. 7) and *cis*-[$\{(C_6H_8)Co(CO)_2\}_2$].[8] The molecule approximates to m symmetry (C_s). The centroids of the π-ligands, the metal atoms, and the terminal carbonyl groups lie in a plane (Table 4) and the dihedral angle between this plane and the mean plane defined by the Fe(CO)$_2$Co bridging system is 90·0°.

TABLE 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Fe ··· Co 2·530(1)

Fe–C(B1)	1·903(4)	Co–C(B1)	1·905(4)
Fe–C(B2)	1·911(5)	Co–C(B2)	1·918(4)
Fe–C(T1)	1·756(6)	Co–C(T2)	1·782(5)
C(B1)–O(B1)	1·183(6)	C(B2)–O(B2)	1·175(6)
C(T1)–O(T1)	1·146(7)	C(T2)–O(T2)	1·140(6)
Fe–Cp *	1·742(4)	Co–NBD(1) †	2·056(5)
Fe–C(1)	2·086(5)	Co–NBD(2) †	2·030(5)
Fe–C(2)	2·121(6)	Co–C(6)	2·189(4)
Fe–C(3)	2·129(6)	Co–C(7)	2·141(5)
Fe–C(4)	2·129(6)	Co–C(8)	2·163(5)
Fe–C(5)	2·083(6)	Co–C(9)	2·119(5)
C(1)–C(2)	1·405(12)	C(6)–C(7)	1·359(7)
C(2)–C(3)	1·401(10)	C(8)–C(9)	1·370(7)
C(3)–C(4)	1·383(9)	C(6)–C(11)	1·517(8)
C(4)–C(5)	1·368(8)	C(8)–C(11)	1·521(7)
C(5)–C(1)	1·433(11)	C(7)–C(10)	1·537(8)
		C(9)–C(10)	1·538(7)
		C(10)–C(12)	1·545(8)
		C(11)–C(12)	1·536(8)

(*b*) Angles

C(B1)–Fe–C(B2)	95·4(2)	C(T2)–Co–C(B1)	96·5(2)
Co–Fe–C(B1)	48·4(1)	C(T2)–Co–C(B2)	95·8(2)
Co–Fe–C(B2)	48·8(1)	NBD(1) †–Co–C(B1)	151·9(3)
Co Fe C(T1)	99·9(2)	NBD(1) †–Co–C(B2)	91·9(3)
C(T1)–Fe–C(B1)	88·8(2)	NBD(1) †–Co–C(T2)	109·8(3)
C(T1)–Fe–C(B2)	89·9(3)	NBD(1) †–Co–NBD(2) †	70·5(3)
Cp *–Fe–C(B1)	122·7(3)	NBD(2) †–Co–C(B1)	91·3(3)
Cp *–Fe–C(B2)	124·0(3)	NBD(2) †–Co–C(B2)	151·1(3)
Cp *–Fe–C(T1)	126·1(3)	NBD(2) †–Co–C(T2)	111·5(3)
Cp *–Fe–Co	134·0(2)	Fe–C(B2)–Co	82·7(2)
Fe–C(T1)–O(T1)	177·9(6)	Fe–C(B2)–O(B2)	141·8(4)
Co–C(T2)–O(T2)	179·3(5)	Co–C(B2)–O(B2)	135·5(4)
Fe–C(B1)–Co	83·2(2)	C(11)–C(6)–C(7)	107·0(5)
Fe–C(B1)–O(B1)	140·0(4)	C(6)–C(7)–C(10)	106·2(5)
Co–C(B1)–O(B1)	136·6(4)	C(9)–C(8)–C(11)	106·7(4)
C(5)–C(1)–C(2)	106·5(6)	C(8)–C(9)–C(10)	106·0(4)
C(1)–C(2)–C(3)	108·1(6)	C(7)–C(10)–C(9)	100·8(4)
C(2)–C(3)–C(4)	107·9(6)	C(7)–C(10)–C(12)	100·6(5)
C(3)–C(4)–C(5)	109·7(6)	C(9)–C(10)–C(12)	100·4(4)
C(4)–C(5)–C(1)	107·8(6)	C)6)–C(11)–C(8)	100·9(4)
C(B1)–Co–C(B2)	95·1(2)	C(6)–C(11)–C(12)	101·3(5)
Fe–Co–C(B1)	48·4(1)	C(8)–C(11)–C(12)	101·0(4)
Fe–Co–C(B2)	48·5(1)	C(10)–C(12)–C(11)	92·8(4)
Fe–Co–C(T2)	109·9(2)		

* Cp is the centroid of the cyclopentadienyl ring. † NBD(1) and NBD(2) are the mid-points of the bonds between C(6)–C(7) and C(8)–C(9) respectively.

The cyclopentadienyl ligand exhibits the expected planarity (Table 4). The C–C distances within the ligand are in accord with those previously reported,[2,7] mean 1·40 Å. The iron to ring-carbon distances are 2·08—

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[5] C. K. Johnson, 1965 ORTEP: Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794 Revised, 1971, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[6] *Chem. Soc. Special Publ.*, No. 11, 1959 and No. 18, 1965.

[7] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc.* (*A*), 1970, 3068.

[8] F. S. Stephens, *J.C.S. Dalton*, 1972, 1752.

2·13 Å, mean 2·11 Å, and the iron–ring-centroid distance is 1·74 Å. These values are similar to those found in *cis*[{(C_5H_5)Fe$(CO)_2$}$_2$] (ref. 7) and other similar complexes.[2,9,10] The norbornadiene ligand has the expected configuration with approximately *mm* (C_{2v}) symmetry, and is bonded to the cobalt atom *via* the carbon–carbon double bonds. The mean distance from the cobalt atom to the mid-points of the double bonds is 2·04 Å, which agrees with the value (2·05 Å) found for [$Co_2(CO)_6(C_7H_8)$].[11] The four atoms involved in the π-bonding [C(6)—(9)] are coplanar and lie 2·12—2·19 Å from the cobalt, mean 2·15 Å. The carbon–carbon double bonds are, as expected, lengthened from the value of 1·333 Å in the free ligand [12] to a mean value of 1·365 Å on co-ordination. These and other dimensions of the ligand agree well with those found in [$Co_2(CO)_6(C_7H_8)$].[11]

TABLE 4

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y', and Z' are orthogonal co-ordinates related to the atomic co-ordinates X, Y, and Z by $X' = X \sin\beta$, $Y' = Y$, $Z' = Z + X \cos\beta$. Deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	*m*	*n*	*p*
Plane (1)				
C(1)—(5)	−0·6754	0·5058	0·5367	1·0181
[C(1) −0·001, C(2) 0·008, C(3) −0·013, C(4) 0·013, C(5) −0·008]				
Plane (2)				
C(6)—(9)	0·7746	0·4276	0·4660	6·7078
[C(6) 0·001, C(7) −0·001, C(8) −0·001, C(9) 0·001]				
Plane (3)				
Fe, Co, C(B1), O(B1)	0·0599	0·7711	0·6339	1·6322
[Fe 0·006, Co 0·005, C(B1) −0·024, O(B1) 0·013]				
Plane (4)				
Fe, Co, C(B2), O(B2)	0·0569	0·5465	0·8355	1·8544
[Fe 0·004, Co 0·004, C(B2) −0·018, O(B2) 0·010]				
Plane (5)				
Fe, Co, C(B1), O(B1), C(B2), O(B2)	0·0643	0·6662	0·7430	1·5798
[Fe 0·203, Co 0·216, C(B1) −0·034, O(B1) −0·176, C(B2) −0·029, O(B2) −0·179]				
Plane (6)				
Fe, Co, Cp,* NBD,† C(T1), O(T1), C(T2), O(T2)	−0·0182	−0·7432	0·6688	0·6925
[Fe 0·018, Co −0·004, Cp <0·001, NBD −0·012, C(T1) <0·001, O(T1) −0·016, C(T2) 0·008, O(T2) 0·006]				

* See footnote to Table 3. † NBD is the centroid of the plane defined by atoms C(6)–C(9).

The mean plane of the Fe$(CO)_2$Co bridging system makes an angle of 45·9° with the plane of the cyclopentadienyl ligand, and one of 47·4° with that of the π-bonded atoms of the diene ligand.

The Fe$(CO)_2$Co bridging system is non-planar, the angle between the two Fe(CO)Co planes being 160·6°. This angle, which is markedly less than that for *cis*-[{(C_6H_8)Co$(CO)_2$}$_2$] (175·1°) [8] and *trans*-[(MeC_5H_4)FeCo$(CO)_4$(C_6H_{10})] (173·4°),[2] is consistent with that (159—164°) for *cis*-[{(C_5H_5)Fe$(CO)_2$}$_2$],[7] and other related *cis*-Fe–Fe carbonyl-bridged compounds.[10,13] This suggests that the effect of the iron atom on the bridge dominates that of the cobalt atom. Bond lengths within the bridging system are much more regular than has been observed in some similar compounds.[14,15] There is, however, a small distortion in angles around the bridge carbons. The Fe–C_b–O_b angles (mean 140·9°) are larger than the Co–C_b–O_b angles (mean 136·1°) indicating a movement of the oxygen atoms of the bridge away from the iron and towards the cobalt, but still maintaining a planar environment about the bridge-carbon atoms. The cause of this may be the result of steric effects or electronic effects arising from the presence of two different metal atoms in the system.

The Fe · · · Co distance of 2·529 Å is consistent with metal–metal distances observed in similar iron and cobalt bridged complexes.[2,7-11,13-15] The iron atom is in an octahedral environment, with the iron to C(B1), to C(B2), and to C(T1) directions defining the axes, and the cyclopentadienyl ligand occupying a {111} face. The theoretical angle between such a face and an axial direction of a regular octahedron is 125·3° and for the present compound the three ring-centroid–iron–carbon angles are 122·7, 124·0, and 126·1° (Table 3). The cobalt-atom environment can be described by a square-based pyramid defined by C(B1), C(B2), and the mid-points of the carbon–carbon double bonds of the norbornadiene ligand, with C(T2) in the axial position. The cobalt atom lies *ca.* 0·43 Å from the basal plane towards the apical atom. This compares with [$Co_2(CO)_6(C_7H_8)$],[11] where one cobalt atom has a similar environment, and the corresponding distance is 0·37 Å.

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