# 两个由异烟酰胺构筑的钴、镍配合物的合成及晶体结构

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摘要:采用溶液培养法,在室温下合成了 2 个新的过渡金属配合物[Co(inta)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Co(H<sub>2</sub>O)<sub>6</sub>](tdc)<sub>2</sub>·2H<sub>2</sub>O (1)和[Ni(inta)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](tdc) ·2H<sub>2</sub>O (2)(inta=异烟酰胺,H<sub>2</sub>tdc=2,5-噻吩二甲酸)。并对其进行了元素分析、红外光谱、紫外光谱、热重和 X-射线单晶衍射测定。这两个配合物通过氢键和  $\pi$ - $\pi$  相互作用形成了三维超分子网状结构。

关键词:晶体结构;钴配合物;镍配合物

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## Synthesis and Crystal Structure of Two Complexes of Cobalt, Nickel Assembled by Isonicotinamide

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**Abstract:** Two transitional metal complex  $[Co(inta)_2(H_2O)_4][Co(H_2O)_6](tdc)_2 \cdot 2H_2O$  (1) and  $[Ni(inta)_2(H_2O)_4](tdc) \cdot 2H_2O$  (2) (inta=isonicotinamide,  $H_2tdc=2,5$ -thiophenedicarboxylic acid) have been synthesized by employing the solution a preparation method at room temperature. They were structurally characterized by elemental analysis, IR spectrum, UV spectrum, TG and single-crystal X-ray diffraction. They are further extended into a three-dimensional supramolecular network structure through hydrogen bonds and  $\pi$ - $\pi$  interactions. CCDC: 862125, 1; 862126, 2.

Key words: crystal structure; cobalt complex; nickel complex

### 0 Introduction

The rational design and synthesis of metal-directed supramolecular frameworks have received much attention in coordination chemistry because of their interesting molecular topologies and tremendous potential applications in host-guest chemistry, catalysis, molecular selection, nonlinear optics, ion exchange and microelectronics<sup>[1-6]</sup>. In this field, the metals often have

different valences, making a number of building blocks to fulfill special needs. Many important properties of coordination polymers depend largely on their structures and topology. Therefore, the selection of special inorganic and organic building blocks is the key to the construction of a desired framework<sup>[7]</sup>. In this respect, the 2,5-thiophenedicarboxylic acid (H<sub>2</sub>tdc) ligand is proved to be a good candidate due to its various bridging abilities and strong coordination

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tendency with transition metals to form 2D and 3D moderately robust networks [8-9]. On the other hand, the introduction of bi- or multi-dentate ligands containing N- or O-donors to the metal-oxalate system may lead to new structural evolution since the binding of these ligands to metal centers may adjust the dimensionality of metal-organic coordination polymers [10-11]. Among the organic N-donors, isonicotinamide (inta) is an excellent rigid ligand for the construction of novel metal-organic coordination frameworks because of its three donor sites [12-13]. In this paper, we report two new compounds, [Co(inta)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Co(H<sub>2</sub>O)<sub>6</sub>](tdc)<sub>2</sub>·2H<sub>2</sub>O (1) and [Ni(inta)<sub>2</sub> (H<sub>2</sub>O)<sub>4</sub>](tdc)·2H<sub>2</sub>O (2), which exhibit 3D supramolecular framework through hydrogen bonds and  $\pi$ - $\pi$  stacking interactions and are reported scarcely.

### 1 Experimental

#### 1.1 General procedures

All materials were commercially purchased and used without further purification. Infrared spectra (KBr pellets) were taken on a Perkin-Elmer 2400LS II spectrometer and elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The TG studies were performed on a Perkin-Elmer TGA7 analyzer.

### 1.2 Synthesis

 $[\text{Co\,(inta)}_2(\text{H}_2\text{O})_4][\text{Co\,(H}_2\text{O})_6](\text{tdc})_2 \cdot 2\text{H}_2\text{O}$  (1). An aqueous solution of  $\text{Co\,Cl}_2 \cdot 6\text{H}_2\text{O}$  (0.2 mmol, 10 mL) was slowly dropped into an acetonitrile solution of isonicotinamide (0.2 mmol, 10 mL) under stirring. After stirring for 30 min, an aqueous solution of sodium tdc

(0.2 mmol, 10 mL) was added into the above solution, the precipitate was filtered and the filtrate was stood for 10 d, obtaining pink block crystals suitable for X-ray structural analysis. The elemental analyses found (%): C, 31.1; H, 4.2; N, 5.9. Calcd. for  $C_{24}H_{40}Co_2N_4O_{22}S_2$  (%): C, 31.4; H, 4.4; N, 6.1.

[Ni(inta)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](tdc) · 2H<sub>2</sub>O (**2**). An aqueous solution of Ni(OAc)<sub>2</sub> · 2H<sub>2</sub>O (0.2 mmol, 10 mL) was slowly dropped into an acetonitrile solution of isonicotinamide (0.2 mmol, 10 mL) under stirring. After stirring for 30 min, an aqueous solution of sodium tdc (0.2 mmol, 10 mL) was added into the above solution, the precipitate was filtered and the filtrate was stood for 10 d, obtaining blue block crystals suitable for X-ray structural analysis. The elemental analyses found (%): C, 39.2; H, 4.5; N, 10.0. Calcd. for  $C_{18}H_{26}N_4NiO_{12}(\%)$ : C, 39.4; H, 4.8; N, 10.2.

### 1.3 Structure determination

Single crystal diffraction data of 1 and 2 were respectively collected on a Bruker SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Mo  $K\alpha$  ( $\lambda$ =0.071 073 nm) radiation at room temperature. The structure was solved by direct methods with SHELXS-97 program<sup>[14]</sup> and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[15]</sup>. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The selected bond parameters are given in Table 1.

Crystal data for **1**:  $C_{24}H_{40}Co_2N_4O_{22}S$ , triclinic, space group  $P\bar{1}$ ,  $M_r$ =918.58, a=0.673 82(5) nm, b=

Table 1 Selected bond lengths (nm) and bond angles (°) complound for 1 and 2

1					
Co(1)-N(1)	0.216 94(16)	Co(1)-N(1A)	0.216 94(16)	Co(1)-O(1W)	0.211 33(16)
Co(1)- $O(1WA)$	0.211 33(16)	Co(1)-O(2W)	0.209 01(15)	Co(1)-O(2WA)	0.209 01(15)
Co(2)-O(3W)	0.208 27(14)	Co(2)-O(3WA)	0.208 27(14)	Co(2)-O(4W)	0.205 75(15)
Co(2)-O(4WB)	0.205 75(15)	Co(2)-O(5WB)	0.214 50(13)	Co(2)-O(5WB)	0.214 50(13)
O(2W)-Co(1)-O(2WA)	180.0	O(2WA)-Co(1)-O(1W)	86.90(7)	O(2W)-Co(1)-O(1WA)	86.90(7)
O(2W)- $Co(1)$ - $O(1W)$	93.10(7)	O(1W)- $Co(1)$ - $O(1WA)$	180.00(8)	O(2W)- $Co(1)$ - $N(1A)$	88.50(6)
$\mathrm{O}(1\mathrm{W})\text{-}\mathrm{Co}(1)\text{-}\mathrm{N}(1\mathrm{A})$	88.45(6)	O(2W)-Co(1)-N(1)	91.50(6)	O(2WA)-Co(1)-N(1)	88.50(6)
O(1W)- $Co(1)$ - $N(1)$	91.55(6)	O(1WA)-Co(1)-N(1)	88.45(6)	N(1A)-Co(1)-N(1)	180.0
O(4WB)-Co(2)-O(4W)	180.00(10)	O(4WB)-Co(2)-O(3W)	85.83(6)	O(4W)-Co(2)-O(3W)	94.17(6)

O(3W)-Co(2)-O(3WB)	180.00(9)	O(4W)-Co(2)-O(3WB)	85.83(6)	O(3W)-Co(2)-O(5WB)	86.78(6)
O(4WB)-Co(2)-O(5W)	86.78(6)	O(4W)-Co(2)-O(5W)	93.22(6)	O(3W)-Co(2)-O(5W)	90.75(5)
O(3W)-Co(2)-O(5WB)	89.25(5)	$\mathrm{O}(5\mathrm{W})\text{-}\mathrm{Co}(2)\text{-}\mathrm{O}(5\mathrm{WB})$	180.00(7)	O(3WB)-Co(2)-O(5W)	89.25(5)
		2			
Ni(1)-O(1W)	0.204 98(17)	Ni(1)-O(2W)	0.205 33(15)	Ni(1)-N(1)	0.211 91(19)
Ni(1)- $O(1WA)$	0.204 98(17)	Ni(1)-O(2WA)	0.205 33(15)	Ni(1)- $N(1A)$	0.211 91(19)
Ni(2)-O(3W)	0.205 31(15)	Ni(2)-O(4W)	0.205 83(19)	Ni(2)-N(3)	0.210 86(19)
Ni(2)-O(3WB)	0.205 31(15)	Ni(2)-O(4WB)	0.205 83(19)	Ni(2)-N(3B)	0.210 86(19)
O(1WA)-Ni(1)-O(1W)	180.0	O(1WA)-Ni(1)-O(2W)	89.41(6)	O(1W)-Ni(1)-O(2W)	90.59(6)
O(2W)-Ni(1)-O(2WA)	180.0	O(1WA)-Ni(1)-N(1)	90.81(6)	O(1W)-Ni(1)-N(1)	89.19(6)
O(2W)-Ni(1)-N(1)	92.19(6)	O(1W)-Ni(1)-N(1A)	90.81(6)	O(2WA)-Ni(1)-N(1)	87.81(6)
O(2W)-Ni(1)-N(1A)	87.81(6)	N(1)-Ni(1)-N(1A)	180.00(9)	O(3WB)-Ni(2)-O(3W)	180.0
O(3WB)-Ni(2)-O(4W)	88.97(6)	O(3W)-Ni(2)-O(4W)	91.03(6)	O(3W)-Ni(2)-O(4WB)	88.97(6)
O(4W)-Ni(2)-O(4WB)	180.0	O(3WB)-Ni(2)-N(3)	87.98(6)	O(3W)-Ni(2)-N(3)	92.02(6)
O(4W)-Ni(2)-N(3)	92.34(6)	O(3W)-Ni(2)-N(3B)	87.98(6)	O(4W)-Ni(2)-N(3B)	87.66(6)
N(3)-Ni(2)-N(3B)	180.000(1)				

Symmetry transformations used to generate the equivalent atoms: 1: A: -x, -y, 1-z; B: -x, -y, -z; 2: A: -x+1, -y, -z+1; B: -x+1, -y, -z+2.

0.699 53(6) nm, c =2.014 64(16) nm,  $\alpha$  =81.316 0(10)°,  $\beta$ =81.502 0(10)°,  $\gamma$ =75.904 0(10)°, V =0.904 34(13) nm³, Z=1, F(000)=474,  $\mu$ (Mo  $K\alpha$ )=1.126 mm $^{-1}$ ,  $D_c$ =1.687 g·cm $^{-3}$ , 4 991 reflections measured, 3 543 unique ( $R_{\rm int}$ =0.012 8), 3 284 observed reflections with I>2 $\sigma$ (I), R=0.029 8, wR=0.075 6, S=1.046.

Crystal data for **2**:  $C_{18}H_{26}N_4NiO_{12}S$ , triclinic, space group  $P\bar{1}$ ,  $M_r$ =581.2, a=0.9068(5) nm, b=0.9165(5) nm, c=1.5533(5) nm,  $\alpha$ =80.695(5)°,  $\beta$ =88.325(5)°,  $\gamma$ =73.535(5)°, V=1.2215(10) nm³, Z=2, F(000)=604,  $\mu$ (Mo  $K\alpha$ )=0.949 mm<sup>-1</sup>,  $D_c$ =1.580 g·cm<sup>-3</sup>, 6765 reflections measured, 4766 unique ( $R_{int}$ =0.0116), 4173 observed reflections with I>2 $\sigma$ (I), R=0.0298, wR=0.0710, S=1.026.

### CCDC: 862125, 1; 862126, 2.

### 2 Results and discussion

### 2.1 IR spectrum

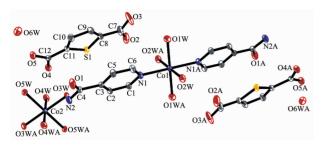
The FTIR spectra of compound **1** (in KBr) show the bands as follows: 3 442, 1 680, 1 558, 1 403, 1 350, 1 128, 785, 760, 620, 542 and 468 cm<sup>-1</sup>. IR spectrum of the compound shows the typical anti-symmetric (1 558 cm<sup>-1</sup>) and symmetric (1 350 cm<sup>-1</sup>) stretching bands of carboxylate groups. The absence of the characteristic band around 1 700 cm<sup>-1</sup> in compound **1** attributed to the

protonated carboxylic group indicates that the presence deprotonation of tdc ligand. In addition, the strong and broad band centered at 3 442 cm<sup>-1</sup> for 1 is attributable to the H-O-H stretching vibration of water molecule on the basis of the known structure.

The FTIR spectra of compound **2** (in KBr) show the bands as follows: 3 358, 1 679, 1 600, 1 555, 1 418, 1 400, 1 351, 1 312, 1 222, 1 151, 1 103, 1 064, 881, 786, 762, 662, 623, 550 and 473 cm<sup>-1</sup>. IR spectrum of the compound shows the typical anti-symmetric (1 555 cm<sup>-1</sup>) and symmetric (1 351 cm<sup>-1</sup>) stretching bands of carboxylate groups. The absence of the characteristic band around 1 700 cm<sup>-1</sup> in compound 1 attributed to the protonated carboxylic group indicates that the present deprotonation of tdc ligand. In addition, the strong and broad band centered at 3 358 cm<sup>-1</sup> for 1 is attributable to the H-O-H stretching vibration of water molecule on the basis of the known structure.

### 2.2 Description of the structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in  $P\bar{1}$  space group. The molecular structure of **1** is shown in Fig.1. There are two different coordination centers, Co(1) and Co(2), in the crystal with different coordination modes. The Co(1) ion is six-coordinated by two nitrogen atoms from



Symmetric code: A: -x, -y, 1-z; B: -x, -y, -z; Hydrogen atoms and crystal water molecules are omitted for clarity

Fig.1 Molecular structure of the title compound 1 different inta ligands (Co(1)-N(1) 0.2169 4(16) nm, Co(1)-N(1A) 0.216 94(16) nm) and four coordinated water molecules (Co(1)-O(1W) 0.211 33(16) nm, Co(1)-

 $O(1WA)~0.211~33\,(16)~nm,~Co(1)-O(2W)~0.209~01\,(15)~nm,~Co(1)-O(2WA)~0.209~01\,(15)~nm),~showing~a~slightly~distorted~octahedral~geometry. The Co(2)~ion is six-coordinated by six coordinated water molecules (Co(2)-O(3W)~0.208~27\,(14)~nm,~Co(2)-O(3WA)~0.208~27\,(14)~nm,~Co(2)-O(4W)~0.205~75\,(15)~nm,~Co(2)-O(4WA)~0.205~75\,(15)~nm,~Co(2)-O(5WA)~0.214~50\,(13)~nm),~showing~a~slightly~distorted~octahedral~geometry~too.$ 

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architecture. There are persistent N–H $\cdots$ O and O–H $\cdots$ O hydrogen bonding interactions (Table 2) in the

Table 2 Hydrogen bonds for compound 1 and 2

$D-H\cdots A$	d(D-H) / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathbf{D}\cdots\mathbf{A})$ / nm	$\angle$ (DHA) / (°)
1				
N(2)- $H(2A)$ ···O(5W)	0.086 0	0.231 6	0.310 8	153.28
$\mathrm{N}(2)\mathrm{-H}(2\mathrm{B})\cdots\mathrm{O}(6\mathrm{W})$	0.086 0	0.225 9	0.291 7	133.32
O(1W)- $H(1WA)$ ··· $O(3)$	0.085 3	0.223 6	0.305 7	161.41
O(1W)- $H(1WB)$ ··· $O(2)$	0.078 9	0.213 6	0.291 9	171.80
O(2W)- $H(2WA)$ ··· $O(2)$	0.086 0	0.189 5	0.275 3	174.37
O(2W)- $H(2WB)$ ··· $O(3)$	0.088 8	0.178 9	0.267 4	174.37
O(3W)- $H(3WA)$ ··· $O(4)$	0.089 0	0.187 2	0.271 2	156.75
O(3W)- $H(4WB)$ ··· $O(1)$	0.087 9	0.176 9	0.264 3	172.85
O(4W)- $H(4WA)$ ··· $O(5)$	0.087 2	0.188 4	0.274 8	170.74
$\mathrm{O}(4\mathrm{W})\mathrm{-H}(4\mathrm{WB})\mathrm{\cdots}\mathrm{O}(6\mathrm{W})$	0.093 0	0.179 3	0.271 4	170.83
O(5W)- $H(5WA)$ ··· $O(4)$	0.084 8	0.192 3	0.273 2	159.03
O(5W)- $H(5WB)$ ··· $O(5)$	0.087 8	0.194 6	0.281 9	172.33
O(6W)- $H(6WA)$ ··· $O(5)$	0.082 7	0.190 6	0.271 6	166.15
O(6W)- $H(6WB)$ ··· $O(4)$	0.083 7	0.198 5	0.281 0	168.19
2				
N(2)-H(2A)···O(5)	0.086 0	0.247 7	0.319 4	141.25
N(2)- $H(2B)$ ···O(4)	0.086 0	0.220 6	0.304 1	163.70
N(4)- $H(4A)$ ···O(6)	0.086 0	0.229 2	0.307 5	151.44
$\mathrm{N}(4)\mathrm{-H}(4\mathrm{B})\mathrm{\cdots}\mathrm{O}(5\mathrm{W})$	0.086 0	0.216 9	0.297 8	156.60
O(1W)- $H(1WA)$ ··· $O(5W)$	0.086 4	0.189 3	0.273 7	165.16
O(1W)- $H(1WB)$ ··· $O(5)$	0.078 7	0.196 9	0.275 2	173.28
O(2W)- $H(2WA)$ ··· $O(6)$	0.085 0	0.184 2	0.268 3	169.81
$O(3W)-H(3WB)\cdots O(6)$	0.083 1	0.193 3	0.275 2	167.88
O(4W)- $H(4WA)$ ··· $O(2)$	0.090 4	0.181 2	0.271 5	176.27
O(4W)- $H(4WB)$ ··· $O(6)$	0.080 6	0.188 6	0.268 4	170.42
O(5W)- $H(5WA)$ ··· $O(5)$	0.081 7	0.197 1	0.275 2	159.64
O(5W)- $H(5WB)$ ··· $O(1)$	0.084 1	0.190 7	0.271 6	161.02
$O(6W)-H(6WA)\cdots O(4)$	0.075 6	0.239 0	0.311 9	162.23
$O(6W)-H(6WB)\cdots O(2)$	0.087 9	0.188 2	0.275 8	173.56

complex, which play an important role in stabilizing the network structure. Moreover, there are  $\pi$ - $\pi$  interactions in compound 1 (Table 3) between inta ligands and free tdc anion. Therefore, through hydrogen bonds and  $\pi$ - $\pi$ 

interactions, the network structures are further extended into a three-dimensional supramolecular framework (Fig.2).

Table 3 Parameters between the planes in compound 1

Plane	Distance between ring centroids / nm	Dihedral angle / (°)
Cg1->Cg2	0.381 2	3.02
Cg1->Cg2C	0.400 3	3.02
Cg2->Cg1D	0.400 3	3.02

Symmetric code: C: x, 1+y, z; D: x, y-1, z; Cg1: N1C1C2C3C5C6, Cg2: S1C8C9C10C11.

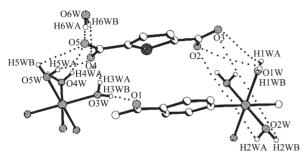
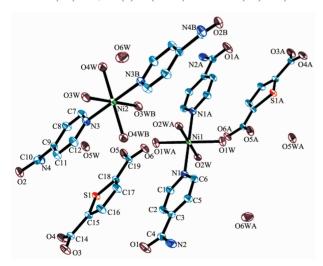


Fig.2 Hydrogen binding interactions in 1

Single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in  $P\bar{1}$  space group. The coordination environment of Ni (II) in complex **2** is shown in Fig.3. There are two same coordination centers, Ni(1) and Ni(2), in the crystal with same coordination modes. The Ni(1) ion is six-coordinated by four coordinated water molecules (Ni(1)-O(1W) 0.204 98(17) nm, Ni (1)-O (1WA) 0.204 98 (17) nm, Ni (1)-O (2W) 0.205 33(15) nm, Ni(1)-O(2WA) 0.205 33(15) nm) and



Symmetric code: A: 1-x, -y, 1-z, B: 1-x, -y, 2-z; Hydrogen atoms and crystal water molecules are omitted for clarity

Fig.3 Molecular structure of the title compound 2

two nitrogen atoms from different inta ligands (Ni(1)-N(1) 0.211 91(19) nm, Ni(1)-N(1A) 0.211 91(19)nm), showing a slightly distorted octahedral geometry.

There are persistent N -H  $\cdots$  O and O -H  $\cdots$  O hydrogen bonding interactions (Table 2) in the complex **2**, which play an important role in stabilizing the network structure. Moreover, there are many significant  $\pi$ - $\pi$  interactions in the packing diagram between the neighboring aromatic cycles contained in inta ligands and free tdc anion. The centroid-to-centroid distances between adjacent aromatic rings is 0.394 3 nm for N3C7C8C9C11C12 and S1C15C16C17C18 aromatic rings. The perpendicular distance is 0.365 0 nm for N3C7C8C9C11C12 and S1C15C16C17C18 aromatic rings. Therefore, through hydrogen bonds and  $\pi$ - $\pi$  interactions, the network structures are further extended into a three-dimensional supramolecular framework (Fig.4).

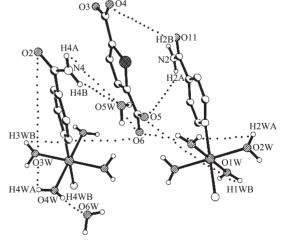


Fig.4 Hydrogen binding interactions in 2

### 2.3 Thermal analysis

TG curve of 1 show that the first weight loss of

58.6% from 17 to 117 °C corresponds to the removal of water and tdc molecules (calcd. 60.5%). Upon further heating, an obvious weight loss (28.50%) occurs in the temperature range of 117~450 °C, corresponding to the release of inta ligands (calcd. 26.6%). After 450 °C no weight loss is observed, which means the complete decomposition of 1. The residual weight should be CoO.

TG curve of **2** shows that the first weight loss of 33.1% from 15 to 151 °C corresponds to the removal of free water and tdc molecules (calcd. 35.5%). Upon further heating, an obvious weight loss (88.5%) occurs in the temperature range of 151~549 °C, corresponding to the release of coordinated water molecules and inta ligands (calcd. 89.9%). After 554 °C no weight loss is observed, which means the complete decomposition of **2**. The residual weight should be NiO.

### 2.4 UV spectrum

The UV spectra for the title compound 1 and inta ligand have been investigated in the solid state. Both the title compound and inta have one absorption band at about 271 nm, which should be assigned to the  $n \rightarrow \pi^{*[16]}$  transition of inta. However, after inta coordinating to the Co<sup>2+</sup> ion, the absorption intensity slightly increases. It is clearly that the absorption band in inta remains in the same position with that in the title compound, showing that they are not affected basically by the metal coordination.

The UV spectra for the title compound 2 and inta ligand have been investigated in the solid state. For compound 2, there is no absorption band.

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