SSRG International Journal of Applied Chemistry
ISSN: 2393 – 9133 /doi:10.14445/23939133/IJAC-V8I1P107

Volume 8 Issue 1, 30-33, Jan-April 2021

Coordination Property of Three Benzoylhydrazine Based Schiff-base Compounds: A Comparative Studied with UV-vis Method

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Received Date: 28 February 2021
Revised Date: 16 March 2021
Accepted Date: 19 April 2021

Abstract *- Three Schiff base compounds L_{1-3} derived from benzoyl hydrazine were synthesized, and the coordination properties were characterized by the UV-vis method. The results showed that the active groups had a great effect on the coordination ability of these compounds. L_1 bearing OH as active groups showed good affinity and selectivity to Al^{3+}, L_2 with NH_2 groups had no obvious selectivity to any metal ions, and L_3 showed good selectivity to Cu^{2+}.*

Keywords — *Schiff base; Coordination property; Metal ions; Fluorescent probe; UV-vis method*

I. INTRODUCTION

Schiff base compounds have many advantages, such as easy synthesis, various properties, and adjustable structure made them good components for the construction of organic metal complexes and antibacterial reagents[1-8]. Schiff base complexes with conjugated structures have important application value in fluorescent materials[9-14], and many excellent probes have been synthesized and reported[9-18].

Among the probes based on different fluorophores, benzohydrazide derivatives are easy to prepare and purify and have been characterized as fluorescent probes for the detection of many environmentally and biologically relative targets[18-23]. Based on the above-mentioned reasons, three Schiff base compounds derived from benzoyl hydrazine were synthesized and characterized in this work.

II. EXPERIMENTAL SECTION

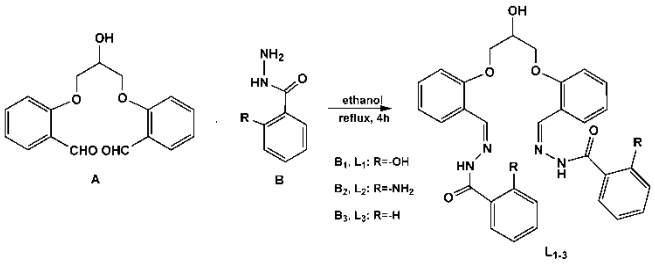
A. Reagents and Instruments

All reagents are commercially available and used directly. The reagents used in the experiment process were commercially available and used directly. The metal ions salts employed are NaCl, KCl, $CaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $CdCl_2$, $HgCl_2$, $FeCl_2{\cdot}4H_2O$, $CrCl_3{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $AgNO_3$, $CoCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $CuCl_2{\cdot}2H_2O$, $PbCl_2$, and $NiCl_2{\cdot}6H_2O$.

MS were recorded on a Thermo TSQ Quantum Access Agillent 1100 system. UV-vis spectra were obtained on a Hitachi U-2910 spectrophotometric. Nuclear magnetic resonance (NMR) spectra were measured with a Bruker AV 400 instrument, and chemical shifts are given in ppm from tetramethylsilane (TMS).

B. Synthesis of P

The synthesis route of $\mathbf{L_{1-3}}$ was shown in Scheme 1.



Scheme 1. Synthesis route of $\mathbf{L_{1-3}}$

Compound **A**[24] and $\mathbf{L_1}$[25] were synthesized according to the reported method, respectively. $\mathbf{L_{2-3}}$ was synthesized as a similar method to $\mathbf{L_1}$.

Compound **A** (0.15 mmol) and **B** (0.31 mmol) were reacted in ethanol (40 mL) and stirred under reflux for 4 h, and then the mixture was cooled to room temperature, the precipitate so obtained was filtered and dried in vacuum. The product was used directly.

$\mathbf{L_1}$[25]: White solid. Yields: 83.4%. MS m/z: 569.14 $[M+H^+]^+$, 591.27 $[M+Na^+]^+$. ^{1}H-NMR (DMSO-d_6): 11.88 (s, 2H), 8.81 (s, 2H), 7.88 (d, 2H), 7.87 (t, 2H), 7.85 (t, 2H), 7.44 (d, 2H), 7.39 (t, 2H), 7.16 (d, 2H), 7.01 (t, 2H), 6.96 (d, 2H), 6.34 (d, 2H), 5.46 (m, 1H), 4.28 (d, 4H) , 4.22 (t, 1H).

$\mathbf{L_2}$: Yellow solid. Yields: 81.5%. MS m/z: 567.16

$[M+H^+]^+$. ^{1}H-NMR (DMSO-d_6): 11.62 (s, 2H), 8.75 (s, 2H), 7.84 (d, 2H), 7.52 (d, 2H), 7.36 (t, 2H), 7.18 (t, 2H), 7.13 (d, 2H), 6.99 (t, 2H), 6.73 (d, 2H), 5.55 (t, 2H), 6.34 (b, 4H), 5.40 (m, 1H), 4.26 (d, 4H), 4.21 (t, 1H).

L$_3$: White solid. Yields: 86.4%. MS m/z: 537.23 $[M+H^+]^+$, 559.41 $[M+Na^+]^+$. ^{1}H-NMR (DMSO-d_6): 11.87 (s, 2H), 8.82 (s, 2H), 7.89 (d, 4H), 7.86 (d, 2H), 7.57 (t, 2H), 7.51 (t, 4H), 7.38 (t, 2H), 7.15 (d, 2H), 7.01 (t, 2H), 5.42 (m, 1H), 4.28 (d, 4H), 4.22 (t, 1H).

C. General Spectroscopic Methods

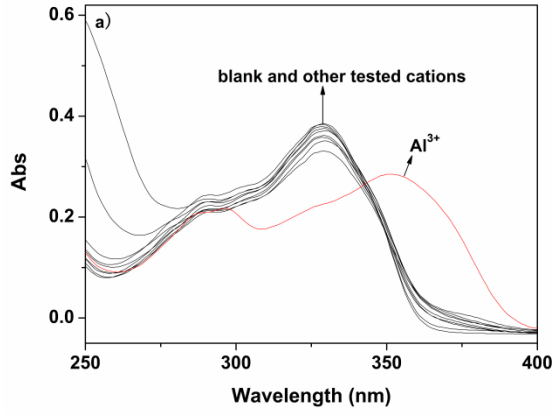
1.0 mM stock solutions were obtained by dissolving salts and **L$_{1\text{-}3}$** in deionized water and dimethylsulfoxide (DMSO), respectively. The testing solutions were freshly prepared before spectroscopic measurements, and the desired concentration was obtained by diluting the stock solutions.

III. RESULTS AND DISCUSSION

A. Selectivity Measurement

The selectivity of compounds **L$_{1\text{-}3}$** was firstly studied by using the UV-vis method. The UV-vis spectra of **L$_{1\text{-}3}$** (10 μM) were investigated in ethanol with the addition of respective metal ions (10 μM) (Fig. 1). The tested metal ions were K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, Al^{3+} and Ag^+.

The addition of Al^{3+} to the solution of **L$_1$** induced an apparent red-shift of absorbance in the UV-vis region, and a new peak at 360 nm appeared (Fig. 1a). The absorbance in the UV-vis region decreased at 325 nm. The addition of Cu^{2+} to the solution of **L$_3$** induced an apparent red-shift of absorbance in the UV-vis region (Fig.1c). From the results, we can know that **L$_1$** and **L$_3$** had better selectivity towards Al^{3+} and Cu^{2+} than other tested metal ions, respectively. The UV-vis selective result of **L$_1$** was in accordance with the fluorescent detection study[25]. However, **L$_2$** showed no obvious selectivity to any target among the tested ions (Fig. 1b). So the coordination property of **L$_1$** and **L$_3$** were studied further.



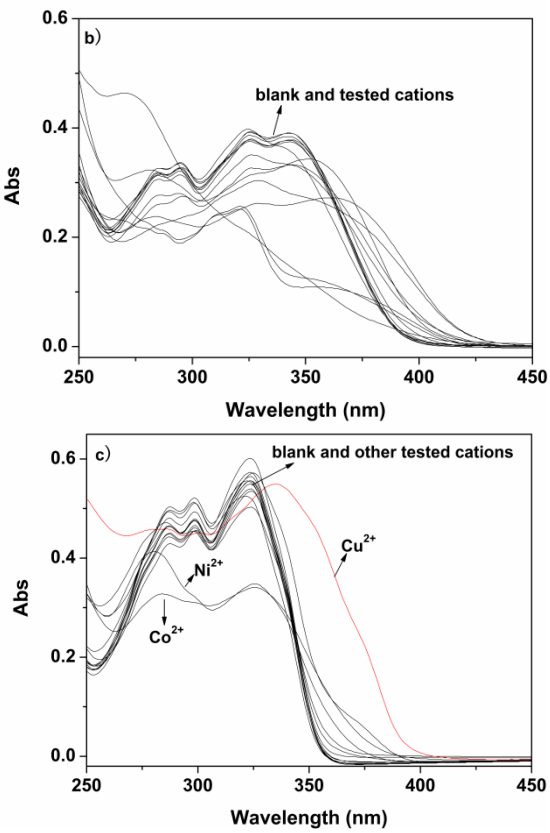


Fig. 1 Selectivity measurements of L$_{1\text{-}3}$ with tested metal ions in ethanol.

B. UV-vis Titration Experiments of L$_1$ with Al^{3+} and L$_3$ with Cu^{2+}

In order to study the reaction of **L$_1$** with Al^{3+} and **L$_3$** with Cu^{2+} further, UV-vis titration experiments were carried out (Fig. 2). From the results, we can see that there is a regular change in the UV-vis spectra at 375 and 430 nm, followed by the introduction of various concentrations of Al^{3+} to the solution of **L$_1$** in ethanol (Fig. 2a). For **L$_3$**, regular changes in the UV-vis spectra were observed at 255 and 365 nm, followed an increase in the content of Cu^{2+} in ethanol of **L$_3$** (Fig. 2b). The study clearly suggested that new complexes of **L$_1$**-Al^{3+} and **L$_3$**-Cu^{2+} were formed.

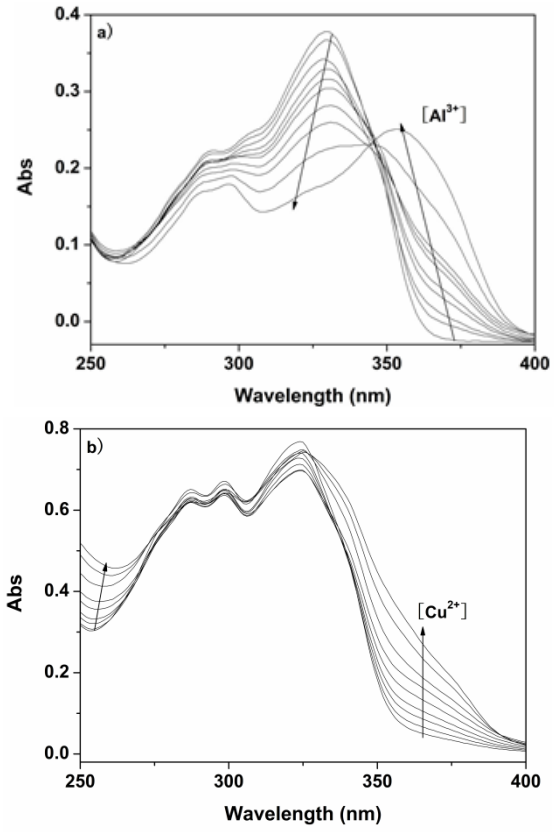
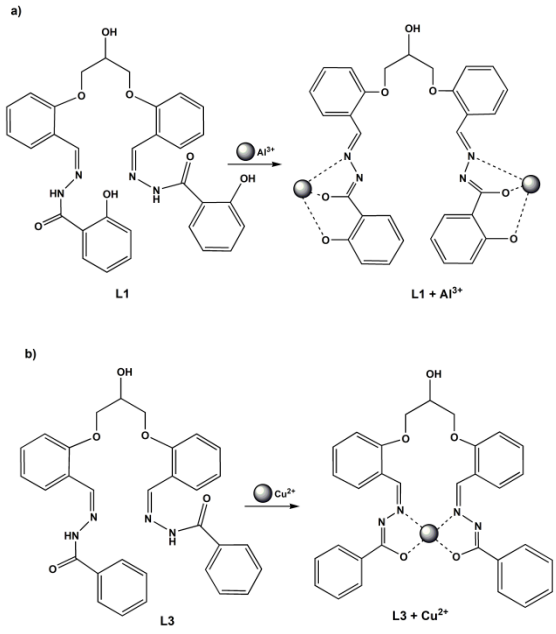


Fig. 2 UV-vis titration experiments of L_1 with Al^{3+} and L_3 with Cu^{2+}.



Scheme 2. Binding mode of a) L_1 with Al^{3+} and b) L_3 with Cu^{2+}.

C. Proposed Binding Modes of L_1 with Al^{3+} and L_3 with Cu^{2+}

Based on the experiment results mentioned above, the binding mode of $\mathbf{L_1}$ with Al^{3+} and $\mathbf{L_3}$ with Cu^{2+} was proposed, as shown in Scheme 2. For the formation of the $\mathbf{L_1}$-Al^{3+} complex, the N (-C=N) and O (-C=O and –OH) participated in the coordination process (Scheme 2a). For $\mathbf{L_3}$, N (-C=N) and O (-C=O) coordinated with Cu^{2+} to form the $\mathbf{L_3}$-Cu^{2+} complex (Scheme 2b).

IV. CONCLUSIONS

In summary, the coordination properties of three Schiff base compounds were studied in detail. The results indicated that substituent groups on chemical compounds had a big effect on the formation of a complex between ligands and metal ions. We believe that this study will significantly promote the development of effective ligands for the selective detection of metal ions.

ACKNOWLEDGMENT

This work was financially supported by the Natural Science Foundation of Hainan Province (No. 820RC626), the Research and Training Foundation of China (No. 202011810017), and the National Natural Science Foundation of China (No. 81760387, 81860381).

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