simple linear correlation with cone angle θ. Furthermore, these results provide strong support for the fundamental tenets of the QALE model: separation of energy of activation into electronic and steric components and the existence of steric thresholds in the ground and transition states. Because of the existence of different steric thresholds, it is very clear that there is no reason to expect a linear dependence of log k on the size of phosphorus(III) ligands except under very special circumstances.

Contribution from the Department of Chemistry
Education and Department of Chemistry,
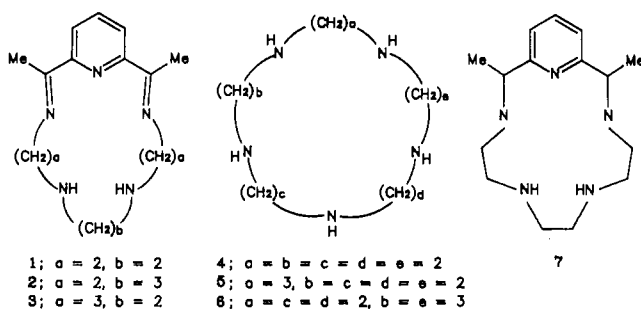Seoul National University, Seoul 151, Korea

Synthesis, Characterization, and X-ray Structure of the Octahedral Nickel(II) Complex of a Pentadentate Hexaaza Macrobicyclic Ligand: Chloro(9-(methoxymethyl)-1,4,6,9,11,14-hexaazabicyclo-[12.2.1]heptadecane)nickel(II) Perchlorate

Myunghyun Paik Suh,* Jungwon Choi, Shin-Geol Kang, and Whanchul Shin

There are several pentadentate macrocyclic ligands and their complexes reported thus far.[1–15] The pentaaza macrocycles (L) containing a pyridine ring (**1–3**) were reported to form pentag-

1; a = 2, b = 2   4; a = b = c = d = e = 2   7
2; a = 2, b = 3   5; a = 3, b = c = d = e = 2
3; a = 3, b = 2   6; a = c = d = 2, b = e = 3

onal-bipyramidal complexes [MLX₂]ⁿ⁺ with Fe(III), Fe(II), or Mn(II) ions, where X stands for a monodentate ligand such as H_2O or NCS^-.[1–9] The Ni(II) complexes with pentaaza macrocyclic ligands **4–7** were reported to form distorted octahedral [NiLX]ⁿ⁺ (X = Cl⁻ or H_2O, n = 1 or 2).[4,15] In this paper, we report a new Ni(II) complex with the hexaaza macrobicyclic ligand $C_{13}H_{30}N_6O$ that serves as a pentadentate ligand. The complex [Ni($C_{13}H_{30}N_6O$)Cl]ClO₄ was synthesized by the simple template condensation reaction of polyamines with formaldehyde. The complex that has a distorted octahedral structure, contains a rarely observed four-membered chelate ring.

Experimental Section

Reagents. All chemicals and solvents used in the syntheses were of reagent grade and were used without purification. For the conductance and spectroscopic measurements, solvents were purified according to the literature method.[16]

Measurements. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau E518 conductometer and RC-216B₂ conductivity bridge. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. Magnetic susceptibility

Table I. Crystallographic Data for [Ni($C_{13}H_{30}N_6O$)Cl]ClO₄

$NiC_{13}H_{30}N_6O_5Cl_2$	space group $C2/c$ (No. 15)
fw = 480.02	T = 18 °C
a = 29.885 (13) Å	λ = 0.7107 Å
b = 9.838 (3) Å	ρ_{obsd} = 1.580 g cm⁻³
c = 15.193 (5) Å	ρ_{calcd} = 1.592 g cm⁻³
β = 109.89 (3)°	μ = 12.25 cm⁻¹
V = 4006 (3) Å³	$R(F_o)$ = 0.049
Z = 8	$R_w(F_o)$ = 0.053

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\text{Å}^2 \times 10^3$) of Non-Hydrogen Atoms for [Ni($C_{13}H_{30}N_6O$)Cl]ClO₄

atom	x	y	z	$U_{eq}{}^a$
Ni	3916.6 (0.2)	5891.7 (0.7)	3943.1 (0.4)	30
Cl	4578.8 (0.4)	4820 (2)	3643 (1)	46
N(1)	3594 (1)	4030 (5)	4250 (3)	38
C(2)	3925 (2)	2813 (7)	4584 (5)	52
C(3)	4168 (2)	3079 (8)	5620 (5)	57
N(4)	3894 (2)	4224 (6)	5875 (3)	48
C(5)	4137 (2)	5555 (8)	6092 (4)	50
N(6)	4313 (1)	6164 (5)	5355 (3)	35
C(7)	4426 (2)	7668 (7)	5541 (4)	47
C(8)	4543 (2)	8333 (8)	4746 (5)	54
N(9)	4160 (2)	8065 (5)	3833 (3)	46
C(10)	3695 (2)	8672 (7)	3783 (6)	55
N(11)	3396 (2)	7478 (5)	3887 (3)	39
C(12)	2966 (2)	7263 (8)	3044 (5)	48
C(13)	3098 (2)	6622 (8)	2256 (4)	50
N(14)	3476 (2)	5536 (5)	2569 (3)	39
C(15)	3306 (2)	4054 (7)	2532 (4)	49
C(16)	3182 (2)	3713 (8)	3398 (5)	49
C(17)	3445 (2)	4289 (7)	5084 (4)	43
C(18)	4320 (3)	8456 (10)	3072 (6)	80
O(19)	4400 (5)	10118 (12)	3297 (8)	70
O(19′)	4585 (4)	9522 (13)	2981 (10)	70
C(20)	4379 (5)	10761 (14)	2624 (11)	130
Cl(2)	3040 (1)	384 (2)	675 (1)	61
O(1)	2679 (3)	221 (12)	−145 (9)	269
O(2)	3404 (2)	−586 (7)	746 (6)	143
O(3)	3238 (2)	1764 (6)	684 (4)	101
O(4)	2922 (3)	209 (9)	1483 (6)	177

$^a U_{eq} = {}^1/_3(\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j)$.

was measured by the NMR method[17] on a Varian EM 360 60-MHz NMR spectrometer using a Wilmad 5-mm coaxial sample unit. For this measurement, Me₂SO and *t*-BuOH were used as the solvent and the reference material, respectively.· Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

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Synthesis. *Caution!* The compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

[Ni(C₁₃H₃₀N₆O)Cl]ClO₄. To a stirred methanol solution (50 mL) of NiCl₂·6H₂O (0.05 mol) were added slowly triethylenetetramine (2,2,2-tet) (0.05 mol), ethylenediamine (0.025 mol), and 36% aqueous formaldehyde solution (0.1 mol). The mixture was heated at reflux for 24 h. The solution was filtered hot to remove insoluble material and then cooled to room temperature. Excess lithium perchlorate dissolved in methanol was added to the filtrate, and then the solution was kept in the refrigerator until violet crystals formed. The crystals were filtered, washed with methanol, and air-dried. The crystals for the X-ray studies were obtained by dissolving the crystals in warm (50–60 °C) water and then allowing the solution to stand at room temperature for 2 days; yield ~50%. Anal. Calcd for NiC₁₃H₃₀N₆Cl₂O₅: C, 32.53; H, 6.30; N, 17.51. Found: C, 31.62; H, 6.26; N, 17.57.

X-ray Study. Crystallographic data are summarized in Table I and details of the crystal parameters along with data collection are deposited in Table SI. Experimental procedures are the same as described previously.[18] The structure was solved by Patterson and Fourier methods. The non-hydrogen atoms were refined anisotropically and only the positional parameters of the hydrogen atoms were refined with the isotropic thermal parameters fixed with the values of 1.3 times those of the bonded atoms. The methoxy group was clearly disordered (54%:46%) and the current model accounted for the experimental data most satisfactorily. The refinement converged at $R = 0.049$ for 2289 observed reflections. The weighted R was 0.053. The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement. w, the weight of the reflection, was defined by $k/(\sigma^2(F_o) + gF_o^2)$, where $\sigma(F_o)$ was from counting statistics and k and g were optimized in the least-squares procedure ($k = 0.868$ and $g = 0.0026$). The largest parameter shift in the final refinement cycle was 0.220 esd for the y coordinate of H(20A). The largest difference peaks of 0.56, 0.53, and 0.51 e Å⁻³ appeared at the centers of the Ni–N(6), Ni–N(9), and Ni–N(1) bonds, respectively. The next highest difference peak (0.48 e Å⁻³) was located in the vicinity of the perchlorate ion. All of the calculations were done by using the program SHELX 76[19] on a VAX 11/780 computer. Atomic scattering factors and the terms of the anomalous-dispersion correction were from ref 20 as incorporated in SHELX 76. The final atomic parameters are listed in Table II. Structure factors are available as supplementary material.

Results and Discussion

The template condensation reaction of 2,2,2-tet, en, and CH₂O in the presence of NiCl₂·6H₂O with a mole ratio of 1:0.5:2:1 in methanol solutions produced the six-coordinate [Ni-(C₁₃H₃₀N₆O)Cl]⁺ cation.[21] The violet perchlorate complex is very stable in the solid state. The complex is soluble in water and Me₂SO to give purple solutions, but insoluble in CH₃CN, CH₃-NO₂, alcohols, and nonpolar solvents. The complex is moderately stable against decomposition in dilute acid solutions. In 1 M HNO₃ solutions, the first-order rate constant for the decomposition is $k_{obs} = 7 \times 10^{-3}$ s⁻¹ at 25 °C. The products for the decomposition are [Ni(H₂O)₆]²⁺ and NO₃⁻ salt of the protonated free ligand. The IR spectra of the complex shows the N–H stretches for the coordinated secondary amines at 3186 and 3290 cm⁻¹. The values of molar conductance of the complex are $\Lambda_M = 45$ Ω⁻¹ cm⁻¹ M⁻¹ in Me₂SO solutions and 245 Ω⁻¹ cm⁻¹ M⁻¹ in aqueous solutions at 20 °C, indicating that the complex behaves as 1:1 and 1:2 electrolytes in the respective solvents. This means that the Cl⁻ ligand of the complex is stable in Me₂SO solutions against dissociation but is labile in aqueous solutions. It has been known that the axial ligands such as halides or NCS⁻ in the six-coordinate Ni(II) complexes of tetradentate macrocyclic ligands are very labile in donating solvents to give square-planar complexes.[18,22] The electronic spectra of the complex show λ_{max} at 554 nm (ϵ =
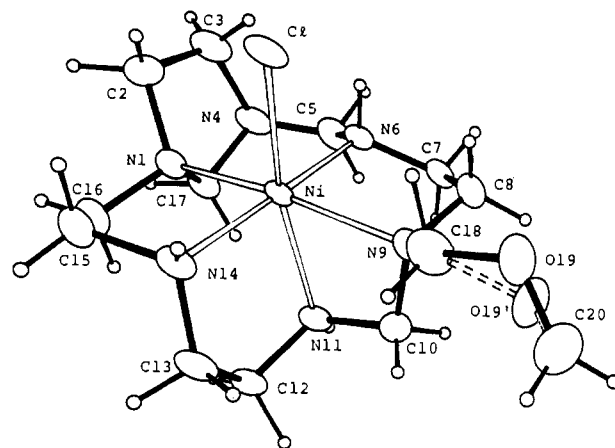
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(21) Without knowing the reason, when 1.0 equiv of en and 4 equiv of CH₂O were employed instead of 0.5 and 2 equiv, respectively, a yellow square-planar complex[25] was produced instead of the title complex. The spectroscopic and preliminary X-ray studies indicated that the complex was a Ni(II) complex of 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1⁸,¹¹]octadecane.
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Figure 1. ORTEP view of the cation for [Ni(C₁₃H₃₀N₆O)Cl]ClO₄ with the atomic numbering scheme.

Scheme I
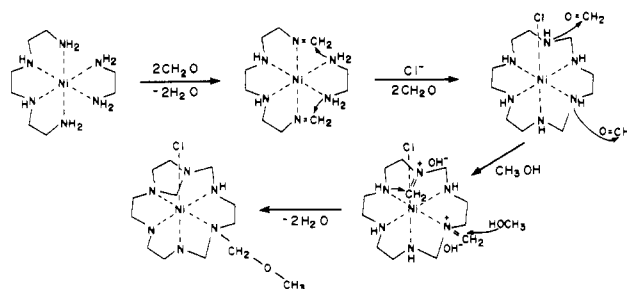
Table III. Selected Bond Lengths (Å) and Angles (deg) for [Ni(C₁₃H₃₀N₆O)Cl]ClO₄

(a) Bond Lengths			
Ni–Cl	2.398 (1)	Ni–N(1)	2.122 (4)
Ni–N(6)	2.084 (4)	Ni–N(9)	2.190 (5)
Ni–N(11)	2.134 (5)	Ni–N(14)	2.082 (5)
N(1)–C(2)	1.482 (7)	N(1)–C(16)	1.482 (7)
N(1)–C(17)	1.498 (7)	C(2)–C(3)	1.513 (10)
C(3)–N(4)	1.482 (9)	N(4)–C(5)	1.426 (9)
N(4)–C(17)	1.466 (8)	C(5)–N(6)	1.502 (7)
N(6)–C(7)	1.456 (8)	C(7)–C(8)	1.503 (9)
C(8)–N(9)	1.489 (8)	N(9)–C(10)	1.480 (8)
N(9)–C(18)	1.442 (10)	C(10)–N(11)	1.475 (8)
N(11)–C(12)	1.487 (8)	C(12)–C(13)	1.507 (9)
C(13)–N(14)	1.474 (8)	N(14)–C(15)	1.475 (8)
C(15)–C(16)	1.517 (9)	C(18)–O(19)	1.597 (15)
O(19)–C(20)	1.170 (19)		

(b) Bond Angles			
N(1)–Ni–Cl	99.4 (1)	N(6)–Ni–Cl	91.7 (1)
N(9)–Ni–Cl	93.4 (1)	N(11)–Ni–Cl	157.3 (1)
N(14)–Ni–Cl	91.4 (2)	N(6)–Ni–N(1)	91.0 (2)
N(9)–Ni–N(1)	166.1 (2)	N(11)–Ni–N(1)	101.7 (2)
N(14)–Ni–N(1)	84.7 (2)	N(9)–Ni–N(6)	82.9 (2)
N(11)–Ni–N(9)	66.7 (2)	N(11)–Ni–N(6)	96.1 (2)
N(14)–Ni–N(6)	175.0 (2)	N(14)–Ni–N(9)	100.7 (2)
N(11)–Ni–N(14)	82.4 (2)	C(2)–N(1)–Ni	114.2 (3)
C(16)–N(1)–Ni	106.2 (4)	C(17)–N(1)–Ni	109.9 (4)
C(5)–N(6)–Ni	120.0 (3)	C(7)–N(6)–Ni	109.4 (3)
C(8)–N(9)–Ni	104.9 (4)	C(10)–N(9)–Ni	91.8 (4)
C(18)–N(9)–Ni	120.5 (5)	C(10)–N(11)–Ni	94.2 (4)
C(12)–N(11)–Ni	110.1 (4)	C(13)–N(14)–Ni	111.6 (3)
C(15)–N(14)–Ni	106.4 (3)	N(11)–C(10)–N(9)	107.1 (5)

14.8) and 363 nm ($\epsilon = 22.6$) in Me₂SO solutions and at 534 nm ($\epsilon = 7.6$) and 350 nm ($\epsilon = 12.7$) in aqueous solutions, which are normally observed for the Ni(II) macrocyclic complexes with tetragonally distorted octahedral structures.[15,23,24] The magnetic susceptibility of the complex measured by the NMR method gives

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magnetic moments of 3.12 μ_B at 26 °C in Me$_2$SO solutions and 3.06 μ_B at 21 °C in aqueous solutions, which is attributed to the d^8 electronic configuration in octahedral geometry. A possible route for the formation of the complex is proposed in Scheme I. The formation of the macrocyclic ligand containing 1,3-diazacyclopentane ring moieties from a reaction similar to this has been already reported by our laboratory.[25,26]

An ORTEP[27] view of the complex with the atomic numbering scheme is presented in Figure 1. The bond lengths and angles are listed in Table III. The title complex has a distorted octahedral geometry. The hexaaza macrobicyclic ligand serves as a pentadentate ligand by coordinating to the Ni(II) ion with two tertiary [N(1) and N(9)] and three secondary [N(6), N(11), and N(14)] nitrogens. N(4) is clearly uncoordinated to Ni(II) at a distance of 3.349 (5) Å from the metal ion. The bond angles at N(4) indicate that the lone pair of the nitrogen atom is directed away from the Ni(II) ion. The 1,3-diazacyclopentane ring of the ligand assumes an envelope conformation with an N(1)–C(2)–C(3)–N(4) torsion angle of 12.8 (5)°. These four atoms form a plane [maximum deviation 0.090 (6) Å] that is nearly perpendicular to the coordination plane with a dihedral angle of 114°. The Cl$^-$ ligand is located at the axial position toward the same direction as the ethylene portion of the 1,3-diazacyclopentane ring moiety in the macrocyclic ligand. The complex contains a rarely observed four-membered chelate ring. There are three five-membered chelate rings and one six-membered chelate ring in the complex also. The four-membered chelate ring shows a good planarity with a maximum deviation of 0.035 (9) Å. The bite distance and bite angle are 2.377 (8) Å and 66.7 (2)°, respectively. Each five-membered chelate ring assumes a half-chair conformation with the N–C–C–N torsion angles in the en moiety ranging from 38.8 (5) to 54.5 (5)°. The six-membered chelate ring assumes a near-chair conformation with the intracyclic torsion angles ranging from 24.9 (4) to 87.8 (5)°, and consequently, the seven-membered ring assumes a boat conformation.

The complex is very much distorted from the regular octahedral geometry. The bond lengths involving the Ni(II) ion are not equal, and the bond angles also vary widely, ranging from 66.7 (2) to 101.7 (2)°. The Cl–Ni–N(11) angle deviates from linearity by 22.7°. This severe distortion seems to be caused by the presence of the strained four-membered chelate ring and by the close contact between the ethylene portion of the 1,3-diazacyclopentane ring moiety and the Cl$^-$ ligand. The Cl···C(2) separation of 3.363 (7) Å in this complex is much shorter than the van der Waals contact of 3.50 Å. The coordination plane is distorted such that N(1), N(6), N(9), and N(14) deviate from their best plane by −0.079 (3), 0.079 (3), −0.108 (5), and 0.107 (5) Å, respectively. The Ni(II) ion is out of the plane by 0.146 (1) Å toward the direction of the Cl$^-$ ligand. The average Ni–N bond length is 2.12 ± 0.04 Å. The Ni–N bonds in the four-membered ring are lengthened by up to 0.106 Å compared to the others, presumably to relieve the strain of the ring.

This study presents the first example of a hexaaza macrocycle that serves as a pentadentate ligand.

Registry No. [Ni(C$_{13}$H$_{30}$N$_6$O)Cl]ClO$_4$, 119769-51-6; triethylenetetramine, 112-24-3; ethylenediamine, 107-15-3; formaldehyde, 50-00-0; methanol, 67-56-1.

Supplementary Material Available: Tables SI–SV, listing a summary of crystal data and data collection parameters, anisotropic thermal parameters, atomic coordinates of the hydrogen atoms, and complete bond lengths and angles involving non-hydrogen and hydrogen atoms (5 pages); tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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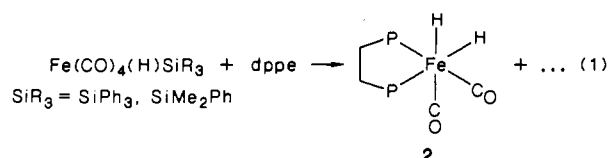(27) Johnson, C. "ORTEPII"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Transition-Metal Silyl Complexes. 29. Formation of Dihydride Complexes from Hydrido(silyl)tetracarbonyliron Derivatives

U. Schubert* and M. Knorr

In a series of papers we have recently shown that phosphine- or phosphite-substituted hydrido(silyl)iron derivatives can be prepared by several routes.[1–4] The choice of the most suitable method depends essentially on the nature of the silyl group and the phosphine. Our successful synthesis of Fe(CO)$_2$(dppe)(H)SiMeCl$_2$ by thermal CO/phosphine exchange starting from Fe(CO)$_4$(H)SiMeCl$_2$[2] seemingly was in line with the report of Bellachioma and Cardaci,[5] who claimed the synthesis of Fe(CO)$_2$(dppe)(H)SiPh$_3$ (**1**) by the same method (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$). However, when we repeated the latter reaction by the reported procedure, we only isolated the dihydride compound **2** in 40% yield (eq 1) and a small amount (10%) of

$$\text{Fe(CO)}_4\text{(H)SiR}_3 \;+\; \text{dppe} \longrightarrow \quad\quad\quad + \;\ldots \quad (1)$$
$$\text{SiR}_3 = \text{SiPh}_3,\; \text{SiMe}_2\text{Ph}$$

2

Fe(CO)$_3$(dppe). We did not find any evidence for **1**. Interestingly, the melting point and the spectroscopic data for **2** are very similar to those reported[5] for the alleged **1**.

The dihydride complex **2** is also obtained from Fe(CO)$_4$(H)SiMe$_2$Ph as a precursor (eq 1). Obviously, dppe-substituted derivatives Fe(CO)$_2$(dppe)(H)SiR$_3$ are only formed from the tetracarbonyl complexes if electron-withdrawing substituents at silicon provide strong Fe–Si bonds (as in the SiMeCl$_2$ derivative).

The real complex **1**, as well as Fe(CO)$_2$(dppe)(H)SiMe$_2$Ph, can be prepared by silane-exchange reaction from Fe(CO)$_2$(dppe)(H)SiMe$_3$ and HSiPh$_3$ or HSiMe$_2$Ph, respectively.[2] Spectroscopic data of the hydrido silyl complexes are included in Table I for comparison. They fit into the series of other complexes of the type Fe(CO)$_2$(dppe)(H)SiR$_3$.[2]

Since **1** is stable toward the conditions employed for reaction 1, it cannot be a precursor for **2**. If reaction 1 is followed ^{1}H NMR spectroscopically (at 20 °C), no intermediates can be observed. To check the possibility that the second hydride ligand of **2** originates from HSiPh$_3$, which might be formed by decomposition of Fe(CO)$_4$(H)SiPh$_3$, we reacted a 1:1:1 mixture of Fe(CO)$_4$(H)SiPh$_3$, dppe, and DSiPh$_3$. ^{1}H NMR spectroscopically, only **2** and no Fe(CO)$_2$(dppe)(H)D was observed. Although this experiment eliminates the possibility that HSiPh$_3$ is involved in reaction 1, we cannot rule out that the second hydride ligand in **2** is transferred from another metal moiety by another mechanism. The mechanism of this reaction and particularly the fate of the silyl ligand will be subject to further investigations. The dihydride complex **2** was independently synthesized by photochemical reaction of Fe(CO)$_3$(dppe) with H$_2$ (eq 2).

$$\text{Fe(CO)}_3\text{(dppe)} + \text{H}_2 \xrightarrow{h\nu} \textbf{2} + \text{CO} \qquad (2)$$
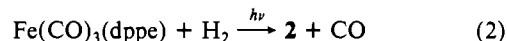
Complex **2** fills the gap between the known dihydride complexes Fe(CO)$_4$H$_2$[6] and Fe(dppe)$_2$H$_2$.[7] In **2**, one of the hydride ligands is trans to a CO ligand and the other hydride ligand is trans to

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