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# A new pyrazoline-based fluorescent sensor for Al<sup>3+</sup> in aqueous solution



SPECTROCHIMICA ACTA

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#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T



- The structure of the pyrazoline was confirmed by single crystal X-ray diffraction.
- This sensor can be used to determine Al<sup>3+</sup> ion with high selectivity.
- It is the first example of Al<sup>3+</sup> ion fluorescent chemosensor based on pyrazoline chromophore.



Pyrazoline derivate 1 for selective detection of Al<sup>3+</sup> with fluorescence quenching

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#### Introduction

Aluminum is the most abundant element in the Earth's crust and its compounds are widely used in the water treatment, in food additives, in medicines and in the production of light alloy, etc. [1]. The toxicity of Al<sup>3+</sup> not only hampers plant performance [2], killing

### ABSTRACT

A new pyrazoline-based fluorescent sensor was synthesized and the structure was confirmed by single crystal X-ray diffraction. The sensor responds to  $A^{3^+}$  with high selectivity among a series of cations in aqueous methanol. This sensor forms a 1:1 complex with  $A^{3^+}$  and displays fluorescent quenching. © 2014 Elsevier B.V. All rights reserved.

> fish in acidified waters [3] but also damages the central nervous system to cause human illnesses like dementia and encephalopathy [4], Parkinson's disease [5], and Alzheimer's disease [6]. Thus, the detection of Al<sup>3+</sup> has attracted increasing interest in the areas of chemical and biological sciences. Compared with some conventional methods, fluorescent sensors for various metal ions have attracted significant focus because of the advantages such as high sensitivity, selectivity, rapid response time and versatility [7]. However, the poor coordination ability of Al<sup>3+</sup> compared to the transition metal ions [8] makes the development of an Al<sup>3+</sup> fluorescent sensor difficult. Only a few Al<sup>3+</sup> selective fluorescent sensors have so far been reported [9–16]. Most of them were operated in

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Scheme 1. Synthesis of pyrazoline derivate 1.



Fig. 1. The molecular structure of compound 1, with displacement ellipsoids drawn at the 30% probability level.

organic solvent, which limited their applications. Therefore, the development of new efficient Al<sup>3+</sup> fluorescent chemosensors, especially those that are simple to synthesise, and can work in aqueous solution with high selectivity and sensitivity is still a challenge.

# 1,3,5-Triaryl-2-pyrazolines, with their rigid but only partly unsaturated central pyrazoline ring, are well-known fluorescent compounds widely used in fluorescent dyes emitting blue fluorescence with high fluorescence quantum yield [17–21] and electroluminescence fields [22–28], However, the pyrazoline-based fluorescent sensor for metal ions is still rare [29–32]. Recently, we had reported two selective pyrazoline-based fluorescent chemosensor for $Cu^{2+}$ [33] and Fe<sup>3+</sup> [34]. In continuing our research to develop new fluorescent chemosensors based on pyrazoline chromophore, we design a new pyrazoline derivative **1.** The primary test showed that **1** possesses a highly selective response of fluorescence quenching toward Al<sup>3+</sup> in MeOH /H<sub>2</sub>O (95:5, v/v) solution.

#### Experimental

#### Reagents

All the reagents were purchased from commercial suppliers and used without further purification. The salts used in stock solutions of metal ions were CoCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, KCl, NaCl, CuCl<sub>2</sub>·2H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CdCl<sub>2</sub>·2H<sub>2</sub>O, HgCl<sub>2</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, MgCl<sub>2</sub>. ·6H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O.

#### Apparatus

NMR spectra were measured on a Varian Mercury 300 spectrometer operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C relative to tetramethylsilane as internal standard. MS spectra were obtained on a Finnigan Trace MS spectrometer. Elemental analyses were performed with a Vario EL-III instrument (Germany). IR

Table	1
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Crystal structure data and structure refinement for **1**.

Empirical formula	C <sub>26</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> S
Formula weight	457.53
Temperature	298(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	24.516(4)
b (Å)	9.1979(13)
c (Å)	20.561(3)
α	90°
β	101.315(2) °
γ	90°
V (Å <sup>3</sup> )	3669.9(6)
Ζ	8
Density (calculated)	1.337 Mg/m <sup>3</sup>
Index ranges	$-35 \le h \le 35, -12 \le k \le 13, -29 \le l \le 29$
F(000)	1616
Crystal size	$0.15 \times 0.12 \times 0.10 \text{ mm}$
$\theta$ range for data collection	1.69-30.99°
Reflections collected	24263
Independent reflections	7184 $[R_{(int)} = 0.1222]$
Max. and min. transmission	0.9826 and 0.9740
Data/restraints/parameters	7184/0/300
Goodness-of-fit on $F^2$	0.842
Absorption correction	None
Final R indices $(I > 2 \sigma(I))$	R1 = 0.0519, wR2 = 0.1026
R indices (all data)	<i>R</i> 1 = 0.1228, <i>wR</i> 2 = 0.1270
Largest diff. peak and hole	0.245 and -0.369 e Å <sup>-3</sup>

spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in cm<sup>-1</sup>. Absorption spectra were determined on UV-2501 PC spectrophotometer. Fluorescence spectra measurements were performed on a Fluoro-Max-P spectrofluorimeter equipped with a xenon discharge lamp, 1 cm quartz cells at room temperature (about 298 K).

#### Synthesis of ethyl 2-(2-(1-(benzo[d]thiazol-2-yl)-4-phenyl-4,5dihydro-1H-pyrazol-3-yl)phenoxy)acetate (1)

The synthetic route of the compound **1** is shown in Scheme **1**. Starting material pyrazoline (**4**) was synthesized according to

literature [33]. A mixture of pyrazoline (4) (0.37 g, 1 mmol), ethyl bromoacetate (0.20 g, 1.2 mmol), KI (0.17 g, 1 mmol), K<sub>2</sub>CO<sub>3</sub> (0.33 g, 2.4 mmol), and acetone (25 ml) was stirred at reflux for 2 h. After cooling, the mixture was filtered and the filtrate was evaporated to afford residue. The residue was crystallized from ethanol to afford **1** (0.27 g) as a white solid, Yield: 60%; Mp: 143-144 °C;IR (KBr, cm<sup>-1</sup>): 3423, 2920, 2359, 1752, 1597, 1540, 1444, 1320, 1280, 1210, 1124, 1083, 809, 754;<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ8.07-8.10 (m, 1H), 7.61-7.63 (m, 1H), 7.49-7.51 (m, 1H), 7.20-7.37 (m, 8H), 7.06-7.10 (m, 2H), 6.77-6.80 (m, 1H), 5.78 (dd, 1H, J = 4.5, 4.5 Hz, pyrazoline-H), 1.23 (t, 3H, CH3-H); 4.62 (s, 2H); 4.18–4.29 (m, 3H), 3.58 (dd, 1H, J = 4.5, 4.5 Hz, pyrazoline-H), 1.23 (t, 3H, CH3-H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 168.2, 163.5,155.9, 152.6, 141.5, 131.7, 131.3, 129.6, 128.8, 127.6, 126.0, 125.6, 122.0, 119.9, 112.3, 65.5, 63.8, 61.5, 47.0, 14.1; ESI-MS: m/ z: 458.7 [M + H]<sup>+</sup>. Anal. calcd for C<sub>26</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>S: C 68.25, H 5.07, N 9.18: found: C 68.22. H 5.04. N 9.14.

#### X-ray crystallography of compound 1

Suitable single crystals of **1** for X-ray structural analysis were obtained by slow evaporation of a solution of **1** in CHCl<sub>3</sub>—CH<sub>3</sub>OH (20:1, v/v) mixture at room temperature. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 296(2)*K*. The structures were solved by direct methods with SHEL-XS-97 program and refinements on *F*<sup>2</sup> were performed with SHEL-XL-97 program by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and  $U_{iso}(H) = 1.2 U_{eq}(C)$ .

#### **Binding titration**

The stock solutions of **1**  $(1.0 \times 10^{-5} \text{ M})$  were prepared by dissolving **1** in MeOH/water(95:5, v/v) containing HEPES buffer(10 mM, pH = 7.0). The cationic stocks were all in MeOH with



Fig. 2. A packing diagram for 1, viewed along the c-axis.



**Fig. 3.** UV-vis spectral changes of compound **1** ( $1 \times 10^{-5}$  M) in MeOH/water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0) upon additions of various metal ions ( $1 \times 10^{-5}$  M).



**Fig. 4.** UV absorbance spectra of **1**  $(1.0 \times 10^{-5} \text{ M})$  upon the addition of various amounts of Al<sup>3+</sup>. The inset shows the absorbance intensity at  $\lambda max = 342 \text{ nm}$  as a function of Al<sup>3+</sup> concentration.

a concentration of  $3.0 \times 10^{-3}$  M for UV–vis absorption and fluorescence spectra analysis. For metal ion absorption and fluorescence titration experiments, each time 3 mL solution of **1** filled in a quartz cell of 1 cm optical path length, and we increased concentrations of metal ions by stepwise addition of different equivalents using a micro-syringe. After each addition of Al<sup>3+</sup> ion, the solution was stirred for 3 min. The volume of cationic stock solution added was less than 100 µL with the purpose of keeping the total volume of testing solution without obvious change. For all measurements of fluorescence spectra of **1**, the excitation was at 360 nm.

#### **Results and discussion**

#### Synthesis and structural characteristics of 1

The sensor **1** was obtained by the reaction of pyrazoline derivative (**4**) with ethyl bromoacetate in acetone under reflux with  $K_2CO_3$  as base and KI as catalyst. The yield of **1** was 60%. The structures of **1** were identified by using <sup>1</sup>H NMR, IR and MS. The structure of **1** was further confirmed by X-ray diffraction analysis.

The molecular view of **1** is shown in Fig. 1. A summary of crystallographic data collection parameters and refinement parameters for 1 are compiled in Table 1.



**Fig. 5.** Fluorescence emission spectra of **1**  $(10^{-5} \text{ M})$  was titrated with Al<sup>3+</sup> (0-2 equiv) in MeOH/water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0).



**Fig. 6.** Job's plot for determining the stoichiometry for **1** and Al<sup>3+</sup> in MeOH/water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0). Total concentration =  $1.0 \times 10^{-5}$  M.

The structure of compound **1** is crystallized in Monoclinic space group C2/c. Two benzene moieties and a benzothiazole moiety are bonded to the pyrazoline ring at the atoms of C8, C10 and N2, respectively. Consistent with a pronounced electronic interaction, the bond lengths of C10–C17, N2–C7 are significantly shorter as would be expected for a single bond. Moreover, the bond lengths of N2–N3, N3–C10, C8–C9 agree well with the equivalent ones in similar structures [35]. In the crystal of **1**, the torsion angle C7–N2–C8–C11 of  $-63.44(10)^{\circ}$  shows C7 in the benzothiazole moiety adopts an antiperiplanar conformation with respect to the C11 atom of the benzene ring. In the asymmetry unit, the pyrazoline ring and benzothiazole is almost coplanar, while the pyrazoline ring is not coplanar with benzene ring(C11-C16) and benzene ring(C17-C22), the dihedral angle between pyrazoline and them is  $6.86(11)^{\circ}$  and  $87.08(12)^{\circ}$ , respectively.

The packing diagram of the compound **1** is shown in Fig. 2. The molecules are connected by weak  $\pi$ - $\pi$  interactions and C—H- $\pi$  interaction. C4–Cg4 3.559(2) Å C9–Cg5 3.501(2) Å C25–Cg3 3.571(2) Å and C25–Cg5 3.616(2) Å.

#### Spectral characteristics

The absorption spectrum of compound 1 exhibits a broad band at 342 nm at room temperature in  $(1 \times 10^{-5} \text{ tM})$  in MeOH/water



Fig. 7. Benesi-Hildebrand linear analysis plots of 1 at different Al<sup>3+</sup> concentration.



**Fig. 8.** Fluorescence spectra of  $1 (1 \times 10^{-5} \text{ M})$  in MeOH/water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0) in the presence of different metal ions (2 equiv). Inset: Photos of **1** in MeOH/water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0) without and with addition of Al<sup>3+</sup> under the irradiation of UV light at 365 nm.

(95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0). Binding affinities of compound **1** toward metal ions (Na<sup>+</sup>, Cr<sup>3+</sup>, Mg<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup> ions) were evaluated by UV–vis spectroscopy measurements. Upon addition of these metal ions, the absorption spectrum changes in different manner as shown in Fig. 3. In the case of Na<sup>+</sup>, Cr<sup>3+</sup>, Mg<sup>2+</sup>, Mg<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, K<sup>+</sup> absorption curve did not change, whereas in the case of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Al<sup>3+</sup> ions, the addition of metal ions caused a increase of absorption intensity at 342 nm. Moreover, upon addition of Fe<sup>3+</sup> and Cu<sup>2+</sup> to a solution of **1**, two new absorption peaks appeared obviously at 292 nm and 288 nm, respectively.

The UV-vis absorption spectra of **1**  $(1 \times 10^{-5} \text{ M})$  in MeOH/ water (95:5, v/v) containing HEPES buffer (10 mM, pH = 7.0) in the presence of various concentrations of Al<sup>3+</sup> ion (0–2 × 10<sup>-5</sup> M) are shown in Fig. 4, and the inset shows the plots of changes as a function of increasing concentrations of Al<sup>3+</sup>. As shown in Fig. 4, the UV absorbance of **1** at 342 nm enhanced from 0.187 to 0.49 when increasing concentration of Al<sup>3+</sup> from 0 to 2 × 10<sup>-5</sup> M, which indicates the formation of a new complex between compound **1** and Al<sup>3+</sup>. A satisfactory linear relationship between UV-vis absorbance and Al<sup>3+</sup> concentration was observed with the correlation coefficient as high as 1.00.



**Fig. 9.** Competitive experiments in the **1** + Al<sup>3+</sup> system with interfering metal ions. [**1**] =  $1 \times 10^{-5}$  M, [Al<sup>3+</sup>] =  $2 \times 10^{-5}$  M, and [M<sup>n+</sup>] =  $2 \times 10^{-5}$  M. Excited at 360 nm and emission collected at 473 nm.



Fig. 10. Partial infrared spectra (KBr) of free 1 and 1 with Al<sup>3+</sup> at room temperature.

The fluorescence titration spectra of **1** in MeOH/water (95:5, v/ v) containing HEPES buffer (10 mM, pH = 7.0) with Al<sup>3+</sup> shows an emission maximum peak at 473 nm (Fig. 5). The fluorescence quantum yield of compound **1** in the absence of Al<sup>3+</sup> was calculated to be 0.33 with respect to quinine sulphate in 0.1 N H<sub>2</sub>SO<sub>4</sub> solution ( $\Phi_s = 0.54$ ) [36]. As Al<sup>3+</sup> ion was gradually titrated, the fluorescence intensity of compound **1** gradually decreased and when the amount of Al<sup>3+</sup> ion added was about  $2 \times 10^{-5}$  M, the fluorescence intensity almost reached minimum. The quantum yield of **1** was calculated to be 0.029 in the presence of Al<sup>3+</sup> ion ( $2 \times 10^{-5}$  M) and almost reduced to 8.7% of the initial one.



Scheme 2. The proposed 1:1 bonding model of the 1-Al<sup>3+</sup> complex.

To determine the stoichiometry of compound **1** and  $Al^{3+}$  ion in the complex, Job's method [37] was employed by using the emission changes at 473 nm as a function of molar fraction of  $Al^{3+}$ . A maximum emission was observed when the molar fraction of  $Al^{3+}$  reached 0.5 (Fig. 6), indicating that  $Al^{3+}$  ions form a 1:1 complex with the sensing compound.

Using the adjusted equation of Benesi–Hildebrand [38] Eq. (1), we made the calculation of stability constant ( $K_a$ ).

$$1/(F - F_0) = 1/(F_\infty - F_0)Ka[G] + 1/(F_\infty - F_0)$$
<sup>(1)</sup>

Applying the Eq. (1), graph obtained was illustrated in Fig. 7. Where  $F_0$  represents the fluorescence intensity in the absence of Al<sup>3+</sup> ion, F is the fluorescence intensity with the Al<sup>3+</sup> ion and [G] represents the concentration of guest Al<sup>3+</sup> ion. The stability constant ( $K_a$ ) value obtained from the Benesi–Hildebrand was  $1.75 \times 10^5 \text{ M}^{-1}$  (error limits  $\leq 10\%$ ). The detection limit, based on the definition by IUPAC ( $C_{\text{DL}}$  = 3 Sb/m) [39], was found to be  $2.27 \times 10^{-7}$  M from 10 blank solutions.

The selectivity and tolerance of compound **1** for Al<sup>3+</sup> ion over other metal cations such as K<sup>+</sup>, Na<sup>+</sup>, Cr<sup>3+</sup>, Mg<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup> ions were investigated by adding metal cations ( $2 \times 10^{-5}$  M) to the solution of compound **1** ( $1 \times 10^{-5}$  M). As depicted in Fig. 8, Al<sup>3+</sup> produced significant quenching in the fluorescent emission of **1**, the other tested metals only show relatively insignificant changes, this means that sensor **1** has a high selectivity to Al<sup>3+</sup> ion.

To further gauge selectivity for  $Al^{3+}$  ion over other metal ions, competition experiments of  $Al^{3+}$  ion mixed with other metal ions were carried out from fluorescence spectra and the results are shown in Fig. 9. The fluorescence intensity of  $1 (1 \times 10^{-5} \text{ M})$  in the presence of 2 equiv of the  $Al^{3+}$  ion was almost unaffected by the addition of 2 equiv of competing metal ions (Cd<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, K<sup>+</sup>, Fe<sup>3+</sup>, and Na<sup>+</sup>). These results suggested that molecule 1 could be used as  $Al^{3+}$  selective fluorescent chemosensor.

To gain a clearer understanding of the structure of  $1-Al^{3+}$  complexes, we used IR spectroscopy to obtain structural information about  $Al^{3+}$  binding in **1**. For the free compound **1**, the carbonyl group of ester showed a characteristic IR peak at 1752 cm<sup>-1</sup>, which corresponds to a structural mode involving asymmetric stretching of the carbonyl group. Upon addition of  $Al^{3+}$ , this carbonyl group IR peak displayed distinct shift from  $1752 \text{ cm}^{-1}$  to  $1634 \text{ cm}^{-1}$  (Fig. 10). This suggested that carbonyl group participates in the coordination with  $Al^{3+}$ . There was a bond formed between  $Al^{3+}$  and the oxygen atom in the C=O bond. The complexation of  $Al^{3+}$  ion and **1** was also supported by  $Al^{3+}$  induced chemical shift of **1** changes in the <sup>1</sup>H NMR spectra (see Figs. S1 and S2 in Supplementary data). In the presence of 1.0 equivalents of  $Al^{3+}$  ions, chemical

shift of proton NMR signals corresponding to the  $-OCH_2CO-$  was shifted by 0.0004 ppm. Other obvious change in the chemical shifts of proton of Ar-H and pyrazoline-H are also can be observed owing to the binding of the Al<sup>3+</sup>.

Based on above IR spectroscopy, NMR spectroscopy studies, and Job's plot, the proposed binding model of  $Al^{3+}$  with **1** was shown in Scheme 2. The chemosensor **1** is the most likely to chelate  $Al^{3+}$  via its oxygen on the ether, oxygen on the carbonyl group, as well as nitrogen on the thiazole and pyrazoline. The capture of  $Al^{3+}$  resulted in the electron or energy transfer from **1** to  $Al^{3+}$ ; thus, **1** showed quenching of the fluorescence for  $Al^{3+}$  and provided a high selectivity for  $Al^{3+}$  over the other tested metal ions.

#### Conclusion

In summary, a new selective fluorescent sensor based on a pyrazoline derivate was synthesized and used for the determination of  $Al^{3+}$  ion with high selectivity in MeOH/water(95:5, v/v) containing HEPES buffer(10 mM, pH = 7.0). This sensor formed a 1:1 complex with  $Al^{3+}$  and showed a fluorescent quenching.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.10.005.

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