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**YTTRIUM(III) COMPLEX WITH 1,10-PHENANTHROLINE LIGAND:  
CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDIES****A. Moodi<sup>1</sup>, M. Khorasani-Motlagh<sup>1</sup>, M. Noroozifar<sup>1</sup>, B.O. Patrick<sup>2</sup>**<sup>1</sup>*Chemistry Department, University of Sistan & Baluchestan, Zahedan, Iran*

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$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  reacts with 1,10-phenanthroline (phen) to yield a complex of 1:2 yttrium:ligand stoichiometry. The yttrium(III) complex is characterized by the elemental analysis, UV—Vis, IR as well as the X-ray diffraction analysis. The crystal of  $[\text{Y}(\text{phen})_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  obtained from a methanol solution crystallizes in the triclinic system, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 10.3236(4) \text{ \AA}$ ,  $b = 10.4566(4) \text{ \AA}$ ,  $c = 12.5270(5) \text{ \AA}$ ,  $\alpha = 97.354(2)^\circ$ ,  $\beta = 108.740(2)^\circ$ ,  $\gamma = 93.458(2)^\circ$ ,  $R_{\text{int}} = 0.046$ . The Y(III) ion is eight-coordinated by four nitrogen, three oxygen atoms and one chlorine atom.

**Keywords:** yttrium(III) complex, crystal structure, 1,10-phenanthroline, X-ray diffraction analysis.

**INTRODUCTION**

The term rare earth elements is sometimes applied to the elements La—Lu plus yttrium. The convenience of including La, which, strictly speaking, is not a lanthanide, is obvious. The reason for including Y is that this element has radii (atomic, metallic, ionic) that fall close to those of Er and Ho, and all of its chemistry is in the trivalent state [ 1 ]. Lanthanide trihalides are the major starting materials for the synthesis of lanthanide derivatives [ 2 ], and  $\beta$ -diketones (1,3-diketones) are also most commonly used for the complexation of lanthanide ions [ 3 ]. On the other hand, the coordination chemistry of these complexes has been largely explored and information on the molecular structure of coordination compounds of rare earth elements in solutions underlies the current technologies for obtaining photoresists in microelectronics, pharmaceutical preparations for photodynamic therapy, contrast reagents for magnetic resonance tomography, and synthetic models for natural ionophores [ 4 ]. Thus, based on different ligands and the central RE (III), many fluorescent complexes have been synthesized. The main ligands include aromatic carboxylic acid, pyridine, and 1,10-phenanthroline (phen) [ 5 ]. Among them, 1,10-phenanthroline is a noncharged ligand that can serve as a synergistic agent and an important issue in the design of lanthanide complexes [ 3 ].

Based on above mention, in this paper we report the synthesis of the bis-phen yttrium(III) complex that was characterized by IR, UV—Vis, elemental analysis, and X-ray diffraction.

**EXPERIMENTAL**

All reagents and solvents used in this study were obtained from Merck and Aldrich Chem. Co. All chemicals were of reagent grade and used without further purification. Doubly distilled water was used throughout the experiment.

IR spectra were recorded on a SIMADZU spectrometer with samples prepared as KBr pellets. UV—Vis spectra were recorded on an Analytik Jena SPECORD S100 spectrometer with a photodiode array detector.

**Preparation of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .**  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  was synthesized according to the reported method for the lanthanide analogue [6].  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (0.200 g, 0.66 mmol) was dissolved in ethanol (5 ml), then a solution of 1,10-phen (0.238 g, 1.32 mmol) in ethanol (15 ml) was added to it while stirred and heated to 60 °C. The resulting solution was refluxed for 8 h. The resulting white precipitate was filtered and washed with ethanol and dichloromethane. The yield was ca. 90 % based on yttrium. *Anal. Calc. for  $\text{C}_{24}\text{H}_{24}\text{Cl}_3\text{N}_4\text{O}_4\text{Y}$ :* C, 45.92; H, 3.86; N, 8.93 %. Found: C, 45.79; H, 3.61; N, 8.72 %. IR (KBr):  $\nu(\text{C}=\text{N}) = 1586 \text{ cm}^{-1}$ ;  $\nu(\text{C}=\text{C}) = 1420\text{—}1515 \text{ cm}^{-1}$ ;  $\nu(\text{C—H}) = 724\text{—}848$ , UV—Vis absorption ( $*\pi \rightarrow \pi$  transitions) (in MeOH): 233, 271 nm; (in  $\text{H}_2\text{O}$ ): 225, 264 nm. The crystal was suitable for the X-ray determination.

**Crystallography.** Colorless, prism crystals of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  were grown by acetonitrile diffusion into a methanolic solution of the Y(III) complex at room temperature. All measurements were made on a Bruker X8 APEX II with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), at a temperature of  $-173 \pm 0.1 \text{ }^\circ\text{C}$  to the maximum  $2\theta$  value of  $60.1^\circ$ . Data were collected in a series of  $\phi$  and  $\omega$  scans in  $0.50^\circ$  oscillations with 10.0-second exposures. The crystal-to-detector distance was 40.03 mm. The structure was solved by a direct method and refined by the least-squares technique [7, 8]. All non hydrogen atoms were refined anisotropically. All hydrogen atoms were included but not refined. Out of 76736 reflections collected, 7264 were unique ( $R_{\text{int}} = 0.046$ ); equivalent reflections were merged. The maximum and minimum peaks on the final difference Fourier map corresponded to  $0.62 \text{ e}^-/\text{\AA}^3$  and  $-0.50 \text{ e}^-/\text{\AA}^3$  respectively.

A perspective view of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  with the eclipsed configuration is depicted in Fig. 1. An overview of the molecular packing in the crystal structure of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  and hydrogen bonding around one molecule are shown in Figs. 2 and 3 respectively. Some details of the collection data are given in Table 1. Selected interaction distances and angles and the hydrogen-bonding geometry for the crystal are given in Tables 2 and 3 respectively. The complete crystallographic information file for the structure of the  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  complex was deposited to CCDC, deposition number 865891, and is available free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

## RESULTS AND DISCUSSION

**Spectral studies.** The elemental analysis of the complex is consistent with its formulation, as is the following X-ray structure, spectroscopic characterizations.

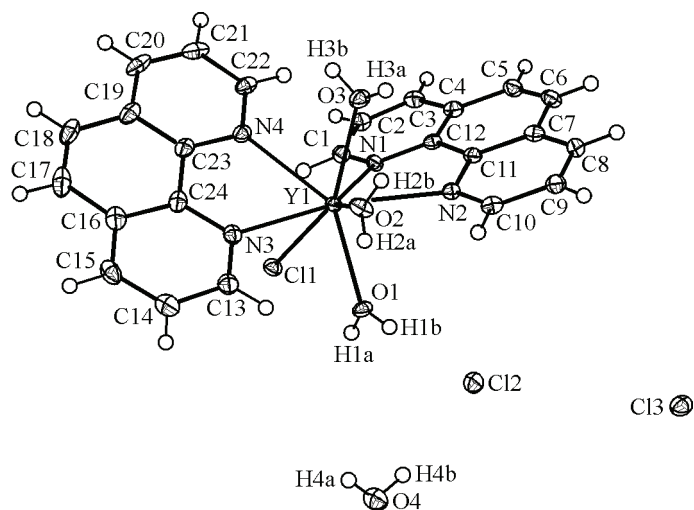


Fig. 1. ORTEP diagram of the  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  complex

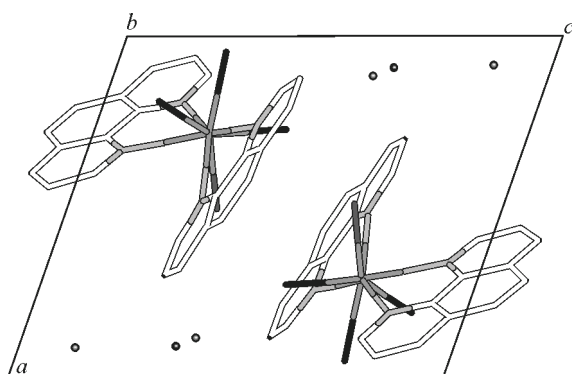


Fig. 2. The unit cell packing (along the *b* axis) of  $[\text{Y}(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$

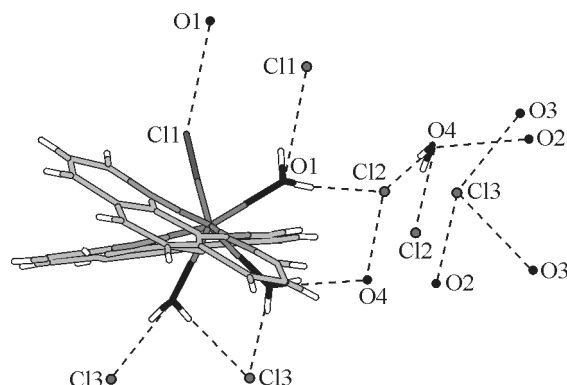


Fig. 3. Hydrogen bonding around one molecule of  $[\text{Y}(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$

IR spectra usually provide a lot of valuable information on coordination reactions. A comparison of the IR spectrum of the title compound with its free ligand shows that the phen bands in the range  $1645\text{--}1400\text{ cm}^{-1}$  attributed to ring stretching vibrations shift to higher frequencies upon chelation

T a b l e 1

Crystal data for  $[\text{Y}(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$

|   |  |
|---|--|
| Empirical formula                         | $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4\text{YCl}_3$ |
| Formula weight                            | 627.73   |
| Crystal system                            | Triclinic  |
| Crystal dimensions, mm                    | $0.12 \times 0.18 \times 0.21$                               |
| Space group                               | $P\bar{1}$ (#2)  |
| $V, \text{\AA}^3; Z$                      | $1262.63(9); 2$  |
| $T, \text{K}$                             | 100  |
| $d, \text{g/cm}^{-3}$                     | 1.651  |
| $F(000)$                                  | 636.00   |
| $a, b, c, \text{\AA}$                     | $10.3236(4), 10.4566(4), 12.5270(5)$                         |
| $\alpha, \beta, \gamma, \text{deg.}$      | $97.354(2), 108.740(2), 93.458(2)$                           |
| $\mu, \text{cm}^{-1}$                     | 26.66  |
| Number of unique data                     | 7264, ( $R_{\text{int}} = 0.046$ )                           |
| Final $R$ indices [ $I > 2.00\sigma(I)$ ] | $R_1 = 0.039; wR_2 = 0.075$                                  |
| Final $R$ indices [for all data]          | $R_1 = 0.054; wR_2 = 0.078$                                  |

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

T a b l e 2

Selected bond lengths ( $\text{\AA}$ ) and bond angles (deg.) of  $[\text{Y}(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$

| Bond      | Dist.      | Bond       | Dist.      | Angle          | (deg.)    | Angle          | (deg.)    |
|-----------|------------|------------|------------|----------------|-----------|----------------|-----------|
| N(1)—Y(1) | 2.5132(19) | O(1)—Y(1)  | 2.3343(17) | N(1)—Y(1)—N(2) | 65.33(6)  | N(4)—Y(1)—N(2) | 134.96(6) |
| N(2)—Y(1) | 2.5390(19) | O(2)—Y(1)  | 2.3407(18) | N(1)—Y(1)—N(3) | 144.94(6) | N(3)—Y(1)—N(4) | 65.67(7)  |
| N(3)—Y(1) | 2.5204(19) | O(3)—Y(1)  | 2.3676(17) | N(1)—Y(1)—N(4) | 85.32(6)  | O(1)—Y(1)—O(2) | 76.14(7)  |
| N(4)—Y(1) | 2.5326(19) | Cl(1)—Y(1) | 2.6869(6)  | N(3)—Y(1)—N(2) | 149.70(6) | O(1)—Y(1)—O(3) | 142.50(7) |

Table 3

Hydrogen-bonding geometry for the crystal of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (Å, deg.)

| Donor...H    | Acceptor | D—H     | H...A   | D...A    | D—H...A |
|--------------|----------|---------|---------|----------|---------|
| O(1)...H(1A) | ..Cl(1)  | 0.79(3) | 2.46(3) | 3.187(2) | 154(3)  |
| O(1)...H(1B) | ..Cl(2)  | 0.80(4) | 2.27(4) | 3.070(2) | 173(4)  |
| O(2)...H(2A) | ..O(4)   | 0.78(3) | 1.89(3) | 2.660(3) | 167(3)  |
| O(2)...H(2B) | ..Cl(3)  | 0.74(3) | 2.37(3) | 3.108(2) | 171(3)  |
| O(3)...H(3A) | ..Cl(3)  | 0.77(3) | 2.34(3) | 3.078(2) | 159(3)  |
| O(3)...H(3B) | ..Cl(3)  | 0.83(3) | 2.25(4) | 3.060(2) | 163(3)  |
| O(4)...H(4A) | ..Cl(2)  | 0.83(4) | 2.32(3) | 3.136(2) | 169(3)  |
| O(4)...H(4B) | ..Cl(2)  | 0.78(3) | 2.40(3) | 3.167(2) | 167(3)  |

[1, 9]. The  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  modes of phen appear in the range  $1558\text{--}1642\text{ cm}^{-1}$ ,  $1418\text{--}1502\text{ cm}^{-1}$  for the ligand, and these peaks shift at  $1586\text{ cm}^{-1}$  and  $1420\text{--}1515\text{ cm}^{-1}$  respectively for the complex [9]. The C—H out-of-plane bending vibration of the free ligand (phen) was located at  $732\text{ cm}^{-1}$  and  $849\text{ cm}^{-1}$  for the complex, the peak shifts to  $724\text{ cm}^{-1}$  and  $848\text{ cm}^{-1}$  [9, 10]. In the IR spectrum of the title compound, a slightly broad band at  $1621\text{ cm}^{-1}$  is due to the H—OH bending and the broad peaks in the range  $2920\text{--}3340\text{ cm}^{-1}$  indicate the presence of  $\nu(\text{O}—\text{H})$  [11]. These peaks may be assigned to the bending and stretching vibrations of coordinated water [9]. The band at  $417\text{ cm}^{-1}$  may be assigned to the  $\rho_w(\text{H}_2\text{O})$  vibration. These results suggest the presence of both coordinated and crystal water in the complex [11]. The non-ligand bands of low intensity in the far infrared region (the bands in the range  $635\text{--}400\text{ cm}^{-1}$ ) can be assigned to  $\nu(\text{Y}—\text{O})$  and  $\nu(\text{Y}—\text{N})$  [12].

The study of the electronic spectrum in the ultraviolet and visible range for the Y(III) complex was carried out in water and methanol solutions. The electronic spectrum of the water solution had a strong band at  $\lambda = 225\text{ nm}$  and a medium band at  $\lambda = 264\text{ nm}$  (Fig. 4). For the methanol solution, a strong band was shown at  $\lambda = 233\text{ nm}$  and a medium one at  $\lambda = 271\text{ nm}$  (Fig. 4). Centered charge transfer including  $\pi \rightarrow \pi$  transitions attributed to the n-donor (phenanthroline) ligand is observed at  $200\text{--}300\text{ nm}$  [9]. The yttrium ion ( $\text{Y}^{3+}$ ) has a stable electronic structure ( $4s^2 4p^6$ ) and there was no  $f\text{--}f$  transitions.

**Crystal structure of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .** The ORTEP drawing of the  $[Y(\text{phen})_2\text{Cl} \cdot (\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$  complex with atom numbering is depicted in Fig. 1. The packing of the unit cell is given in Fig. 2. Crystal structure data and selected bond lengths and angles are given in Tables 1 and 2 respectively. The hydrogen-bonding geometry for the crystal is given in Table 3.

The coordination sphere of the complex comprises two bidentate ligands: two N,N' chelates. The yttrium atom is eight-coordinate, bound to one chloride, three oxygen, and four nitrogen atoms. The

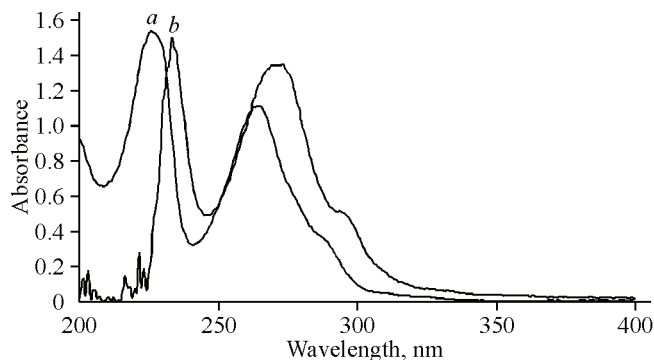


Fig. 4. UV-Vis absorption spectra of water (a) and methanol solutions (b) of  $[Y(\text{phen})_2\text{Cl}(\text{OH}_2)_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$

average Y—N bond distance (2.526 Å) is longer than that in the eight-coordinate  $[Y(H_2O)_2 \cdot (NO_3)_2(terpy)](NO_3) \cdot 2H_2O$  complex [ 1 ] and  $[Y(H_2O)_6(bpy)]^{3+}$  [ 1 ] (average 2.49(1) Å). The average Y—N distance is close to the Y—N distance in  $[Y(NO_3)_3(phen)_2]$  [ 1 ], in which  $Y^{III}$  is ten-coordinate, and shorter than that in the eight-coordinate dinuclear species  $[Y_2(OH)_2(H_2O)_4(phen)_4]Cl_4 \cdot 2phen \cdot MeOH$  [ 1 ]. The N—Y—N bite angles of 65.67(6)° for N(3)—Y—N(4), 65.33(6)° for N(1)—Y—N(2) are typical of  $Y^{III}$ -phen [ 1, 13 ] complexes. The Y—Cl bond length in the complex is 2.6869(6) Å and is close to the Y—Cl distance in  $[Y(DMU)_6][YCl_6]$  [ 14 ]. The Y—O distances range from 2.33 Å to 2.37 Å. The average Y—O bond distance (2.35 Å) in the complex is shorter than the values of 2.48(2) and 2.47(2) Å found for  $[Y(NO_3)_3(bpy)_2]$  [ 1 ] and  $[Y(NO_3)_3(phen)_2]$  [ 1 ] respectively, in which  $Y^{III}$  is ten-coordinated, and the average Y—O bond distances in nine-coordinate yttrium-(III) complexes containing bidentate chelating nitrate groups [ 1 ].

The angle between the two phen planes is 36.41°. The distances of Y to phen(1) and phen(2) rings are 0.610 Å and 0.250 Å respectively. The two different ligations of two phen ligands result in a slightly distorted square antiprismatic surrounding of the yttrium atom. This structural type is quite common in lanthanide  $\beta$ -diketonate chemistry with complexes such as  $[Y(mpa)_3(bipy)]$  [ 12 ]  $[Ln(acac)_3(phen)]$  (Ln = La, Lu [ 12 ] or Eu [ 12 ]),  $[La(acac)_3(H_2O)_2]$  [ 12 ] and  $[Eu(thd)_3(Py)_2]$  (py = pyridine) [ 12 ].

Interestingly, there is a  $\pi$ — $\pi$  stacking interaction between the phen ligands with a face-to-face distance of 3.4 Å. Its cohesion is strengthened by the existence of the  $\pi$ — $\pi^*$  interaction between three benzene rings of the phen ligands from two adjacent molecule blocks. This value of (C...C) is  $\approx$  3.6 Å for phen ligands in  $NdCl_3(phen)_2$ ,  $EuCl_3(phen)_2$ , and  $[Ln(phen)_2Cl_3(H_2O)]$  (Ln = Nd, Eu) [ 15 ]. The centroid-to-centroid distance for the  $\pi$ — $\pi$  stacking interaction between the planes of the nearest neighboring phen ligands and 4-amino-benzenesulfate in  $[Pr(H_2O)_3(C_6H_6O_3NS)_2(C_{12}H_8N_2)_2]NO_3 \cdot 4H_2O$  (( $C_6H_6O_3NS$ ) = 4-aminobenzenesulfonato-O, ( $C_{12}H_8N_2$ ) = 1,10-phenanthroline) [ 16 ] is 3.560(2)—3.630(2) Å.

It is worth noting that hydrogen bonding interactions are usually important in the stabilization of a supramolecular architecture [ 16 ]. All the active H atoms in the structure of the Y(III) complex (four aqua and three chloro) take part in the hydrogen bonding shown in the complex scheme presented in Fig. 3. The hydrogen-bonding geometry is reported in Table 3. From Table 3, it is seen that there are two types of hydrogen bonds: O—H...Cl and O—H...O. It is clear that the O—H...O hydrogen bonding interactions between water molecules and chloride anions of the complex organize a three-dimensional structure. Hydrogen bond interactions occur between water species together and between water species and chlorine anions. The average bond lengths of O...Cl is 3.103 (2) Å to 3.1870(19) Å that is semi-longer than the O...Cl values (3.072(3)—3.118(4) Å) for  $[Ln(phen)_2Cl_3(H_2O)]$  (Ln = Nd, Eu) [ 15 ]. The bond length of H...O (1.89(3) Å) is shorter than the H...O values for  $[Y(5-Nip)(5-HNip)(H_2O)_2] \cdot 2H_2O$  (5-H<sub>2</sub>Nip = 5-nitroisophthalic acid) [ 17 ]. The O—H...O bond angle is (167(3)°) identical to the value (167(4)°) for  $[Y(crot)_3(aq)_2] \cdot 4(bpa)$  (crot = crotonato, aqua = H<sub>2</sub>O, bpa = 2,2'-bipyridylamine) [ 18 ] and different O—H...O values for  $[Y(5-Nip)(5-HNip)(H_2O)_2] \cdot 2H_2O$  (5-H<sub>2</sub>Nip = 5-nitroisophthalic acid) [ 17 ].

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