

喹啉氧基乙酰胺的 Li(I)/Na(I)配合物及其高氯酸盐的结构和荧光性质

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摘要: 合成并通过 X 射线单晶衍射表征了配合物 $[\text{Li}(\text{L})_2]\text{ClO}_4$ (**1**) 和 $[\text{Na}(\text{L})_2]\text{ClO}_4$ (**2**) 的结构 (L 为 2-(5-氯-喹啉-8-基氧基)-1-吡咯烷酮)。单晶衍射结果表明, 配合物 **1** 与 **2** 同构, 金属离子与来自 2 个酰胺配体 L 的 N_2O_4 电子供体配位, 形成扭曲的八面体配位构型。此外, 还测定了配体高氯酸盐 $(\text{HL})\text{ClO}_4 \cdot \text{H}_2\text{O}$ 的结构, 并详细研究了 3 个化合物的荧光性质。

关键词: 主族金属配合物; 酰胺型配体; 喹啉; 晶体结构; 荧光

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Li(I)/Na(I) Complexes and Perchlorate Salt of 2-(5-Chloroquinolin-8-yloxy)-1-(pyrrolidin-1-yl)ethanone: Syntheses, Crystal Structures and Fluorescence Properties

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Abstract: Two complexes, $[\text{Li}(\text{L})_2]\text{ClO}_4$ (**1**) and $[\text{Na}(\text{L})_2]\text{ClO}_4$ (**2**) based on L (L=2-(5-chloroquinolin-8-yloxy)-1-(pyrrolidin-1-yl)ethanone) were synthesized and characterized by the X-ray diffraction analyses. The results show that complex **1** was isostructural with **2**. The metal ion in each complex with a distorted octahedron geometry is surrounded by two acetamide ligands with N_2O_4 donor set. In addition, the structure of the perchlorate salt of L, namely $(\text{HL})\text{ClO}_4 \cdot \text{H}_2\text{O}$ was demonstrated. The fluorescence properties of all compounds have been investigated in detail. CCDC: 1573564, **1**; 1573565, **2**; 1573566, $(\text{HL})\text{ClO}_4 \cdot \text{H}_2\text{O}$.

Keywords: main-group metal complexes; amide type ligand; quinoline; crystal structure; fluorescence

The complexes with the amide group have gained much attention due to their structural diversities, intriguing properties and applications in various fields^[1-2]. Such ligands with flexible structure, could form stable complexes with varies of transition metal or rare earth metal ions^[3-6]. To the best of our knowledge, however, the investigations on the complexes with main-group metal ions are relatively scarce. Thus, in this work, Li(I)/Na(I) complexes were obtained via the reaction of 2-(5-chloroquinolin-8-yloxy)-1-(pyrrolidin-1-yl)ethanone (L) with Li(I)/Na(I) perchlorate, which

have been characterized by X-ray diffraction. In CH_3CN solution, both complexes show similar fluorescence emission as L. However, under the same synthetic conditions, $(\text{HL})\text{ClO}_4 \cdot \text{H}_2\text{O}$ was accidentally produced in the case of Al(III) perchlorate, which exhibits quite different fluorescence spectra from that of L.

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were

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purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra ($\nu=4000\sim400\text{ cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer, in the measurements of emission and excitation spectra the pass width is 5 nm.

1.2 Preparations of **1**, **2** and (HL)ClO₄·H₂O

The ligand L^[7-8] (0.1 mmol) and LiClO₄, NaClO₄ or Al(ClO₄)₃ (0.1 mmol) were dissolved in the ethyl acetate/acetone (10 mL, 1:2, V/V) solution, respectively. The mixture was filtered and spontaneously volatilized at room temperature to obtain crystals of **1**, **2** and (HL)ClO₄·H₂O, respectively.

1: Colorless needles. Anal. Calcd. for C₃₀H₃₀Cl₃LiN₄O₈(%): C, 52.38; H, 4.40; N, 8.14. Found(%): C, 52.27; H, 4.52; N, 7.9. FT-IR (cm⁻¹): $\nu(\text{C}=\text{O})$ 1 650, $\nu(\text{C}=\text{N})$ 1 588, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 236.

2: Colorless plates. Anal. Calcd. for C₃₀H₃₀Cl₃NaN₄O₈(%): C, 51.19; H, 4.30; N, 7.96. Found(%): C, 51.07; H, 4.45; N, 7.78. FT-IR (cm⁻¹): $\nu(\text{C}=\text{O})$ 1 656, $\nu(\text{C}=\text{N})$ 1 593, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 238.

(HL)ClO₄·H₂O: Yellow rods. Anal. Calcd. for C₁₅H₁₅Cl₂N₂O₇ (%): C, 44.35; H, 3.72; N, 6.90. Found

(%): C, 44.13; H, 3.96; N, 6.67. FT-IR (cm⁻¹): $\nu(\text{C}=\text{O})$ 1 641, $\nu(\text{C}=\text{N})$ 1 594, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 231.

1.3 X-ray crystallography

The X-ray diffraction measurements for **1**, **2** and (HL)ClO₄·H₂O were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo K α radiation ($\lambda=0.071\ 073\text{ nm}$) by using φ - ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[9]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[10]. All non-hydrogen atoms were refined anisotropically. The C13 and C14 atoms of **1** occupied two positions, with the occupancy value of C13(C14)/C13B(C14B) being 0.692/0.308. The similar feature of C14 atom in **2** is observed, with the occupancy value of C14/C14B being 0.717/0.283. The H atoms for water molecule in (HL)ClO₄·H₂O are located from difference Fourier map and refined with restraints in bond length and thermal parameters. All the other H atoms were positioned geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements for **1**, **2** and (HL)ClO₄·H₂O are summarized in Table 1.

CCDC: 1573564, **1**; 1573565, **2**; 1573566, (HL)ClO₄·H₂O.

Table 1 Selected crystallographic data for **1**, **2** and (HL)ClO₄·H₂O

	1	2	(HL)ClO ₄ ·H ₂ O
Empirical formula	C ₃₀ H ₃₀ Cl ₃ LiN ₄ O ₈	C ₃₀ H ₃₀ Cl ₃ NaN ₄ O ₈	C ₁₅ H ₁₅ Cl ₂ N ₂ O ₇
Formula weight	687.87	703.92	409.21
T / K	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a / nm	1.315 4(2)	1.393 5(3)	0.704 0(2)
b / nm	0.923 66(13)	0.866 26(16)	0.902 8(3)
c / nm	1.428 0(2)	1.299(3)	1.457 8(5)
$\alpha / (^\circ)$			99.866(6)
$\beta / (^\circ)$	114.440(2)	112.796(3)	102.255(7)
$\gamma / (^\circ)$			96.336(6)
V / nm^3	1.579 5(4)	1.591 3(5)	0.881 6(5)
Z	2	2	2
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.446	1.469	1.542
$F(000)$	712	728	424

Continued Table 1

Unique reflections (R_{int})	2 673 (0.026 8)	2 805 (0.021 3)	3 084 (0.023 0)
Goodness-of-fit (GOF) on F^2	1.068	1.093	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1=0.049\ 7$, $wR_2=0.129\ 1$	$R_1=0.038\ 8$, $wR_2=0.100\ 0$	$R_1=0.067\ 4$, $wR_2=0.187\ 5$
R indices (all data)	$R_1=0.062\ 5$, $wR_2=0.140\ 2$	$R_1=0.055\ 3$, $wR_2=0.110\ 6$	$R_1=0.100\ 5$, $wR_2=0.214\ 2$

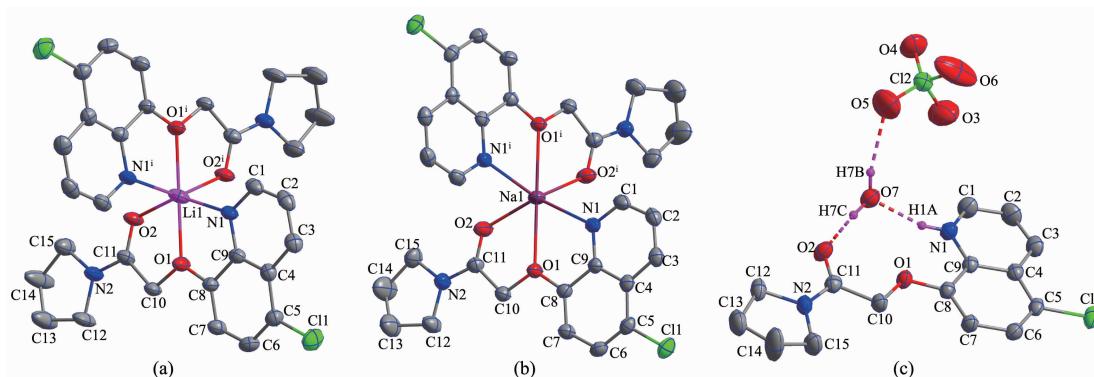
2 Results and discussion

2.1 Crystal structures

A diamond drawing of **1**, **2** and (HL)ClO₄·H₂O is shown in Fig.1. Selected bond distances are summarized in Table 2. Complexes **1** and **2** are isostructural and crystallize in the monoclinic, space group $P2_1/n$. Thus the structure of **1** is discussed in detail for an example. As shown in Fig.1a, the asymmetric unit of **1** contains a half of coordination cation with the Li(I)

ion lying on the two-fold rotate axis, and a half of free perchlorate anion for charge balance. The Li(I) ion in **1** is surrounded by two acetamide ligands with N₂O₄ donor set, thus giving a distorted octahedron geometry^[11-12]. As expected, there exist no classic hydrogen bonds in both complexes.

In (HL)ClO₄·H₂O, the distances of C=N and C=O are slightly shorter than those in **1** and **2**, probably due to the protonation of quinoline N atom and the formation of hydrogen bonds, respectively. In the



Disordered perchlorate anion and carbon atoms are not shown for clarity in (a) and (b); Symmetry codes: $i -x+1/2, y, -z+3/2$ for **1** and **2**

Fig.1 Diamond drawing of **1** (a), **2** (b) and (HL)ClO₄·H₂O (c) with 30% thermal ellipsoids

Table 2 Selected bond lengths (nm) and angles (°) in **1**, **2** and (HL)ClO₄·H₂O

1					
Li1-O1	0.212 84(16)	Li1-O2	0.207 9(4)	Li1-N1	0.226 4(5)
O2 ⁱ -Li1-O2	103.0(3)	O1 ⁱ -Li1-O1	173.4(4)	O2-Li1-O1 ⁱ	109.95(16)
O2-Li1-O1	74.35(10)	O1-Li1-N1	72.11(11)	O2-Li1-N1 ⁱ	87.76(7)
N1-Li1-N1 ⁱ	100.8(3)	O1-Li1-N1 ⁱ	103.53(17)	O2-Li1-N1	146.45(7)
2					
Na1-O1	0.245 27(14)	Na1-O2	0.229 85(19)	Na1-N1	0.247 1(2)
O2 ⁱ -Na1-O2	112.97(12)	O1 ⁱ -Na1-O1	178.09(10)	O2-Na1-N1	130.95(6)
O2-Na1-O1 ⁱ	114.89(6)	O2-Na1-N1 ⁱ	86.57(6)	O1-Na1-N1	64.71(5)
O2-Na1-O1	66.27(5)	O1-Na1-N1 ⁱ	114.16(6)	N1i-Na1-N1	114.73(10)
(HL)ClO ₄ ·H ₂ O					
N1-C1	0.129 6(6)	N1-C9	0.135 8(5)	O1-C8	0.135 0(5)
O1-C10	0.142 1(5)	O2-C11	0.122 2(5)	N2-C11	0.131 7(6)

Symmetry codes: $i -x+1/2, y, -z+3/2$ for **1** and **2**.

crystal, the cation (HL)⁺ and free perchlorate anion are linked by crystal water molecule via intermolecular N-H \cdots O (N1-H1A \cdots O7, with D \cdots A distance being 0.261 1(5) nm, D-H \cdots A angle being 163.0°) and O-H \cdots O hydrogen bonds (O7-H7C \cdots O2, with D \cdots A distance being 0.267 3(5) nm, D-H \cdots A angle being 173.0°; O7-H7B \cdots O5, with D \cdots A distance being 0.295 3(4) nm, D-H \cdots A angle being 160.0°).

2.2 IR spectra

The spectral regions for both complexes are more or less similar due to the similarity in coordination modes of the ligand with the metal centre. The free ligand L exhibit three absorption bands at 1 682, 1 598 and 1 241 cm⁻¹, assigned to $\nu(\text{C=O})$, $\nu(\text{C=N})$ and $\nu(\text{C-O-C})$, respectively^[13-16]. However, in complexes **1** and **2**, such three absorption bands shift evidently to lower frequency, indicating that the oxygen atoms of the carbonyl group, quinoline nitrogen atoms and ethereal oxygen atoms take part in coordination to the central metal ion. In addition, compared with that of the ligand, the stretching vibration frequency of the C=O (at 1 641 cm⁻¹) and C=N (at 1 594 cm⁻¹) of (HL)ClO₄·H₂O shifted by 41 cm⁻¹ and 4 cm⁻¹, indicating the existence of hydrogen bonds involving carbonyl group and the protonation of the quinoline nitrogen atom^[17].

2.3 UV spectra

The UV spectra of **1**, **2** and (HL)ClO₄·H₂O in CH₃CN solution (concentration: 10 $\mu\text{mol}\cdot\text{L}^{-1}$) were measured at room temperature (Fig.2). The spectra of L features two main band located around 244 nm (ε =

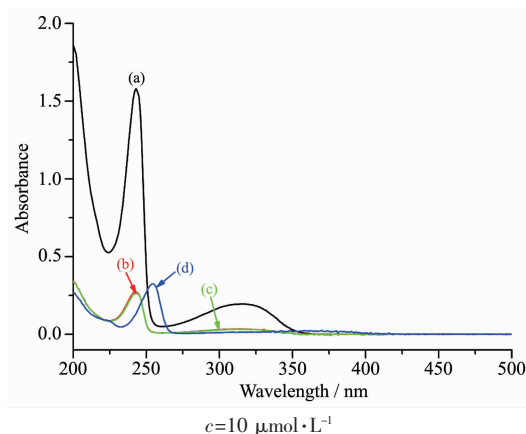
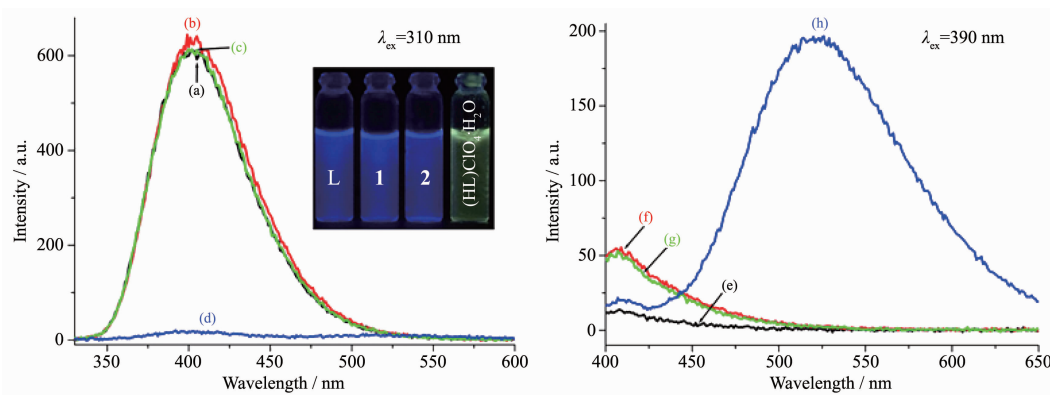


Fig.2 UV spectra of L (a), **1** (b), **2** (c) and (HL)ClO₄·H₂O (d) in CH₃CN solution at room temperature

156 000 L·mol⁻¹·cm⁻¹) and 316 nm (ε =19 500 L·mol⁻¹·cm⁻¹), which could be assigned to characteristic π - π^* transition centered on quinoline ring and the acetamide unit, respectively^[18]. Similar bands are observed in **1** (242 nm, ε =26 948 L·mol⁻¹·cm⁻¹; 314 nm, ε =3 389 L·mol⁻¹·cm⁻¹) and **2** (243 nm, ε =26 072 L·mol⁻¹·cm⁻¹; 314 nm, ε =3 198 L·mol⁻¹·cm⁻¹). The hyperchromicities indicate that the ligand L take part in the coordination in **1** and **2**. However, a significant red-shift (254 nm, ε =32 400 L·mol⁻¹·cm⁻¹; 371 nm, ε =1 850 L·mol⁻¹·cm⁻¹) can be observed in the case of (HL)ClO₄·H₂O, probably due to the protonation of quinoline N atom^[19].

2.4 Fluorescence spectra

The fluorescence spectra of **1**, **2** and (HL)ClO₄·H₂O in CH₃CN solution (concentration: 10 $\mu\text{mol}\cdot\text{L}^{-1}$) were measured at room temperature (Fig.3). When



$c=10\ \mu\text{mol}\cdot\text{L}^{-1}$; Inset: solution colour of L, **1**, **2**, and (HL)ClO₄·H₂O under 365 nm UV lamp

Fig.3 Fluorescence emission spectra of L (a, e), **1** (b, f), **2** (c, g), and (HL)ClO₄·H₂O (d, h) in CH₃CN solution at room temperature excited at different wavelengths

excited at 310 nm, complexes **1** and **2** show a broad emission at 403 nm as the free ligand L^[18], while (HL)ClO₄·H₂O exhibits almost no emission under the same tested conditions (Fig.3A). On the contrary, (HL)ClO₄·H₂O could display intense green emission (at 525 nm) observed by naked eyes at excitation of 390 nm (Fig. 3B). The protonation of nitrogen atoms can greatly enhance the electron-withdrawing ability of quinoline, which may lead to a little bit delocalize. Meanwhile, the delocalization of the electron cloud density can help to stabilize the molecules in the excited states, which is contributed to the shifts of the fluorescence spectra to longer wavelength^[20].

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