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Hexamagnesium dicobalt undecadeuteride $Mg_6Co_2D_{11}$: containing $[CoD_4]^{5-}$ and $[CoD_5]^{4-}$ complex anions conforming to the 18-electron rule

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Abstract

$Mg_6Co_2D_{11}$ crystallizes in space group *Pnma*, $a = 8.1000(2)$ Å, $b = 10.0643(2)$ Å, $c = 18.5664(4)$ Å, $V = 1513$ Å^3, $Z = 8$. The partly disordered structure contains 14 symmetry-independent deuterium atoms, of which 9 are coordinated to cobalt in square-pyramidal $[CoD_5]^{4-}$ and saddle-like $[CoD_4]^{5-}$ complex anions, and 5 are bonded to magnesium only. The Co–D bond distances range between 1.52(1) Å and 1.62(2) Å. The limiting ionic formula can be written as $4Mg_6Co_2D_{11} = 5MgD_2 \cdot 19Mg^{2+} \cdot 2[CoD_5]^{4-} \cdot 6[CoD_4]^{5-}$. The 63-parameter structure was solved *ab initio* and refined from joint synchrotron and neutron high resolution powder diffraction data.

1. Introduction

The Mg–Co–H system contains at least two ternary hydride phases, a tetragonal β phase of composition Mg_2CoH_5 and built up by square-pyramidal $[CoH_5]^{4-}$ complex anions [1], and an orthorhombic γ phase (space group *Cmcm*, lattice parameters $a = 4.648$ Å, $b = 8.115$ Å, $c = 10.083$ Å [2]) of unknown composition and structure. Work on the latter phase showed [3, 4] that its composition was close to Mg_3CoH_5. In this paper we report on its structure and exact composition, $Mg_6Co_2H_{11}$. Its fourfold superstructure can be described in terms of space group *Pnma* with 63 free positional

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parameters, and is one of the most complex structures ever solved *ab initio* from powder diffraction data. The compound contains a mixture of $[CoH_5]^{4-}$ and $[CoH_4]^{5-}$ complex anions, and is the first known example of a complex metal hydride built up by transition metal complexes having two different geometries.

2. Experimental details

2.1. Synthesis

$Mg_6Co_2H_{11}$ was synthesized by mixing magnesium (Fluka) and cobalt (Alfa) powders in a 2:1 molar ratio, pressing them into pellets and sintering them at 753–773 K for 1 day under a hydrogen atmosphere at 40–50 bar pressure. The large unreacted magnesium grains were removed by passing the powder through a sieve, while the unreacted cobalt grains were removed by a magnet. X-ray Guinier films revealed no lines which could be attributed to magnesium, cobalt, MgH_2 or Mg_2CoH_5 [2]. The deuteride was synthesized by sintering a mixture of magnesium (Cerac) and cobalt (Merck) powders in the molar ratio 3.2:1 at 763 K under deuterium (D_2, 99.8%; Air Liquide) at a pressure of 27 bar for a period of 15 h using a method described previously [5]. X-ray Guinier films of this sample exhibited no evidence of impurity phases.

2.2. X-ray powder diffraction

Guinier films (Co $K\alpha_1$ radiation) were indexed by use of the program TREOR [6] on a C-centred orthorhombic cell with refined parameters $a = 4.648(4)$ Å, $b = 8.115(6)$ Å, $c = 10.083(8)$ Å. The observed extinctions were in accordance with the proposed [2] space group *Cmcm*, and the lattice parameters agreed with those already published [2, 4]. A few relatively weak peaks, reproducibly present in well-crystallized samples, could not be accounted for with this cell, indicating a possible superstructure. It was therefore decided to improve the resolution of the X-ray data by performing experiments at Brookhaven National Synchrotron Light Source (NSLS). Data on the hydride sample (quartz glass capillary; diameter, 0.5 mm) were collected at beam line X14 with a sagittally focusing Si(111) monochromator and a flat Ge(111) analyser [7] at three different wavelengths (1.6095, 1.6195 and 1.6295 Å) close to the absorption edge of cobalt in order to improve the contrast between the cobalt and magnesium atoms. Data with better statistics were also collected in the low angle region at beam line X7a in order to detect other possible superlattice peaks.

The average structure was solved in the C-centred subcell from Patterson and Fourier maps by using the contrast provided by the anomalous scattering of cobalt. It revealed the presence of deformed magnesium cubes centred by cobalt atoms, joined by edges and forming layers connected by corners. A careful analysis of the superstructure diffraction peaks showed that the cell had to be quadrupled along a, and that the true space group was *Pnma*.

A refinement of the metal atom superstructure based on the 1.6295 Å data set with the program DBWS 9006 (ref. 8; see also ref. 9) converged at $R_p = 26.9\%$ (without background) and $R_B = 8.3\%$. A small amount of cubic Mg–Co δ phase [2] was detected as impurity. Broad weak peaks were observed at 2θ angles of 41°, 43.2°, 79.9° and 105°. They could not be attributed to Mg_2CoH_5, MgH_2, magnesium and cobalt, or to their oxides, and, with the exception of the first peak, were excluded from the refinements.

2.3. *Neutron powder diffraction*

The neutron diffraction experiments were performed on the deuterated specimen on the DMC diffractometer [10] at the SAPHIR reactor at PSI in Villigen (high resolution mode; specimen mass, 3 g; cylindrical vanadium container of 8 mm inner diameter; $\lambda = 1.7070$ Å) and on the D2B diffractometer at ILL in Grenoble (normal mode, better angular resolution than DMC for $2\theta > 75°$, $\lambda = 1.5939$ Å). The neutron scattering lengths $b(\mathrm{Mg}) = 0.5375 \times 10^{-12}$ cm, $b(\mathrm{D}) = 0.6674 \times 10^{-12}$ cm, $b(\mathrm{Co}) = 0.253 \times 10^{-12}$ cm were taken from ref. 11. The possible sites of the deuterium atoms were found by assuming a minimal Co–D distance of 1.55 Å and an Mg–D distance of 1.90 Å. From the proposed 20 symmetry-independent sites, 14 were found to be occupied. The structure refinements were performed on both data sets by using the program DBWS 9006. Cubic MgO and CoO were detected as impurity phases.

2.4. *Joint refinement*

The final refinements were performed simultaneously on three data sets by using the program SIMREF [12]: (1) hydride, synchrotron radiation (NSLS), $\lambda = 1.6295$ Å, $2\theta = 18$–110°; (2) deuteride, neutron radiation (PSI), $\lambda = 1.7070$ Å, $2\theta = 8$–120°; (3a) deuteride, neutron radiation (ILL), $\lambda = 1.5939$ Å, $2\theta = 8$–105°; (3b) deuteride, neutron radiation (ILL), $\lambda = 1.5939$ Å, $2\theta = 105$–147.5°.

The refinement of 102 parameters, including 63 positional and 13 isotropic displacement parameters (3 in data set 1, 5 in data sets 2 and 3) converged to the following agreement indices (all values calculated after background subtraction):

data set 1	$R_p = 26.4\%$	$R_B = 9.1\%$	$S = 1.01$*
data set 2	$R_p = 11.3\%$	$R_B = 7.2\%$	$S = 1.50$
data set 3a	$R_p = 9.5\%$	$R_B = 6.7\%$	$S = 0.91$*
data set 3b	$R_p = 14.6\%$	$R_B = 11.7\%$	$S = 1.25$
all data sets	$R_p = 12.0\%$	$R_B = 9.0\%$	$S = 1.05$*

The goodness-of-fit values marked by asterisks suggest that the weighting scheme was not optimal. The Durbin–Watson d statistics [13] exhibited positive serial correlations between the adjacent intensity points in all data sets, indicating that the estimated standard deviations were underestimated. The structural parameters refined jointly from synchrotron and neutron data were, however, sufficiently accurate to allow conclusions about the crystal chemistry to be drawn (see below).

The occupancy factors of all deuterium sites except D25 did not differ significantly from unity and were fixed at this value during the final refinement. The occupancy of D25 refined to the value 0.53(3) and was fixed for electronic reasons at 0.5 during the final refinement (see below).

The results of the refinement are summarized in Table 1. Interatomic distances are given in Table 2. The observed and difference diffraction patterns for data sets 1 and 2 are shown in Fig. 1. The environment of the cobalt atoms is shown in Fig. 2, the layers of magnesium cubes centred by cobalt are shown in Figs. 3 and 4, and the environment of the D31–D35 atoms is shown in Fig. 5.

TABLE 1

Results of joint refinement on one synchrotron ($Mg_6Co_2H_{11}$) and two neutron ($Mg_6Co_2D_{11}$) diffraction data sets (estimated standard deviations in parentheses)

Atom	position	x	y	z	U_{iso} ($\times 10^{-2}$ Å^2)
Co1	8d	0.7401(5)	0.0005(5)	0.9345(3)	0.45(5)
Co2	8d	0.7500(8)	0.9990(8)	0.1881(3)	U_{Co1}
Mg1	4c	0.8032(15)	0.25	0.9671(5)	1.2(1)
Mg2	4c	0.1651(11)	0.25	0.0565(7)	U_{Mg1}
Mg3	4c	0.7986(15)	0.25	0.1546(6)	U_{Mg1}
Mg4	4c	0.7170(12)	0.25	0.6911(7)	U_{Mg1}
Mg5	8d	0.5759(8)	0.0693(7)	0.0613(6)	1.08(6)
Mg6	8d	0.9176(7)	0.9598(5)	0.0620(6)	U_{Mg5}
Mg7	8d	0.0943(10)	0.0643(9)	0.1901(5)	U_{Mg5}
Mg8	8d	0.4213(11)	0.9261(10)	0.1858(6)	U_{Mg5}
D11	8d	0.3455(16)	0.0921(12)	0.6119(6)	1.97(6)
D12	8d	0.3010(15)	0.0974(14)	0.0021(6)	U_{D11}
D13	8d	0.3325(15)	0.0974(13)	0.1236(7)	U_{D11}
D14	8d	0.0937(12)	0.0989(11)	0.5528(6)	U_{D11}
D21	8d	0.3127(16)	0.0847(14)	0.8738(7)	U_{D11}
D22	8d	0.3580(16)	0.0907(14)	0.2663(6)	U_{D11}
D23	8d	0.1057(14)	0.1058(13)	0.3110(7)	U_{D11}
D24	8d	0.3185(15)	0.0939(13)	0.7493(7)	U_{D11}
D25[a]	8d	0.0832(28)	0.0896(24)	0.8161(16)	U_{D11}
D31	4c	0.5704(21)	0.25	0.5624(13)	2.2(1)
D32	4c	0.5663(23)	0.25	0.3232(10)	U_{D31}
D33	4c	0.0637(24)	0.25	0.7066(11)	U_{D31}
D34	4c	0.1341(17)	0.25	0.4336(11)	U_{D31}
D35	4c	0.4152(19)	0.25	0.4400(12)	U_{D31}

Space group *Pnma* (No. 62). Cell parameters (data set 1,hydride): $a=8.1120(1)$ Å, $b=10.0800(1)$ Å, $c=18.6028(3)$ Å. Cell parameters (data set 2, deuteride): $a=8.1000(4)$ Å, $b=10.0643(5)$ Å, $c=18.5664(9)$ Å. The value of U_{iso} for cobalt is taken from the refinement of data set 1, for magnesium and deuterium from data set 3. $R_B=9.0\%$, $R_p=12.0\%$, $S=1.05$ for 850 reflections in data set 1, 869 reflections in data set 2 and 1475 reflections in data set 3.

[a] Half occupied position.

TABLE 2

Bond distances in $Mg_6Co_2D_{11}$ (estimated standard deviations in parentheses) (all deuterium–deuterium distances are greater than 2.1 Å)

Co1–D12	1.521(12)	Co2–D21	1.532(12)
D11	1.556(10)	D22	1.550(12)
D14	1.574(9)	D24	1.563(12)
D13	1.603(12)	D23	1.574(12)
		D25^a	1.622(18)
Mg1	2.640(6)	Mg4	2.526(8)
Mg2	2.642(6)	Mg3	2.631(8)
Mg5	2.668(7)	Mg7	2.686(11)
Mg8	2.681(11)	Mg6	2.718(11)
Mg7	2.757(11)	Mg8	2.755(11)
Mg6	2.791(11)	Mg5	2.819(12)
Mg5	2.802(12)	Mg8	2.823(12)
Mg6	2.811(7)	Mg7	2.847(10)
D31–2Mg6	2.126(4)	D32–2Mg7	1.889(8)
Mg1	2.288(15)	Mg3	2.241(17)
Mg2	2.329(17)	Mg2	2.382(16)
D33–2Mg8	1.855(10)	D34–2Mg5	1.873(7)
Mg4	2.259(16)	Mg3	2.090(15)
Mg4	2.784(15)	Mg1	2.218(15)
D35–Mg1	1.943(17)		
Mg3	1.968(17)		
Mg2	2.000(13)		

^{a}Half occupied position.

3. Discussion

The structure of $Mg_6Co_2D_{11}$ contains 14 symmetry-independent deuterium atoms, of which 9 are coordinated to cobalt atoms, and 5 are bonded to magnesium atoms only. As shown in Fig. 2, one of the cobalt sites, Co1, has four deuterium ligands in a saddle-like configuration that derives from a square-pyramidal configuration by removal of one basal ligand. The other cobalt site, Co2, is surrounded by five ligand sites in a square-pyramidal configuration, of which one of the basal sites (D25) is half occupied. Thus Co2 is surrounded by 4.5 deuterium ligands on the average, *i.e.* the structure is partly disordered. As shown in Figs. 3 and 4 the five deuterium atoms not bonded to cobalt are situated on a mirror plane. Four of them (D31, D32, D33, D34) are coordinated by four magnesium atoms in a saddle-like configuration, and one (D35) has a triangular magnesium coordination (see Fig. 5) similar to that in binary MgD_2 (rutile-type structure). The connectivity of the deformed alkaline earth cubes centred by the transition metal is the same as that found recently in $SrMg_2FeD_8$ [14].

These structural features suggest that $Mg_6Co_2D_{11}$ can be rationalized in terms of a one-to-three mixture of $[CoD_5]^{4-}$ and $[CoD_4]^{5-}$ complex anions

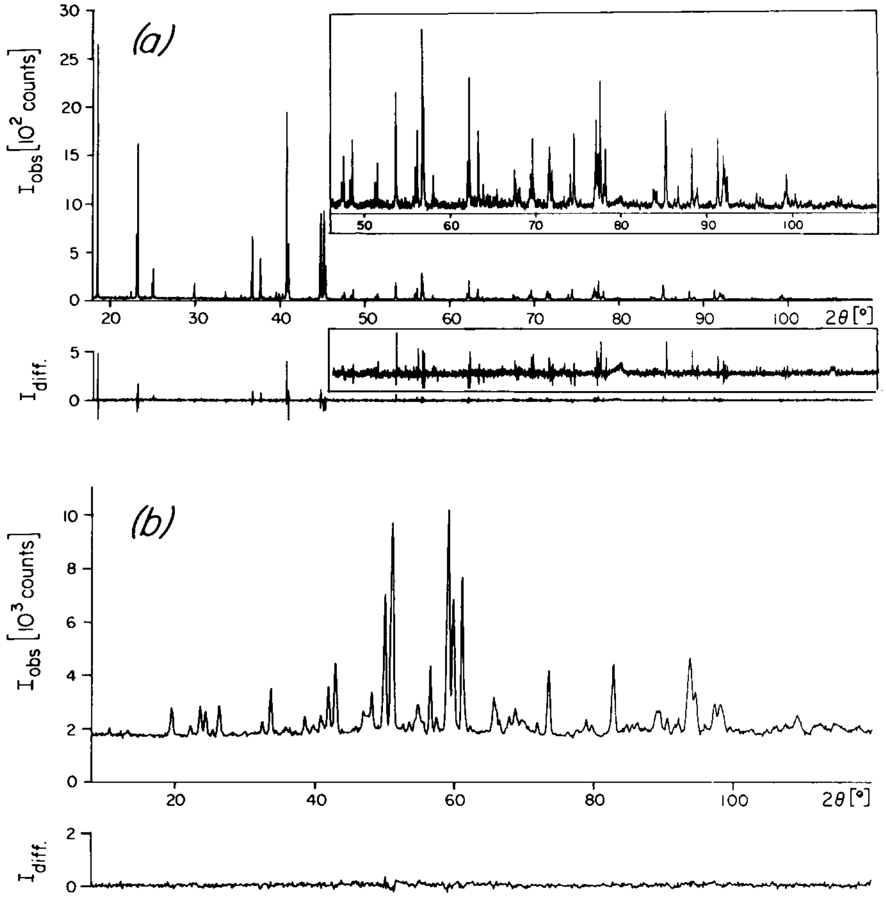
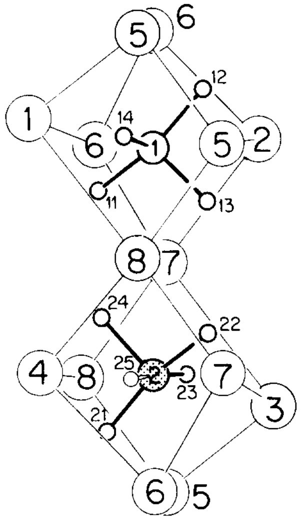


Fig. 1. Observed and difference diffraction patterns for (a) synchrotron ($Mg_6Co_2H_{11}$, $\lambda = 1.6295$ Å) and (b) neutron ($Mg_6Co_2D_{11}$, $\lambda = 1.7070$ Å) data. The intensity scale of the insets is ten times enlarged.

respectively, of magnesium cations, and of magnesium dideuteride, corresponding to the limiting ionic formula $4Mg_6Co_2D_{11} = 5MgD_2 \cdot 19Mg^{2+} \cdot 2[CoD_5]^{4-} \cdot 6[CoD_4]^{5-}$. This description implies that the compound conforms to the 18-electron rule, as does Mg_2CoD_5 which is built-up by square-pyramidal $[CoD_5]^{4-}$ complex anions only [1]. The exact distribution of the $[CoD_4]^{5-}$ and $[CoD_5]^{4-}$ complex anions in $Mg_6Co_2D_{11}$, however, remains to be determined. The metal–deuterium bond distances in the $[CoD_4]^{5-}$ anions (1.52–1.60 Å), and the average bond distances in the disordered $[CoD_5]^{4-}$ anions (1.53–1.62 Å), compare favourably with those in the $[CoD_5]^{4-}$ anions of Mg_2CoD_5 (1.590(17) Å apical, 1.515(3) Å basal) [1]. The geometry of the $[CoD_4]^{5-}$ 18-electron complex in $Mg_6Co_2D_{11}$ is similar to that of the ruthenium complex in Mg_2RuD_4 which was originally formulated [15] as a monomeric $[RuD_4]^{4-}$ 16-electron complex, and later [16] as a polymeric



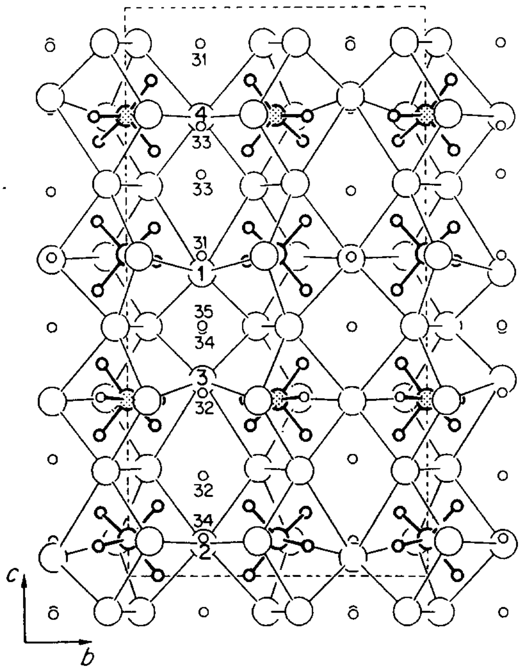


Fig. 2. Environment of Co1 and Co2 atoms in $Mg_6Co_2D_{11}$, viewed approximately along [100]: ◯, magnesium; ○, Co1; ◍. Co2; ∘, deuterium. Atom numbers according to Table 1. The half-occupied D25 position is indicated by an open bond.

Fig. 3. Projection of a layer of deformed cubes of magnesium atoms in $Mg_6Co_2D_{11}$ along [100]: ◯, magnesium; ○, Co1; ◍, Co2; ∘, deuterium. All cobalt atoms at $x \approx 0.25$. Atom numbers given only for atoms situated on the mirror plane.

$[RuD_4]_n{}^{4n-}$ conforming to the 18-electron rule. The transition metal (T)–deuterium bond angles in these two complexes, however, differ: $[D–T–D]_{trans} = 154.7°$ ($[CoD_4]^{5-}$), 170.3° ($[RuD_4]_n{}^{4n-}$); $[D–T–D]_{cis} = 101.6°$ ($[CoD_4]^{5-}$), 84.2° $[RuD_4]_n{}^{4n-}$. The shortest Co–Co distances in $Mg_6Co_2D_{11}$ are 4.57 Å. The shortest Co–Mg distances (Co1–Mg1, 2.64 Å; Co2–Mg4, 2.53 Å) are close to the sum of covalent bond radii. None of the D–D contacts is shorter than 2.1 Å.

$Mg_6Co_2D_{11}$ is the first known example of a complex deuteride showing two types of transition metal ligand geometries. The only other known complex deuteride with crystallographically independent transition metal sites is K_2ReD_9 [17], containing two $[ReD_9]^{2-}$ anions which have both tricapped trigonal prismatic geometry.

Finally it is worth pointing out that the structure of $Mg_6Co_2D_{11}$ has 63 free atomic positional parameters, and thus is one of the most complex crystal structures ever solved *ab initio* from powder diffraction data. The success was largely due to the availability of diffraction data of highest

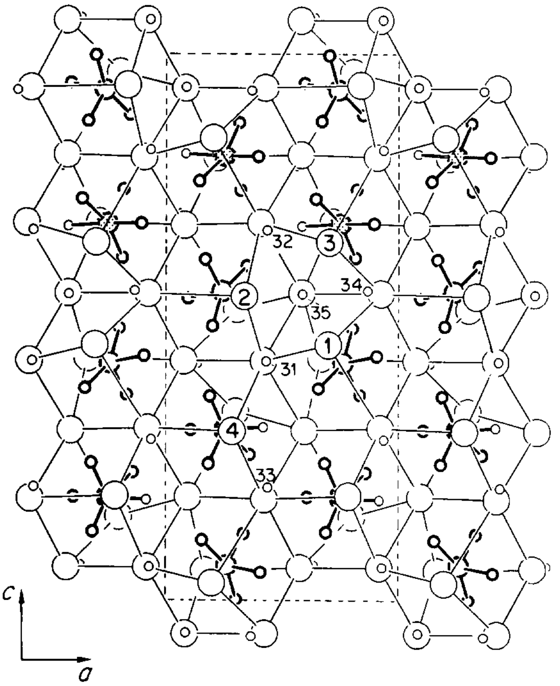


Fig. 4. Projection of a layer of deformed cubes of magnesium atoms in $Mg_6Co_2D_{11}$ along [010]: ○, magnesium; ○, Co1; ◍, Co2; ○, deuterium. Cobalt atoms at $y \approx 0$. Atom numbers given only for atoms situated on the mirror plane.

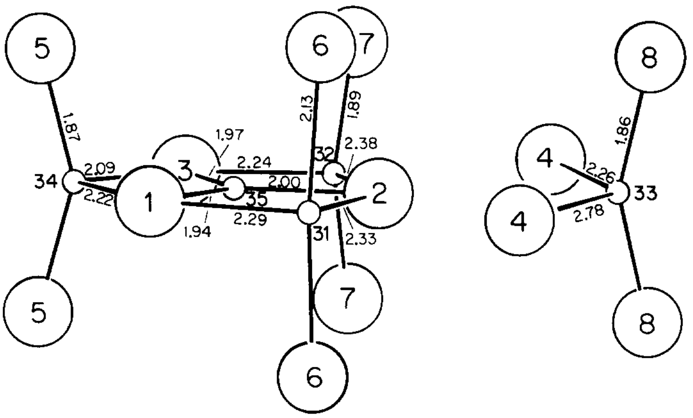


Fig. 5. Environment of D31, D32, D34 and D35 atoms (left) and D33 atom (right) in $Mg_6Co_2D_{11}$: ○, magnesium; ○, deuterium; bond lengths in ångströms.

resolution and the possibility of performing joint refinements on several data sets, and shows the potential of powder diffraction methods to characterize complex crystal structures.

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