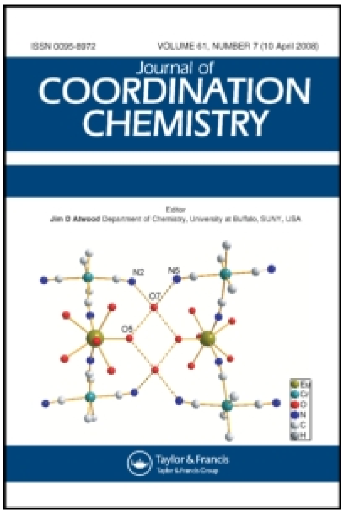

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A new 3D polyoxometalate based on saturated Wells-Dawson polyanions and calcium cations

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A new 3D polyoxometalate based on saturated Wells–Dawson polyanions and calcium cations

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A new polyoxometalate based on saturated Wells-Dawson polyanions and calcium cations, $H_2[Ca_2(P_2W_{18}O_{62})(H_2O)_5]\cdot 7.5H_2O$ (**1**), has been synthesized in aqueous solution and characterized by single-crystal X-ray diffraction and IR. Compound **1** is a new example of 3D framework based on Wells-Dawson anions that act as chelate ligands to coordinate with calcium cations. Cyclic voltammetry reveals that the pH of the supporting electrolytic solution has a marked effect on the electrochemical behavior.

Keywords: Wells–Dawson; Alkaline earth metal; Polyoxometalate; Electrochemistry

1. Introduction

Polyoxometalates (POMs) continue to attract significant interest for structural architectures and potential applications in the fields of catalysis, medicine, magnetism, electrochemistry, photochemistry and geochemistry [1–4]. Syntheses of inorganic solid-state materials built by polyoxometalate building blocks and metal coordination complexes are well developed [5–12]. A variety of solid-state materials containing chain, layer and multi-dimensional frameworks constructed from components based on POMs anions and coordination complex cations have been reported [13–17]. Compared with other classical POMs, such as the Keggin and Anderson types with dimensional expansion, multiple dimensional structures based on Wells-Dawson type polyanions are comparatively rare. Although it has abundant terminal oxygen atoms that can coordinate to metal ions in the extended structure, it is difficult to use the Wells-Dawson type anion as a building block to construct high-dimensional frameworks due to its larger volume. Using transition metal complex subunits as bridging ligands in the Wells-Dawson infinitely extended structure have been described [17–20], are synthesized by hydrothermal methods. From the standpoint of molecular design, we have attempted to make use of simple synthesis to realize such molecular assemblies.

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We are trying to construct various polyoxometalates linked by alkaline earth metal coordination polymers [12, 21–26]. In this article we report one extended heteropoly compound $H_2[Ca_2(P_2W_{18}O_{62})(H_2O)_5] \cdot 7.5H_2O$ (**1**), which shows a 3D framework structure constructed from saturated Wells–Dawson anions that act as chelate ligands to coordinate calcium cations.

2. Experimental

2.1. *Material and synthesis*

The $K_6P_2W_{18}O_{62} \cdot 10H_2O$ was prepared according to the literature method [27] and confirmed by IR spectrum. All other chemicals used for synthesis were of reagent grade and used without further purification.

A mixture of $K_6P_2W_{18}O_{62} \cdot 10H_2O$ (1.46 g, 0.30 mmol), $CaCl_2$ (0.07 g, 0.60 mmol) and H_2O (20 mL) was stirred for 20 min until the solid was completely dissolved at room temperature. The pH was adjusted to 3.46 with acetic acid under vigorous stirring. The resulting solution was allowed to react for 5 h, then filtered and left to evaporate at room temperature. Several weeks later, colorless crystals were obtained.

2.2. *Physical measurements*

IR spectrum was recorded on a Nicolet 170 SXFT–IR spectrometer using KBr pellets from 4000~400 cm^{-1}. Electrochemical measurements were performed on a LK98 microcomputer-based electrochemical system (LANLIKE, Tianjin, China). A three-electrode system was employed for cyclic voltammetry; a 4 mm diameter glassy carbon disk electrode (GCE) (home-made) was used as a working electrode, a platinum wire served as the counter electrode and an Ag/AgCl electrode as the reference electrode.

A single crystal of **1** (with dimensions of $0.11 \times 0.11 \times 0.08\ mm^3$) was used for data collection. Intensity measurement was made on an Apex-II CCD image plate area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 (2)K. The structure was solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL-97 crystallographic software package [28]. A summary of the crystallographic data and structure refinements is given in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

The structure of **1** is built on saturated Wells-Dawson polyoxoanions $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ and Ca^{2+} into a three-dimensional framework. The polyanions $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in **1** have normal Wells-Dawson structure, constructed by two $[\alpha\text{-}PW_9O_{34}]^{9-}$ units (each generated from $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ by removal of three corner-shared WO_6 octahedra), which are linked through corner-sharing with the elimination of six oxygen

Table 1. Crystallographic data and structure refinement for **1**.

Compound no.	**1**
Formula	$H_{27}Ca_2O_{74.50}P_2W_{18}$
Fw	4670.62
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.933(5)
b	14.878(6)
c	20.048(8)
α	70.253(5)
β	80.800(5)
γ	64.425(4)
Volume (Å^3), Z	3275(2), 2
D_{Calcd} (Mg m^{-3})	4.737
$F(000)$	4050
θ(°)	2.07 to 25.00
Reflections collected	15553
Goodness-of-fit	0.943
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0732$, $wR_2 = 0.1881$
Independent reflections	10730 ($R_{int} = 0.1097$)

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ca(1)–O(1W)	2.70(3)	Ca(1)–O(10)#1	2.75(2)
Ca(1)–O(3W)	2.84(2)	Ca(1)–O(2W)	2.86(3)
Ca(1)–O(32)#2	2.882(18)	Ca(1)–O(5)	2.912(19)
Ca(1)–O(11)	2.94(2)	Ca(2)–O(3W)#3	2.78(2)
Ca(2)–O(7)	2.66(2)	Ca(2)–O(12W)	2.87(6)
Ca(2)–O(17)#4	2.83(2)	Ca(2)–O(11W)	2.89(6)
Ca(2)–O(1W)#3	2.87(3)	Ca(2)–O(6)#3	3.10(2)
Ca(2)–O(3)#5	2.94(3)	W(5)–O(5)	1.725(18)
W(4)–O(55)	2.44(2)	W(10)–O(10)	1.721(19)
W(7)–O(7)	1.78(2)	W(12)–O(42)	1.85(2)
W(11)–O(11)	1.69(2)	W(14)–O(14)	1.66(2)
W(13)–O(49)	2.027(17)	O(1W)–Ca(1)–O(10)#1	129.7(8)
O(15W)–O(16W)	1.42(6)	O(10)#1–Ca(1)–O(3W)	123.7(6)
O(1W)–Ca(1)–O(3W)	71.1(8)	O(10)#1–Ca(1)–O(2W)	73.4(7)
O(1W)–Ca(1)–O(2W)	74.6(9)	O(32)#2–Ca(1)–O(5)	161.1(6)
O(3W)–Ca(1)–O(2W)	144.6(8)	O(10)#1–Ca(1)–O(11)	66.7(6)
O(7)–Ca(2)–O(17)#4	72.9(7)	O(2W)–Ca(1)–O(11)	137.8(7)
O(7)–Ca(2)–O(12W)	103.5(13)	O(7)–Ca(2)–O(3W)#3	129.8(7)
O(12W)–Ca(2)–O(1W)#3	60.5(14)	O(3W)#3–Ca(2)–O(12W)	87.2(13)
O(3W)#3–Ca(2)–O(11W)	81.4(12)	O(7)–Ca(2)–O(11W)	75.2(12)
O(7)–Ca(2)–O(3)#5	106.2(7)	O(17)#4–Ca(2)–O(11W)	114.5(12)
O(17)#4–Ca(2)–O(3)#5	61.5(6)	O(11W)–Ca(2)–O(3)#5	75.4(12)
O(7)–Ca(2)–O(6)#3	67.7(6)	O(3W)#3–Ca(2)–O(6)#3	74.0(6)
O(1W)#3–Ca(2)–O(6)#3	113.7(7)	O(12W)–Ca(2)–O(6)#3	64.3(13)

Symmetry transformations used to generate the equivalent atoms: #1: $-x+2$, $-y$, $-z-2$; #2: $x+1$, y, z; #3: $-x+2$, $-y-1$, $-z-1$; #4: $-x+1$, $-y$, $-z-1$; #5: $-x+1$, $-y-1$, $-z-1$.

atoms [29, 30]. The polyanion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ has D_{3h} point group symmetry and contains only two structurally distinct types of W atoms: six "polar" atoms and twelve "equatorial" atoms. W–O distances are in the range of 1.66(2)–1.78(2)Å for Ot oxygens, 1.85(2)–2.027(17)Å for μ_2-bridging oxygens, 2.29(2)–2.44(2)Å for μ_3-bridging oxygens and 2.350(19)–2.435(18)Å for μ_4-bridging oxygens. The central P atoms are PO_4 with P–O distances in the range 1.507(19)–1.58(2)Å, and the O–P–O angles vary from 105.4(10)° to 115.2(11)°. All these bond lengths are within the normal ranges and in close agreement with those described in the literature [20–23].

There are two kinds of calcium coordination in the building block $[Ca_2(P_2W_{18}O_{62})(H_2O)_5]^{2-}$ of the asymmetric structural unit of **1** (figure 1), which is composed of one $[Ca(1)(H_2O)_3]^{2+}$, one $[Ca(2)(H_2O)_2]^{2+}$, and one $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ subunit. The Ca^{2+}(1) and Ca^{2+}(2) coordination cations are connected with oxygens of the polyanion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ through W–O–Ca–O–W bridges (figure 2). By means of this architecture, the adjacent polyanions are polymerized by the two bridging Ca^{2+},

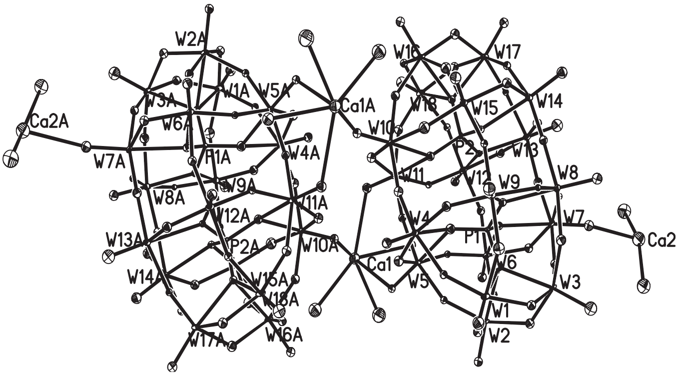

Figure 1. ORTEP view of the heteropolyanion of **1** with atom labeling showing 30% probability displacement ellipsoids.

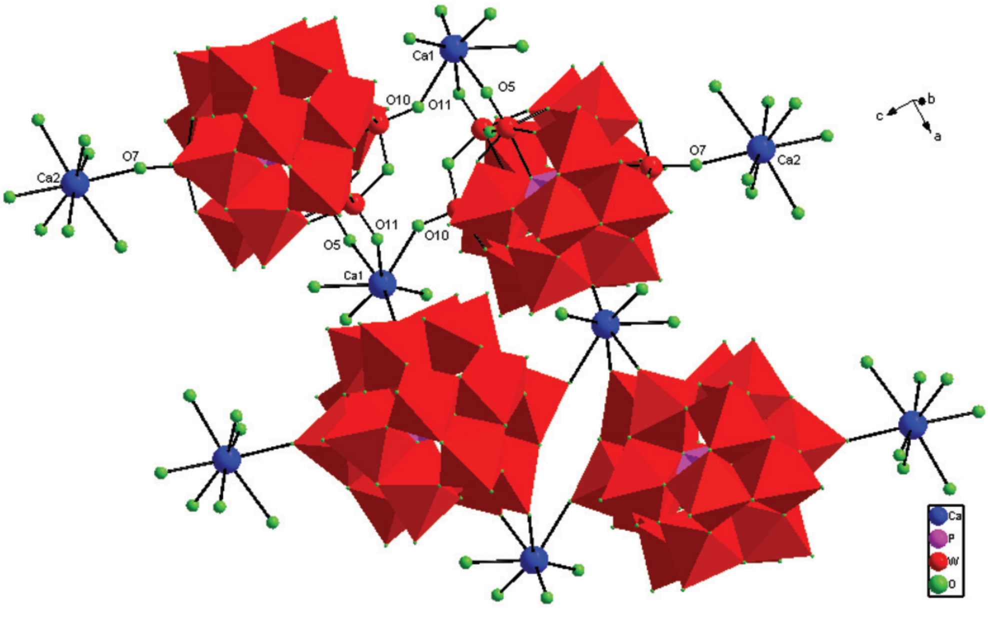

Figure 2. The molecular coordination mode of **1**.

giving **1** (figure 3). An additional interesting feature is that the Ca(1) and Ca(2) are related to each other by Ca(1)–O1W–Ca(2) and Ca(1)–O3W–Ca(2) bridges to strengthen the 3D framework structure.

As can be seen from bond distances and angles relevant to Ca^{2+}(1) coordination sphere, the Ca^{2+}(1) ion is coordinated to seven oxygens, three from H_2O molecules (O1W, O2W, and O3W) and the remaining from O5, O11, O10#1, and O32#2 of two polyoxoanions. The Wells-Dawson anion is a chelate ligand coordinating a Ca^{2+}(1) via two terminal oxygen atoms of tungsten (O5 and O11), which belong to two hemisphere "equatorial" sites in the same polyanion. The Ca(1)–O lengths are in the range 2.70(3)–2.94(2)Å, average 2.84 Å. The average Ca(1)–O(H_2O) bond distance, 2.80 Å, is 0.07 Å, a little shorter than the average Ca(1)–O (oxygen atoms of W–O) bond distance, 2.87 Å. The bond angle O32#2–Ca(1)–O5 is 161.1(6)°. The central Ca^{2+}(1) is 0.5827 Å above the least-square plane defined by O1W, O2W, O3W, O11 and O10#1, with a greatly distorted pentagonal bipyramid geometry [figure 4(a)]. The coordination of Ca^{2+}(2) is different from Ca^{2+}(1), with a distorted square prismatic geometry in which

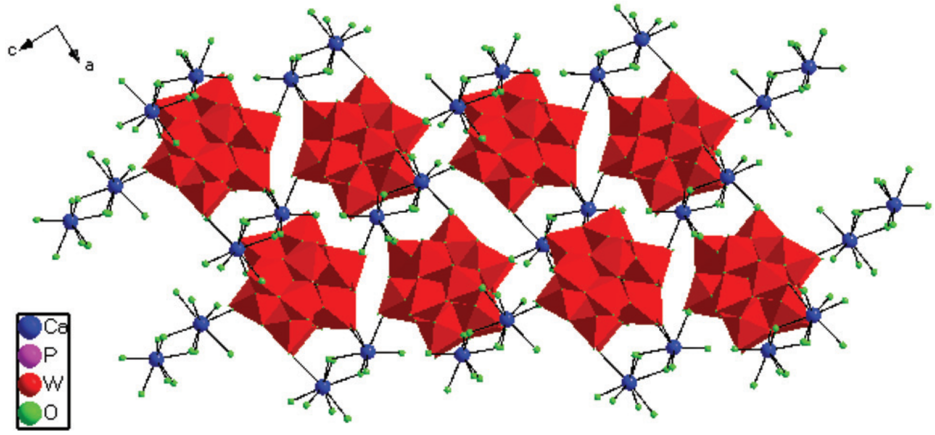

Figure 3. View of the 2D network structure in **1**. Some water molecules and hydrogen atoms are omitted for clarity.

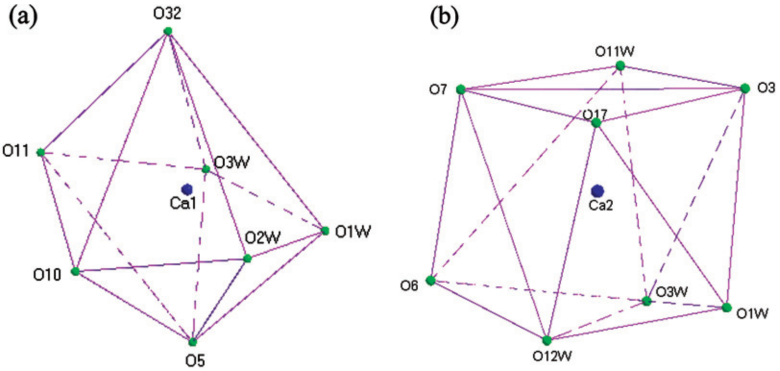

Figure 4. Coordination polyhedron around Ca^{2+}(1) and Ca^{2+}(2) in **1**.

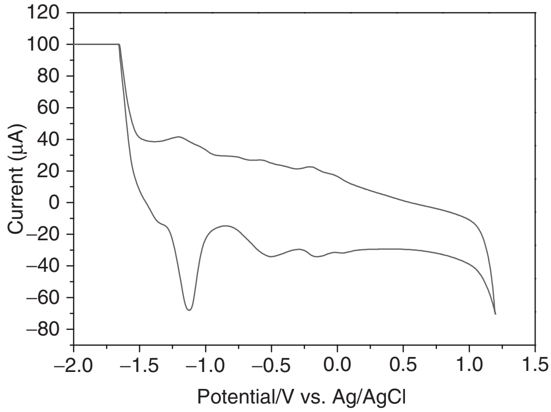

Figure 5. Cyclic voltammogram of 0.20 mM $H_2[Ca_2(P_2W_{18}O_{62})(H_2O)_5]\cdot 7.5H_2O$ at pH 5.85 in 0.50 M NaCl aqueous solution; scan rate: 80 mV s^{-1}.

four oxygens from coordinated water and four from terminal oxygens of two polyanions occupy eight sites [figure 4(b)]. The two bottom surfaces of the square prism are occupied by O7, O11W, O3#5, O17#4 group and O6#3, O12W, O1W#3, O3W#3 group, respectively. The distances of $Ca^{2+}(2)$ and the two bottom planes are 1.6383 and 1.7065 Å, respectively. The Ca(2)–O bond lengths are in the range 2.66(2)–3.10(2)Å, average 2.87 Å. The average Ca(2)–O(H_2O) bond distance, 2.85 Å, is a little shorter than the average Ca(2)–O (oxygen atoms of W–O) bond distance, 2.88 Å. All these experimental data confirm that the coordination of $Ca^{2+}(1)$ and $Ca^{2+}(2)$ is distorted greatly, owing to the interaction between the oxygen atoms of the larger volume of Dawson-type polyanion and the metal cations.

3.2. *Electrochemistry*

It is easy to obtain well-defined redox waves in aqueous electrolytes due to the stability of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in aqueous solution. The electrochemical behavior of the parent Dawson-type heteropolyanion, $\alpha/\beta\text{-}K_6P_2W_{18}O_{62}\cdot 14H_2O$, has previously been described [30].

Compound **1** has been studied by cyclic voltammetry. Figure 5 shows the evolution of the cyclic voltammogram for **1** in the presence of 0.50 M NaCl aqueous solution as supporting electrolyte (pH = 5.85), and four pairs of redox waves appears with the midpoint peak potentials ($E_{p1/2}$) of −1.1545, −0.5303, −0.1536 and −0.0332 V, where $E_{p1/2} = (E_{pc} + E_{pa})/2$, E_{pc} and E_{pa} are cathodic and anodic peak potentials. The peak potential separations of these four pairs of redox peaks are 50, 38, 36 and 32 mV, with two semi-reversible charge-transfer processes and two reversible two-electron reduction processes. The reversibility criterion used was $\Delta E_p = E_{pa} - E_{pc} = 59/n$ mV (n, number of electrons).

The following experiments were carried out in the same media varying the pH, with 0.10 M HCl and 0.10 M NaOH aqueous solution (figure 6). At pH 2.50, the peak current is the strongest among the pH region studied here, and compared with the redox wave at pH 5.85, the peak potential is shifted in the positive direction. This may be due to protonation of the heteropolyanion which makes the heteropoly anion stable. In the pH range 3.83∼8.00, the peak potentials are in agreement with that at pH 5.85.

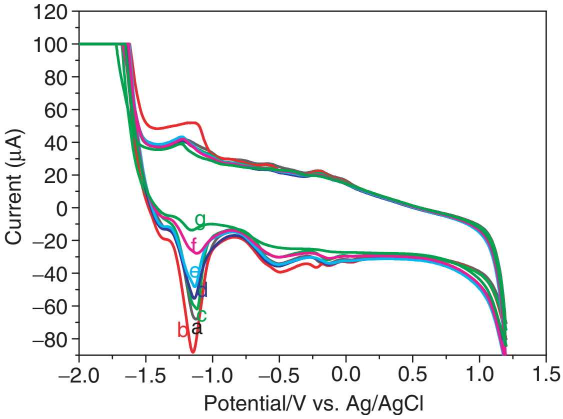

Figure 6. Cyclic voltammograms of 0.20 mM $H_2[Ca_2(P_2W_{18}O_{62})(H_2O)_5] \cdot 7.5H_2O$ with the $2 < pH < 11$ region in 0.50 M NaCl aqueous solution; scan rate: $80\,mV\,s^{-1}$. Curves a, pH = 5.85; b, pH = 2.50; c, pH = 3.83; d, pH = 4.03; e, pH = 6.76; f, pH = 8.00; g, pH = 10.55.

Three pairs of redox peaks gradually diminish at pH 10.55, which may be due to decomposition of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in strong basicity.

From the above analysis, $P_2W_{18}O_{62}^{6-}$ is stable in pH values from 2.00 to 8.00, but the solution pH has marked influence on the polyanion of **1**. These results are in good agreement with previous analysis [31, 32].

3.3. *IR spectrum*

There are four characteristic asymmetric vibrations resulting from $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, namely $\upsilon_{as}(P\text{–}\mu_3\text{–}Oa)$, $\upsilon_{as}(W\text{–}\mu\text{–}Ot)$, and $\upsilon_{as}(W\text{–}\mu_2\text{–}Ob)$ (the vibration band $W\text{–}\mu_2\text{–}Ob$ is split into two peaks), at 1090, 958, 910 and 777 cm^{-1}, respectively. In comparison with the IR spectrum of precursor $\alpha\text{-}H_2P_2W_{18}O_{62} \cdot nH_2O$ [18], the $\upsilon_{as}(W\text{–}\mu\text{–}Ot)$ and $\upsilon_{as}(W\text{–}\mu_2\text{–}Ob)$ red shift 3 cm^{-1}; the possible reason is that Ca^{2+} has stronger interactions to the oxygens of the polyanions, consistent with the X-ray analysis.

4. Conclusion

In **1**, there are two kinds of calcium cations which are linked by Ca–O–Ca bridges to strengthen the 3D framework structure. Compound **1** is a new Wells-Dawson anion and alkaline-earth metal cations complex.

Supplementary material

CSD-419014 contains the supplementary crystallographic data for this article. The data can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Email: Crysdata@fiz-karlstruhe.de).

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