Synthesis and Luminescent Properties of Eu³⁺, Gd³⁺, and Tb³⁺ Complexes with Quinoline-4-carboxylic Acids

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Received May 17, 2019; revised May 17, 2019; accepted May 25, 2019

Abstract—New complex compounds $LnL_3 \cdot nH_2O$ (n = 5-10) have been synthesized on the basis of Eu^{3+} , Gd^{3+} , and Tb^{3+} salts and quinoline-4-carboxylic acid derivatives obtained via the Pfitzinger reaction. Composition and structure of the ligands and the resulting complex compounds have been confirmed by NMR and IR spectroscopy, thermogravimetry, and complexometric titration. Europium complex with 1,2,3,4-tetrahydroacridine-9-carboxylic acid has exhibited efficient luminescence.

Keywords: quinoline-4-carboxylic acid derivatives, Pfitzinger reaction, lanthanides, luminescent properties, complexation

DOI: 10.1134/S1070363219120144

The demand to the development of novel polyfunctional complexes exhibiting efficient luminescence (in particular, lanthanides complexes with organic ligands favoring efficient energy transfer to the emission level of the ion and improving the luminescence efficiency) has recently emerged [1–8]. Synthesis and photoluminescent properties of lanthanides complexes with a series of 8-oxyquinoline derivatives [9–13] as well as with quinoline-2,3-dicarboxylic acid [14] have been reported. However, the lanthanides complexes with substituted quinoline-4-carboxylic acids have not been systematically studied.

Complexes of Eu³⁺, Gd³⁺, and Tb³⁺ with aromatic and heterocyclic ligands have been recognized as compounds exhibiting efficient luminescence. Extending the studies of heteroatomic ligands containing carboxylic groups [15] and luminescent lanthanides carboxylates [16–20], we explored the possibility of targeted synthesis and photoluminescent properties of Eu³⁺, Gd³⁺, and Tb³⁺ complexes with substituted quinoline-4-carboxylic acids.

First, we synthesized 2-(4-methoxyphenyl)quinoline-4-carboxylic 1 (quin-OCH₃), 2-(4-bromophenyl)quinoline-4-carboxylic 2 (quin-Br), and 1,2,3,4-tetrahydroacridine-9-carboxylic 3 [quin(CH₂)₄] acids. Acids 1–3 were synthesized (Scheme 1) via the Pfitzinger reaction (cf. [21]) using a modified procedure [22]. Purity and structure of compounds **1–3** were confirmed by means of comprehensive spectroscopy studies: IR and NMR (¹H, ¹³C, and ¹⁵N including DEPTQ, ¹H–¹³C HSQC, and ¹H–¹³C HMBC). ¹H NMR spectra of acids **1–3** contained a signal at 13.99–14.01 ppm, typical of the carboxylic group. A similar typical signal of the carboxylic group was found in the ¹³C DEPTQ NMR spectra of acids **1–3** at 167.5–168.7 ppm. ¹⁵N NMR spectrum of compound **1** contained a signal of the quinoline nitrogen at 312.0 ppm which revealed the cross peaks with H³ (8.41 ppm) and H⁸ (8.11 ppm) protons in the HMBC ¹H–¹⁵N spectrum. The principal chemical shifts and heteronuclear correlations for compounds **1** and **3** are shown in Scheme 2; complete sets of the observed correlations are collected in Tables 1 and 2.

Complexes of Eu³⁺, Gd³⁺, and Tb³⁺ with acids **1–3** were synthesized from alcoholic solutions containing the lanthanide(III) ligand and the ligand (HL) in the 1 : 3 ratio (Scheme 3). The composition of the obtained complexes corresponded to the LnL₃·*n*H₂O (n = 5-10) formula, their yield being 41–84%.

Complexes 4–12 were pale-yellow powders. Their composition and structure were confirmed by means of IR spectroscopy, and the metal content was determined by complexometric titration. According to the obtained data, the composition of compounds 4–12 was as fol-



$$\begin{split} R^1 = H, \ R^2 = 4\text{-}CH_3OC_6H_4 \ (quin-OCH_3) \ \textbf{(1)}, \ 4\text{-}BrC_6H_4 \ (quin-Br) \ \textbf{(2)}; \\ R^1 + R^2 = (CH_2)_4 \ [quin(CH_2)_4] \ \textbf{(3)}. \end{split}$$

Scheme 2.



lows: Gd(quin-OCH₃)₃·5H₂O (**4**), Tb(quin-OCH₃)₃·7H₂O (**5**), Eu(quin-OCH₃)₃·5H₂O (**6**), Gd(quin-Br)₃·7H₂O (**7**), Tb(quin-Br)₃·6H₂O (**8**), Eu(quin-Br)₃·7H₂O (**9**), Gd[quin(CH₂)₄]₃·5H₂O (**10**), Tb[quin(CH₂)₄]₃·10H₂O (**11**), and Eu[quin(CH₂)₄]₃·6H₂O (**12**).

The complexes composition was determined by thermogravimetry. In the case of the Eu[quin(CH₂)₄]₃·6H₂O complex (**12**), two exothermic effects were observed at 20–226 and 227–331°C, corresponding to the elimination of 4 outer-sphere water molecules and 2 inner-sphere water molecules, respectively (Fig. 1). A strong exothermic effect observed at 332–575°C corresponded to thermal decomposition of the complex and sequential elimination of three ligand molecules. The residual mass corresponded to europium oxide.

In contrast to IR spectra of compounds 1-3, those of the complexes did not contain the group of bands at 2800–2400 cm⁻¹ assignable to the carboxylic acid dimers, which indirectly confirmed the complex formation. The

stretching C=O band of the protonated carboxylic group at 1650–1715 cm⁻¹ was shifted to shorter wavelengths, typical of the stretching of ionized carboxylic group $v_{as}(COO^{-})$ and $v_{s}(COO^{-})$. Since the difference in the frequency of the asymmetric and symmetric stretching Δv in the complexes spectra did not exceed 220 cm⁻¹, the ligands in the complexes were ionized and exhibited bidentate coordination with the lanthanide(III) ions via two oxygen atoms of the deprotonated carboxylic group [23].

To explore the possibility of the application of the obtained complexes as luminophors, we recorded their luminescence spectra. The efficient luminescence demanded the closeness of the energies of the triplet ligand level and the emission level of the lanthanide ion, the triplet level of the ligand should be higher in energy by $1800-3500 \text{ cm}^{-1}$ [24].

Triplet levels of acids 1-3 were determined from the phosphorescence spectra of their complexes with Gd^{3+} . The T_1 energy was considered equal to that of the long-

δ _H , ppm	δ _C , ppm	
	HSQC ¹ H– ¹³ C	HMBC ¹ H– ¹³ C
3.84 s (3H, MeO)	55.4* (MeO)	160.9 (C-OMe)
7.11 d (2H, H ³ , H ⁵ , 4-MeOC ₆ H_4 , ³ J = 8.7 Hz)	114.4* (C ³ , C ⁵ 4-MeOC ₆ H ₄)	114.4* (C ³ , C ⁵ , 4-MeOC ₆ H ₄), 160.9 (C–OMe), 128.7* (C ² , C ⁶ , 4-MeOC ₆ H ₄), 130.3 (C ¹ , 4-MeOC ₆ H ₄)
7.63–7.67 m (1H, H ⁶)	127.4* (C ⁶)	123.1 (C ⁴ a), 130.2* (C ⁷)
7.80–7.83 m (1H, H ⁷)	130.2 (C ⁷)	125.4* (C ⁵), 148.4 (C ^{8a})
8.11 d (1H, H ⁸ , ${}^{3}J = 8.6$ Hz)	129.6* (C ⁸)	123.1 (C ^{4a}), 127.4* (C ⁶)
8.26 d (2H, H ² , H ⁶ , 4-CH ₃ OC ₆ H_4 , ³ J = 8.7 Hz)	128.7* (C ² , C ⁶ 4-CH ₃ OC ₆ H ₄)	114.4* (C ³ , C ⁵ , 4-MeOC ₆ H ₄), 128.7* (C ² , C ⁶ ,4-CH ₃ OC ₆ H ₄), 155.5 (C ²), 160.9 (C-OMe)
8.41 s (1H, H ³)	118.7* (C ³)	123.1 (C ⁴ a), 130.3 (C ¹ , 4-MeOC ₆ H ₄), 137.5 (C ⁴), 155.5 (C ²), 167.7 (COOH)
8.61 d (1H, H ⁵ , <i>J</i> = 8.6 Hz)	125.4* (C ⁵)	$\begin{vmatrix} 123.1 & (C^{4a}), 130.2^* & (C^7), 137.5 & (C^{4a}), 148.4 \\ & (C^{8a}) \end{vmatrix}$
13.99 br. s (1H, COOH)	-	_

^a Hereafter (asterisk) marks the signals in the opposite phases.

wave emission band in the spectra: 17241 (1), 17094 (2), and 19920 (3) cm⁻¹. The energy of the triplet level of acids 1–3 was lower in comparison with the resonance level of the Tb³⁺ ion (${}^{5}D_{4} 20500 \text{ cm}^{-1}$), and efficient intramolecular energy transfer to the Tb³⁺ was impossible; that was confirmed by the experimental data.

The energy of triplet levels T_1 of acids **1** and **2** was lower than that of resonance level of Eu³⁺ ion (⁵D₀)

17250 cm⁻¹), and the luminescence was not observed for complexes **6**, **9** of Eu³⁺ with those ligands. The energy of triplet level T₁ of acid **3** was optimal for Eu³⁺ ion, and the corresponding complex **12** exhibited efficient luminescence. The luminescence spectrum of complex **12** {Eu(H₂O)₂[quin(CH₂)₄]₃·4H₂O} is shown in Fig. 2; characteristic emission of the Eu³⁺ ion (${}^{5}D_{0}-{}^{7}F_{1}$, ${}^{5}D_{0}-{}^{7}F_{2}$, ${}^{5}D_{0}-{}^{7}F_{3}$, ${}^{5}D_{0}-{}^{7}F_{4}$) was to be seen. The luminescence ef-

Scheme 3.



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S nnm	$\delta_{\rm C}$, ppm		
o _H , ppm	HSQC ¹ H– ¹³ C	HMBC ¹ H– ¹³ C	
1.80–1.86 m (2H, H ²)	22.0 (C ²)	22.2 (C ³), 26.3 (C ¹), 33.3 (C ⁴), 125.7 (C ⁹ a)	
1.86–1.92 m (2H, H ³)	22.2 (C ³)	22.0 (C ²), 26.3 (C ¹), 33.3 (C ⁴), 159.0 (C ⁴ a)	
2.87–2.90 m (2H, H ¹)	26.3 (C ¹)	22.0 (C ²), 22.2 (C ³), 125.7 (C ⁹ a), 139.5 (C ⁹), 159.0 (C ⁴ a)	
3.02–3.05 m (2H, H ⁴)	33.3 (C ⁴)	22.0 (C ²), 22.2 (C ³), 125.7 (C ^{9a}), 145.5 (C ^{10a}), 159.0 (C ^{4a})	
7.54–7.58 m (1H, H ⁶)	126.6* (C ⁶)	124.3* (C ⁷), 128.3* (C ⁸), 129.2* (C ⁵), 145.5 (C ^{10a})	
7.67–7.72 m (2H, H ⁵ , H ⁷ overlap)	124.3* (C ⁷), 129.2* (C ⁵)	122.0 (C ⁸ a), 124.3* (C ⁷), 126.6* (C ⁶), 128.3* (C ⁸), 129.2* (C ⁵), 139.5 (C ⁹), 145.5 (C ¹⁰ a)	
7.92 d (1H, H ⁸ , ${}^{3}J = 8.3$ Hz)	128.3* (C ⁸)	122.0 (C ^{8a}), 124.3* (C ⁷), 126.6* (C ⁶)	
14.00 br. s (1H, COOH)	_	_	

Table 2. Correlations observed in the HSQC ¹H-¹³C and HMBC ¹H-¹³C spectra of 1,2,3,4-tetrahydroacridine-9-carboxylic acid 3

ficiency is generally determined by comparing its integral intensity with that of the corresponding lanthanide benzoate [16–20]. In the considered case, the integral intensity of the $Eu(H_2O)_2[quin(CH_2)_4]_3 \cdot 4H_2O$ complex luminescence was 3.36 times stronger than that of europium benzoate.

In summary, we prepared the complexes of Eu³⁺, Gd³⁺, and Tb³⁺ with 2-(4-methoxyphenyl)quinoline-4-carboxylic, 2-(4-bromophenyl)quinoline-4-carboxylic, and 1,2,3,4-tetrahydroacridine-9-carboxylic acids. It was found that europium complex with 1,2,3,4-tetrahydroacridine-9-carboxylic acid exhibited the luminescent properties 3.36 times stronger in comparison with europium benzoate.



Fig. 1. Thermogram of the $Eu(H_2O)_2[quin(CH_2)_4]_3 \cdot 4H_2O$ complex (12). (1) TG, (2) DSC, (3) DTG.

EXPERIMENTAL

NMR spectra (¹H, ¹³C DEPTQ, HSQC ¹H–¹³C, HMBC ¹H–¹³C, and HMBC ¹H–¹⁵N) were recorded using a Bruker Avance III HD NanoBay spectrometer (400 MHz) in DMSO-*d*₆, operating at 400, 101, and 40.55 MHz (¹H, ¹³C, and ¹⁵N, respectively). TMS or residual signals of the solvent were used as internal references; in the case of the ¹⁵N spectrum, liquid nitromethane served as external reference (380.23 ppm). IR spectra were recorded using a Bruker Vertex 70 spectrometer (4000– 350 cm⁻¹, ATR with a diamond crystal). Excitation and emission spectra were recorded using a Fluorat-02-Pamorama instrument equipped with a fiber-optic at-



Fig. 2. Luminescence spectrum of the $Eu(H_2O)_2[quin(CH_2)_4]_3$ · 4H₂O complex (**12**).

tachment for solid samples. The spectra at liquid nitrogen atmosphere (77 K) were recorded using a cryostat.

Purity of the obtained compounds was monitored by TLC on Sorbfil-A plates (eluent: acetone–hexane 1 : 1, the spots were visualized with iodine vapors and UV light.). Thermogravimetric analysis was performed using a NETSCH STA 409 PC/PG instrument at heating from 25 to 750°C (air atmosphere, 10 deg/min). Elemental analysis (C, H, N) was performed using a Vario MICRO cube instrument. The metals content was determined via titration of a weakly acidic solutions with 0.05 M. EDTA solution in the presence of 0.1% alcoholic solution of Xylene Orange.

Acids 1–3 were prepared via a procedure adopted from Ref. [22]. 0.034 mol of the corresponding ketone and 30 mL of 33% aqueous solution of potassium hydroxide $(d = 1.32 \text{ g/cm}^3, 0.23 \text{ mol})$ was added to a suspension of 5.0 g (0.034 mol) of isatin in 30 mL of 96% ethanol. The mixture was refluxed during 8 h, cooled down, and acidified with HCl to pH = 2. After 24 h, the precipitate was filtered off and washed with cold EtOH. The obtained substance was refluxed during 10 min in an alkaline alcoholic solution with activated carbon; the solution was filtered through a paper filter, cooled, acidified with HCl to pH = 2, and kept in a fridge overnight. The formed precipitate was filtered off, washed with EtOH, and dried.

2-(4-Methoxyphenyl)quinoline-4-carboxylic acid (1). Yield 5.03 g (53%). IR spectrum, v, cm⁻¹: 1599 (C=C, C=N), 1651 (C=O). ¹H NMR spectrum, δ, ppm: 3.84 s (3H, 4-CH₃OC₆H₄), 7.11 d (2H, H³, H⁵, 4-CH₃OC₆H₄, ${}^{3}J = 8.7$ Hz), 7.63–7.67 m (1H, H⁶), 7.80–7.83 m (1H, H⁷), 8.11 d (1H, H⁸, ${}^{3}J$ = 8.6 Hz), 8.26 d (2H, H², H⁶, 4-CH₃OC₆ H_4 , ${}^{3}J = 8.7$ Hz), 8.41 s (1H, H³), 8.61 d (1H, H⁵, J = 8.6 Hz), 13.99 br. s (1H, COOH). ¹³C DEPTQ NMR spectrum, δ_C, ppm: 55.4* (MeO), 114.4* (C³, C⁵, 4-CH₃OC₆H₄), 118.7* (C³), 123.1 (C⁴a), 125.4* (C⁵), 127.4* (C⁶), 128.7* (C², C⁶, 4-CH₃OC₆H₄), 129.6* (C⁸), 130.2* (C⁷), 130.3 (C¹, 4-CH₃OC₆H₄), 137.5 (C⁴), 148.4 (C^{8a}), 155.5 (C²), 160.9 (COMe), 167.7 (COOH). ¹⁵N NMR spectrum: δ_N 312.0 ppm. Found, %: C 73.13; H 4.75; N 4.98. C₁₇H₁₃NO₃. Calculated, %: C 73.11; H 4.69; N 5.02.

2-(4-Bromophenyl)quinoline-4-carboxylic acid (2). Yield 10.60 g (95%). IR spectrum, ν, cm⁻¹: 1586 (C=C, C=N), 1713 (C=O). ¹HNMR spectrum, δ, ppm: 7.69–7.73 m (1H, H⁶), 7.75 d (2H, H³, H⁵, 4-BrC₆H₄, *J* = 8.5 Hz), 7.83–7.87 m (1H, H⁷), 8.16 d (1H, H⁸, *J* = 8.3 Hz), 8.25 d (2H, H², H⁶, 4-BrC₆H₄, *J* = 8.5 Hz), 8.46 s (1H, H³), 8.64 d (1H, H⁵, J = 8.6 Hz), 14.01 br. s (1H, COOH). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 119.0 (C³), 123.6 (CBr), 123.9 (C⁴a), 125.5 (C⁸), 128.1 (C⁶), 129.3 (C⁵), 129.7 (C², C⁶, 4-BrC₆H₄), 130.5 (C⁷), 132.0 (C³, C⁵, 4-BrC₆H₄), 136.9 (C⁴), 137.9 (C¹, 4-BrC₆H₄), 148.2 (C^{8a}), 154.7 (C²), 167.5 (COOH). ¹⁵N NMR spectrum: $\delta_{\rm N}$ 311.7 ppm. Found, %: C 58.54; H 3.13; N 4.28. C₁₆H₁₀BrNO₂. Calculated, %: C 58.56; H 3.07; N 4.27.

1,2,3,4-Tetrahydroacridine-9-carboxylic acid (3). Yield 5.02 g (65%). IR spectrum, v, cm⁻¹: 1595 (C=C, C=N), 1653 (C=O). ¹H NMR spectrum, δ , ppm: 1.80–1.86 m (2H, H²), 1.86–1.92 m (2H, H³), 2.87–2.90 m (2H, H¹), 3.02–3.05 m (2H, H⁴), 7.54–7.58 m (1H, H⁶), 7.67–7.72 m (2H, H⁵, H⁷, signals overlap), 7.92 d (1H, H⁸, ³*J*=8.3 Hz), 14.00 br. s (1H, COOH). ¹³C DEPTQ NMR spectrum, $\delta_{\rm C}$, ppm: 22.0 (C²), 22.2 (C³), 26.3 (C¹), 33.3 (C⁴), 122.0 (C^{8a}), 124.3* (C⁷), 125.7 (C^{9a}), 126.6* (C⁶), 128.3* (C⁸), 129.2* (C⁵), 139.5 (C⁹), 145.5 (C^{10a}), 159.0 (C^{4a}), 168.7 (COOH). Found, %: C 74.02; H 5.80; N 6.18. C₁₄H₁₃NO₂. Calculated, %: C 73.99; H 5.77; N 6.16.

Complexes 4–12. 10 mL of an alcoholic solution of potassium hydroxide was added to 10 mL of an alcoholic solution of 3 mmol of acid 1-3. 10 mmol of an alcoholic solution of 1 mmol of TbCl₃, Gd(NO₃)₃, or EuCl₃ was added dropwise at stirring to the obtained solution. The precipitate was filtered off, washed with cold alcohol, and dried in air.

Gd(quin-OCH₃)₃·5H₂O (4). Yield 0.5084 g (47%). IR spectrum, v, cm⁻¹: 1609 [v_{as} (COO⁻)], 1397 [v_{s} (COO⁻)]. Found, %: C 56.48; H 4.63; Gd 14.51; N 3.84. GdC₅₁H₄₉N₃O₁₄. Calculated, %: C 56.45; H 4.55; Gd 14.49; N 3.87.

Tb(quin-OCH₃)₃·7H₂O (5). Yield 0.7584 g (68%). IR spectrum, v, cm⁻¹: 1608 [v_{as} (COO⁻)], 1390 [v_{s} (COO⁻)]. Found, %: C 54.51; H 4.78; N 3.76; Tb 14.17. TbC₅₁H₅₃N₃O₁₆. Calculated, %: C 54.55; H 4.76; N 3.74; Tb 14.15.

Eu(quin-OCH₃)₃·5H₂O (6). Yield 0.7268 g (67%). IR spectrum, v, cm⁻¹: 1601 [v_{as} (COO⁻)], 1402 [v_{s} (COO⁻)]. Found, %: C 56.74; H 4.65; Eu 14.09; N 3.85. EuC₅₁H₄₉N₃O₁₄. Calculated, %: C 56.72; H 4.57; Eu 14.07; N 3.89.

Gd(quin-Br)₃·7H₂O (7). Yield 0.7039 g (56%). IR spectrum, v, cm⁻¹: 1603 [v_{as} (COO⁻)], 1420 [v_{s} (COO⁻)]. Found, %: C 45.50; H 3.55; Gd 12.43; N 3.29. GdC₄₈H₄₄Br₃N₃O₁₃. Calculated, %: C 45.48; H 3.50; Gd 12.40; N 3.31.

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Tb(quin-Br)₃·6H₂O (8). Yield 0.9342 g (75%). IR spectrum, v, cm⁻¹: 1615 [v_{as} (COO⁻)], 1402 [v_{s} (COO⁻)]. Found, %: C 46.05; H 3.44; N 3.38; Tb 12.68. TbC₄₈H₄₂Br₃N₃O₁₂. Calculated, %: C 46.07; H 3.38; N 3.36; Tb 12.70.

Eu(quin-Br)₃·7H₂O (9). Yield 1.0646 g (84%). IR spectrum, v, cm⁻¹: 1585 [v_{as} (COO⁻)], 1404 [v_{s} (COO⁻)]. Found, %: C 45.65; H 3.58; Eu 12.07; N 3.35. EuC₄₈H₄₄Br₃N₃O₁₃. Calculated, %: C 45.67; H 3.51; Eu 12.04; N 3.33.

Gd[quin(CH₂)₄]₃·5H₂O (10). Yield 0.3845 g (41%). IR spectrum, v, cm⁻¹: 1593 [v_{as} (COO⁻)], 1396 [v_{s} (COO⁻)). Found, %: C 54.26; H 5.37; Gd 16.94; N 4.53. GdC₄₂H₄₉N₃O₁₁. Calculated, %: C 54.30; H 5.32; Gd 16.93; N 4.52.

Tb[quin(CH₂)₄]₃·10H₂O (11). Yield 0.7477 g (73%). IR spectrum, v, cm⁻¹: 1594 [v_{as} (COO⁻)], 1399 [v_{s} (COO⁻)]. Found, %: C 49.43; H 5.86; N 5.80; Tb 15.57. TbC₄₂H₅₉N₃O₁₆. Calculated, %: C 49.42; H 5.83; N 4.12; Tb 15.57.

Eu[quin(CH₂)₄]₃·6H₂O (12). Yield 0.7051 g (76%). IR spectrum, v, cm⁻¹: 1587 [v_{as} (COO⁻)], 1404 [v_{s} (COO⁻)]. Found, %: C 53.55; H 5.49; Eu 16.13; N 4.49. EuC₄₂H₅₁N₃O₁₂. Calculated, %: C 53.56; H 5.46; Eu 16.14; N 4.46.

FUNDING

This study was financially supported by the Ministry of Education and Science of Russian Federation (project no. 4.5547.2017/8.9, V.V. Dotsenko, I.V. Aksenova; project no. 4.1196.2017/4.6, N.A. Aksenov) and carried out using the equipment of Research Center "Diagnostics of Structure and Properties of Nanomaterials – Center for Collective Usage" and Center for Collective Usage "Ecological-Analytical Center" (universal identifier RFMEFI59317X0008) of Kuban State University.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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