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A Tetranuclear Rhomblike Cluster of Manganese(II). Crystal Structure and Magnetic Properties of the Heteropoly Complex $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$

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Introduction

One of the abilities of the polyoxometalate complexes is that of encapsulating magnetic clusters of transition metal ions between diamagnetic fragments of metal oxides.[1] We are interested in the compounds obtained by reaction of divalent metal ions with the trivacant tungstophosphate ligands B-$\alpha\{PW_9O_{34}\}^{9-}$ and $\{P_2W_{15}O_{56}\}^{12-}$ derived from the well-known Keggin and Dawson–Wells polyoxoanions.[2] Up to now, the Co(II), Cu(II), and Zn(II) derivatives are known.[3] Their individual polyoxometalate entities encapsulate a tetrametallic unit M_4O_{16}. These compounds are of current interest in magnetochemistry as model systems for the study of the exchange interactions since the two heteropoly fragments guarantee an effective isolation of the magnetic cluster, imposing at the same time a rhomblike geometry for which situations of orbital orthogonality or spin frustration are favored.[4] As a result, clusters with ferromagnetic or intermediate ground spin states are obtained. Indeed, ferromagnetic exchange interactions have been found in the Co^{II} derivatives, while the Cu^{II} derivatives have an $S = 1$ ground state resulting from spin frustration.[5] We have also found that the $Cu^{II}/PW_9O_{34}{}^{9-}$ system is less stable, giving rise (at $T \geq 60$ °C) to a Keggin-substituted heteropolyanion formulated as $[PW_{10}Cu_2(H_2O)_2O_{38}]^{7-}$ which contains pairs of CuO_6 octahedra sharing edges or vertexes.[6]

With the aim of extending this series to other magnetically interesting ions, we have attempted to prepare the Ni^{II} and Mn^{II} complexes of the Keggin derivative. In the former case, an unexpected polyoxotungstate containing a triangular Ni cluster with ferromagnetic exchange interactions has been obtained.[7] For the manganese member, the usual polyoxoanion structure has been found. We report here the synthesis, crystal structure, and magnetic properties of this complex.

Table I. Crystal Data and Data Collection and Refinement Parameters for $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (**1**)

Crystal Data	
empirical formula (fw)	$Mn_4P_2W_{18}O_{90}H_{44}K_{10}$ (5466)
space group (No.)	$P2_1/n$ (14)
a, Å	15.866(7)
b, Å	21.404(3)
c, Å	12.360(5)
β, deg	92.13(2)
V, Å^3	4195(3)
Z	2
density (calcd), g/mL	4.33
crystal shape and color	prismatic, light amber
dimens, mm^3	0.2 × 0.4 × 0.5
Data Collection	
temp, °C	22
radiation	graphite monochromated
λ (Mo Kα), Å	0.710 73
linear abs coeff, cm^{-1}	263
scan type	$\theta/2\theta$
scan range, deg	$2.0 < 2\theta < 55.0$
data collected	$\pm h,+k,+l$
tot. no. of data	9913
no. of unique data with $I > 3\sigma(I)$	7292
data corrections	Lorentz, polarization, absorption
Final Refinement	
p ($w = 4F^2/\sigma(I)^1 + (pF^2)^2$)	0.07
no. of refined params	334
R^a	0.058
$R_w{}^b$	0.073

^{a} $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Experimental Section

Synthesis. Compound **1** was synthesized by a modification of the method reported by Finke et al.[3e] for the Co^{II} and Zn^{II} derivatives of the series $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. A 2-g sample of $Na_8HPW_9O_{34}\cdot 19H_2O$ (dried at 140 °C during 1 h) was slowly added to a solution containing 0.2366 g of $MnSO_4\cdot H_2O$ in 15 mL of H_2O. This orange solution was gently heated, and any insoluble material was removed by warm filtration through paper. Excess solid KCl (5 g) was added to the orange solution resulting in the immediate precipitation of an orange solid, which was collected in a sintered-glass frit and redissolved in H_2O. After several recrystallizations, an orange crytalline powder was obtained (0.1064 g), redissolved in 20 mL of H_2O, and allowed to crystallize in a closed beaker. Three months later, amber prismatic single crystals of compound **1** were collected and air-dried. The IR spectrum of **1** closely resembles those exhibited by the Co^{II} and Zn^{II} derivatives of the series.[3e] Anal. Calcd for $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$: K, 7.1; W, 60.5; Mn, 4.0. Found: K, 7.0; W, 60.0; Mn, 3.9.

X-ray Crystallography. A pale amber crystal having approximate dimensions of 0.2 × 0.4 × 0.5 mm^3 was mounted on an Enraf-Nonius CAD4 computer-controlled diffractometer. Preliminary examination and data collection were performed with Mo Kα radiation equipped and a graphite-crystal incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $11° < 2\theta < 25°$. During data collection three standard reflections were measured every 100 reflections and showed no significant decay (total 1.3%). Lorentz and polarization corrections were applied to the intensity data. Later an empirical absorption correction[8] was also applied. Other important features of data collection and refinements are summarized in Table I. From the systematic absences of $h0l$ with $h + l = 2n$ and $0k0$ with $k =$

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Table II. Positional Parameters for $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (**1**)

atom	*x*	*y*	*z*	B^a Å^2
W1	0.30880(4)	0.35348(3)	0.26653(6)	0.58(1)
W2	0.70529(4)	0.23981(3)	0.97879(6)	0.55(1)
W3	0.35348(4)	0.38858(3)	0.55761(6)	0.59(1)
W4	0.11191(4)	0.33845(3)	0.15355(6)	0.62(1)
W5	0.25405(4)	0.00715(3)	0.22708(6)	0.73(1)
W6	0.00877(4)	0.29558(3)	0.36161(6)	0.63(1)
W7	0.70766(4)	0.45725(3)	0.49001(6)	0.71(1)
W8	0.05158(4)	0.32812(3)	0.63036(6)	0.47(1)
W9	0.69789(4)	0.04261(3)	0.20655(6)	0.54(1)
Mn1	0.4316(2)	0.0597(1)	0.9642(2)	0.72(5)
Mn2	0.4755(2)	0.0248(1)	0.2194(2)	0.78(5)
K1	0.2137(5)	0.0776(3)	0.5869(6)	4.2(1)
K2	0.0541(4)	0.1229(3)	0.2889(7)	4.5(2)
K3	0.3476(4)	0.1725(3)	0.3021(6)	4.4(1)
K4	0.0265(3)	0.1825(3)	0.8751(5)	3.1(1)
K5	0.7712(3)	0.2140(2)	0.2762(4)	2.06(9)
P	0.6431(3)	0.0757(2)	0.9313(4)	0.43(7)
O1	0.8908(8)	0.1870(6)	0.714(1)	1.2(2)*
O2	0.2514(9)	0.1889(6)	0.493(1)	1.5(2)*
O3	0.9507(8)	0.1385(6)	0.100(1)	1.3(2)*
O4	0.5792(8)	0.1391(6)	0.526(1)	1.3(2)*
O5	0.2031(9)	0.0601(7)	0.360(1)	1.7(2)*
O6	0.9444(8)	0.2393(6)	0.306(1)	0.9(2)*
O7	0.1407(9)	0.1054(7)	0.975(1)	1.8(3)*
O8	0.5104(8)	0.2051(6)	0.242(1)	1.2(2)*
O9	0.7046(8)	0.0330(6)	0.345(1)	1.1(2)*
O10	0.7858(8)	0.1857(6)	0.053(1)	0.9(2)*
O11	0.7534(8)	0.2096(6)	0.850(1)	0.9(2)*
O12	0.8568(7)	0.1214(5)	0.903(1)	0.7(2)*
O13	0.6400(8)	0.1221(6)	0.196(1)	0.8(2)*
O14	0.5726(8)	0.1728(6)	0.742(1)	0.8(2)*
O15	0.1985(8)	0.0228(6)	0.137(1)	0.8(2)*
O16	0.7229(8)	0.1584(6)	0.660(1)	1.2(2)*
O17	0.8279(8)	0.0659(6)	0.718(1)	0.9(2)*
O18	0.1055(8)	0.2398(6)	0.399(1)	1.3(2)*
O19	0.8729(8)	0.0257(6)	0.040(1)	1.1(2)*
O20	0.6417(7)	0.2333(6)	0.103(1)	0.7(2)*
O21	0.8017(7)	0.0927(6)	0.187(1)	0.7(2)*
O22	0.6847(8)	0.0438(6)	0.616(1)	0.8(2)*
O23	0.4914(8)	0.2166(6)	0.016(1)	0.8(2)*
O24	0.2333(7)	0.0249(6)	0.839(1)	0.8(2)*
O25	0.6819(7)	0.0800(6)	0.821(1)	0.7(2)*
O26	0.6147(7)	0.1423(5)	0.961(1)	0.6(2)*
O27	0.7137(7)	0.0561(5)	0.014(1)	0.5(2)*
O28	0.5695(7)	0.0296(5)	0.9292(9)	0.4(2)*
O29	0.5307(7)	0.0591(5)	0.688(1)	0.5(2)*
O30	0.3475(8)	0.0470(6)	0.242(1)	0.8(2)*
O31	0.4427(8)	0.1356(6)	0.865(1)	1.2(2)*
O32	0.3112(8)	0.0763(6)	0.007(1)	1.3(2)*
O33	0.4848(7)	0.1024(5)	0.1069(9)	0.4(2)*
O34	0.4009(8)	−0.0031(6)	0.834(1)	1.0(2)*
O35	0.499(1)	0.0758(8)	0.368(1)	2.4(3)*
O36	0.395(1)	0.0538(8)	0.528(1)	2.8(3)*
O37	0.806(1)	0.1320(9)	0.458(2)	3.6(4)*
O38	0.086(3)	0.134(2)	0.686(3)	11(1)*
O39	0.989(2)	0.147(1)	0.505(3)	8.0(8)*
O40	0.663(1)	0.2457(9)	0.442(2)	3.3(4)*
O41	0.170(1)	0.190(1)	0.190(2)	4.4(4)*
O42	0.441(1)	0.2251(9)	0.490(2)	3.4(4)*
O43	0.280(1)	0.156(1)	0.761(2)	3.9(4)*
O44	0.986(2)	0.011(1)	0.821(2)	6.8(7)*
O45	0.311(1)	0.207(1)	0.050(2)	4.6(5)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected M–M Distances and M–O–M Angles within the M_4O_{16} Tetrameric Clusters of the Series $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ [a]

compd	M–M, ÅÅ	M–O–M, deg	ref
M = Co X = P	1–2 = 2*–1 = 3.192 2–1* = 1*–2* = 3.164 1–1* = 3.305	1*–33–2* = 1–33–2 = 100.5 1–28–2 = 1*–28–2* = 93.7 1*–28–2 = 1–28–2* = 92.6 1–28–1* = 1*–28–1 = 97.0 1–34–2* = 1*–34–2 = 102.6	3d
M = Zn X = As	1–2 = 2*–1 = 3.248 2–1* = 1*–2* = 3.243 1–1* = 3.455	1*–33–2* = 1–33–2 = 99.6 1–28–2 = 1*–28–2* = 96.5 1*–28–2 = 1–28–2* = 94.8 1–28–1* = 1*–28–1 = 103.5 1–34–2* = 1*–34–2 = 101.2	3d
M = Cu X = P	1–2 = 2*–1 = 3.263 2–1* = 1*–2* = 3.426 1–1* = 3.087	1*–33–2* = 1–33–2 = 97.8 1–28–2 = 1*–28–2* = 89.3 1*–28–2 = 1–28–2* = 89.5 1–28–1* = 1*–28–1 = 97.5 1–34–2* = 1*–34–2 = 98.1	3f
M = Mn X = P	1–2 = 2*–1 = 3.294 2–1* = 1*–2* = 3.290 1–1* = 3.447	1*–33–2* = 1–33–2 = 99.6 1–28–2 = 1*–28–2* = 91.4 1*–28–2 = 1–28–2* = 91.6 1–28–1* = 1*–28–1 = 95.5 1–34–2* = 1*–34–2 = 100.6	this work

[a] The numbering scheme corresponds to that of Figure 1b.

$2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14).[9] All calculations were performed on a VAX computer using MolEN.[10] Scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_c;[12] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[13] The structure was solved by direct methods using MULTAN[14] (which showed tungsten and phosphorus atoms) and was developed with successive full-matrix least-squares refinements and difference Fourier syntheses, which showed all the remaining atoms. Only the 7292 reflections with $I > 3\sigma(I)$ were used in the refinements. The standard deviation of an observation of unit weight was 1.63. The difference Fourier was flat and featureless (the highest peak had a height of 3.78 e/Å^3, and the map was continuous at ca. 3.1 e/Å^3). Plots of $\sum w(|F_o| - |F_c|)$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. Atomic parameters and selected bond distances and angles are given in Tables II and III, respectively.

Spectral and Magnetic Measurements. IR spectra were recorded on a Perkin-Elmer 882 IR spectrophotometer. The magnetic measurements were carried out with a magnetometer (905 VTS, SHE Corp.) equipped with a SQUID sensor. The temperature range was 2–300 K and the magnetic field 0.1 T.

Results and Discussion

Crystal Structure of $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (1). The $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion has the general structure of the series $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (M = Co, Cu, Zn): two B-α $\{PW_9O_{34}\}^{9-}$ units (formal fragments of a Keggin anion) are "sandwiching" a centrosymmetric tetrametallic unit M_4O_{16} formed by four MO_6 octahedra sharing edges (Figure 1). The anion has a charge of −10, since two water molecules (O35) are coordinated to two M atoms and the rest of the oxygens correspond to oxide ions. In the present compound, all counterions are potassium ions (in five crystallographically independent sites). Potassiums are coordinated by oxygen atoms belonging to heteropolyanions plus several lattice water molecules (corresponding to O36 to O45). In fact, all potassium ions bridge different heteropolyanions. We have chosen a labeling scheme analogous to that used by Evans et al. for cobalt and zinc derivatives[3d] to facilitate structural comparisons. Indeed, the

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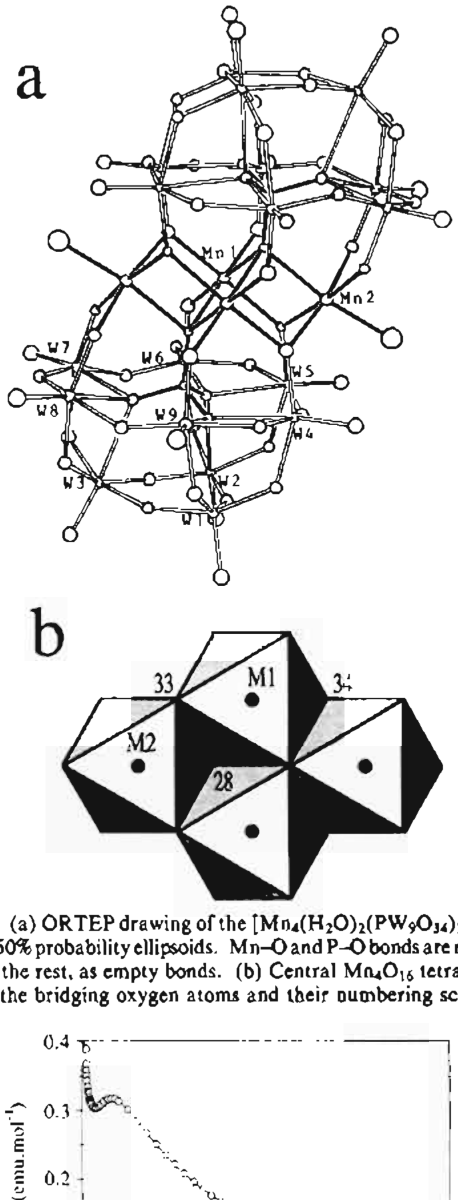


Figure 1. (a) ORTEP drawing of the $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion, showing 50% probability ellipsoids. Mn–O and P–O bonds are represented as filled; the rest, as empty bonds. (b) Central Mn_4O_{16} tetrameric unit showing the bridging oxygen atoms and their numbering scheme.

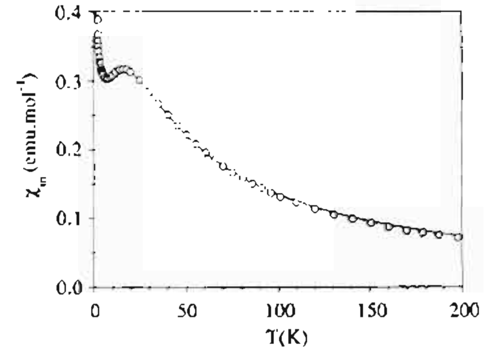


Figure 2. Plot of the molar susceptibility (χ_m) versus T for compound **1**. The solid line represents the best fit to eq 2.

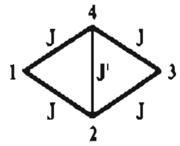
structure of the title heteropolyanion is very similar to that of the analogous Co compound. As should be expected, the largest differences correspond to the M_4O_{16} unit (M = Co, Mn) (see Table III). The only additional significant difference is found for several of the W=O terminal bonds: in our case, all nine values are closer to their average value of 1.72(2) Å, whereas for the Co compound there are a series of terminal W=O bonds shorter than usual and consequently an average value affected by a larger standard deviation (1.69(5) Å).[3d]

Magnetic Properties. As can be seen in Figure 2, the magnetic susceptibility shows a rounded maximum at $T \approx 16$ K, which agrees with the presence of antiferromagnetic exchange interactions in the tetranuclear manganese cluster, followed by a minimum at $T \approx 7$ K and a divergence at lower temperatures, indicative of the presence of a small amount of paramagnetic impurities of monomeric Mn^{II}.

The magnetic exchange interactions in this complex can be described by the isotropic Heisenberg Hamiltonian

$$H = -2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1) - 2J'S_2S_4 \quad (1)$$

where J and J' refer to the magnetic exchange interactions of the sides and shortest diagonal of the rhomb according to the numbering scheme



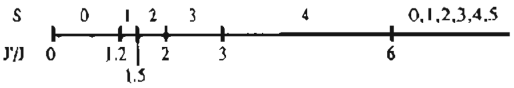
The magnetic data of the title compound have been fitted to the following equation, where the first term refers to the susceptibility of the cluster and the second one to that of a paramagnetic Mn^{II} contribution:

$$\chi = (1 - C)\chi_{cluster} + C[(N_A g^2\mu_B^2/3k_B)S(S+1)] \quad (2)$$

In this expression N_A, μ_B, and k_B have their usual meanings, $(1 - C)$ and C are the molar fractions of Mn_4 clusters and $S = {}^5/_2$ monomeric impurities, respectively, and $\chi_{cluster}$ is the susceptibility for a tetranuclear $S = {}^5/_2$ spin cluster which can be derived from the Kambé method.[15]

A very satisfying description of the magnetic data over the whole temperature range (solid line in Figure 2) has been obtained from the following set of parameters: $g = 2.0$, $J = -1.7$ cm^{-1}, $J' = 0.3$ cm^{-1}, and $C = 0.019$, that is 1.9% of the paramagnetic Mn^{II} impurity. From these parameters a cluster energy diagram with a nonmagnetic $S = 0$ ground state separated from the first excited state ($S = 1$) by an energy of ca. 3.4 cm^{-1} is obtained.

Since the two types of exchange interactions found in the Mn_4 cluster are antiferromagnetic, this cluster should experience spin frustration as a consequence of the interplay of the two different exchange interactions.[16] Thus, for this kind of system it can be seen that the spin multiplicity of the ground state (S) increases as the ratio J'/J is increased (see the following scheme):



Up to $J'/J \approx 1.2$ the antiferromagnetic $S = 0$ state is the ground state. In the present case, the J'/J value falls within this range ($J'/J = 0.18$), so that J' is not strong enough compared to J to give rise to an intermediate-spin ground state. This result contrasts with that obtained for the analogous Cu_4 cluster, which shows an intermediate-spin ground state $S = 1$, as a consequence of the larger J'/J value ($J'/J = 3.6$).[4b] Such a difference may be easily understood from the structural features of the M_4O_{16} entities (see Table III). Thus, the CuO_6 sites are axially distorted in such a way that the long axes of the four octahedra are parallel; as a result, the Cu–Cu distance along the diagonal of the rhomb is sensitively shorter than that along the sides (3.09 Å compared to ~3.25 Å).[3f] This geometry favors the overlap between the magnetic orbitals (of $d_{x^2-y^2}$ type) involved in the diagonal exchange interactions since these are pointing toward the oxo bridges. Conversely, for the Mn compound the sites are less distorted and the situation for the intermetallic distances is reversed. Then, the smaller value of J' compared to J may be related to the larger Mn–Mn distance for the diagonal of the rhomb. Finally, the weak antiferromagnetic exchange values displayed by this complex

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are a result of the Mn–O–Mn angles, which are in the range 90–100° (see Table III).

Several examples of tetranuclear manganese clusters have been reported in the last few years. These kinds of complexes are of current interest in bioinorganic chemistry since it is believed that such species catalyze water oxidation in photosystem II.[17] Their structural and physical properties have been recently reviewed.[18] Generally, these clusters contain a μ_2-oxo-bridged core which stabilizes the Mn(III) and Mn(IV) oxidation states. This is a consequence of the strong basicity of the oxide ligands.[19] Only three tetranuclear Mn(II) clusters have been reported previously. Two of them were obtained from a Schiff-base macrocycle containing a cubanelike Mn_4(alkoxy)$_4$ core, in one case,[20] and two neighboring dimeric pairs bridged by alkoxy groups, in the other.[21] The third example shows a cubanelike Mn_4(fluoride)$_4$ core.[22] To our knowledge the manganese complex reported in this work is the first example of an oxo-bridged manganese cluster either in oxidation state +II or in the planar rhomblike structure. From a magnetic point of view, the weak antiferromagnetic exchange parameters of our complex are comparable to those calculated for the fluoro-bridged Mn^{II} complex (of about -1 cm^{-1}), in agreement with the similar near 90° superexchange paths (the Mn–F–Mn bond angles are about 100°).

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Supplementary Material Available: For $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (1), tables of general displacement parameter expressions (*U*'s) and complete bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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