

Determination of chromium (III) ions in water samples by UV-vis spectrometry based on benzyl-functionalized benzimidazolylidene ligand

Zhenning Yan, Ling Jiang, Cuiying Xu and Jianming Liu

ABSTRACT

Chromium is one of the most notorious environmental pollutants. The development of a sensitive and selective chromium detection method is an important issue. In this paper, cation recognition properties of two benzyl-functionalized benzimidazolylidene ligands towards metal ions were investigated by UV-vis spectrophotometry. The results showed that the receptors had a higher selection of Cr^{3+} . The important analytical parameters, such as pH, quantity of the reagents, and their effects on the studied system were investigated. Under the optimum conditions the absorbance of the Cr^{3+} -L complex obeys Beer's law in the Cr^{3+} concentration range of 0.05–2.60 $\mu\text{g}/\text{mL}$ with the limit of detection of 0.026 and 0.034 $\mu\text{g}/\text{mL}$ for L1 and L2, respectively. Infrared (IR) spectrum and density functional theory (DFT) calculations were used to explore the coordinating sites and the complex strength of two ligands towards Cr^{3+} . The thermodynamic parameters showed that complex formation is a spontaneous exothermic process. The proposed method was successfully applied to the determination of Cr^{3+} content in water and alloy samples. The proposed method is seen as a simple and effective way of determining Cr^{3+} concentration.

Key words | benzyl-functionalized benzimidazolylidene derivative, Cr^{3+} ion, DFT calculations, IR spectrometry, thermodynamic parameters of complex, UV-vis spectrometry

Zhenning Yan (corresponding author)

Cuiying Xu
College of Chemistry and Molecular Engineering,
Zhengzhou University,
Zhengzhou, Henan 450001,
China
E-mail: yanzzn@zzu.edu.cn

Ling Jiang

School of Material and Chemical Engineering,
Zhengzhou University of Light Industry,
Zhengzhou, Henan 450001,
China

Jianming Liu

Key Laboratory of Green Chemical Media and
Reactions (Ministry of Education), School of
Chemistry and Environmental Science,
Henan Normal University,
Xinxiang, Henan 453007,
China

INTRODUCTION

The necessity of selective determination of transition and heavy metal ions has increased immensely during the last few decades due to increasing environmental issues. Among these metal ions, chromium (III), at trace levels, is a micronutrient that plays an important role in the activation of insulin to maintain the correct levels of glucose in the blood. But its accumulation in the human body results in toxicity. Chromium is commonly used in numerous industrial processes including pigment production, electroplating and tanning. Thus, large quantities of chromium compounds can be released into the environment and drinking water (Kumar & Shim 2008). One of the pathways by which chromium enters the human body is through the intake of water. The threshold limit for chromium uptake is 0.1 $\text{mg}\cdot\text{m}^{-3}$ in

air and 0.05 $\text{mg}\cdot\text{dm}^{-3}$ in water (Zhao *et al.* 2013). Therefore, the determination of chromium ion concentration is important in water samples, and also in environmental and industrial applications (Memon *et al.* 2005; Zhang *et al.* 2008).

Detection of chromium in water samples has been measured by a variety of techniques including inductively coupled plasma-mass spectroscopy, electrothermal atomic absorption spectrometry, atomic emission spectroscopy, fluorescence imaging, potentiometric membrane sensor, voltammetry, etc. Although these methods are accurate and sensitive, they are expensive, time consuming, and necessitate complicated sample pretreatment procedures. The identification and quantitative analysis of metal ions by ultraviolet-visible (UV-vis) spectroscopy have been proven

to be an attractive technique (Desvargue & Czarnik 1997; Murkovic & Wolfbeis 1997), due to its simplicity and the low cost of rapid analysis without requirement of any sophisticated instrumentation (Safavi & Bagheri 2004; Kuswandi *et al.* 2006). As a routine quantitative method, UV–vis spectrometry is widely applied to metal complexes in solution to determine metal concentration. Emphasis is focused on the development of new molecules with special organic structures whose donor groups provide a suitable coordinating site, aiming at enhancing the selectivity of the method. Although there are many reports about the determination of metal ions using UV–vis spectrometry, relatively few studies have been carried out for the Cr³⁺ ion. Chromium (III) recognition properties of organic glutamine-based derivatives (Zhao *et al.* 2013), calixarene derivatives with coumarin, benzoxazole or benzothiazole units (Wang *et al.* 2009), branched polyethyleneimine (Jia *et al.* 2014), azocalix [4]arene (Lu *et al.* 2005) and rhodamine spirolactam derivative (Bao *et al.* 2015) have been reported. However, there needs to be improved sensitivity and recognition selectivity for the Cr³⁺ ion over other transition metal ions.

In recent years, we have been testing suitable methods for measuring contaminants in water, which is important for environmental assessment and protection. Herein, cation recognition properties of two benzyl-functionalized benzimidazolylidene ligands towards different metal ions were investigated by UV–vis spectrophotometry. The ligand is a class of N-heterocyclic carbene (NHC) ligand. NHC is an electron-rich nucleophilic scaffold, in which the carbene center enjoys the benefits from stabilization related to both the σ -electron-withdrawing and π -electron-donating nature of the nitrogen centers. Because of their unique electronic dedication, they can bind to a broad range of transition metals (Adhikary *et al.* 2012). Some silver, gold and platinum complexes of these ligands have been synthesized and structurally characterized, and their potential uses as catalysts, medicine, and luminescent materials have also been studied (Zhang *et al.* 2009; Adhikary *et al.* 2012). However, research on the spectroscopic properties of these ligands and their interactions with heavy metal ions has been limited. The objective of this work is to investigate UV–vis absorption characteristics of two benzyl-functionalized benzimidazolylidene ligands (L1 and L2, Figure 1) and their complexes coordinated with

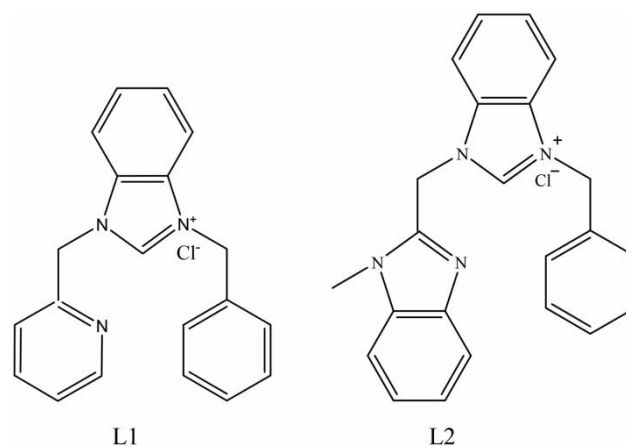


Figure 1 | Structure of ligands.

heavy metal ions. The initial results along with their application in sensing Cr³⁺ ions are reported in this paper.

METHODS

Reagents and solutions

L1 and L2 were synthesized according to the procedures in the literature (Adhikary *et al.* 2012; Liu *et al.* 2012). Other chemical reagents were of analytical grade. Nitrate and chloride salts of all metals were purchased from Shanghai Chemical Company and used without further purification. Double distilled water was used throughout the experiments.

Standard stock solutions of ligand (1.0×10^{-3} M) and metal ion salt (1.0×10^{-4} M) were prepared with C₂H₅OH/H₂O (1:1 by volume). Working solutions were prepared by appropriate dilution of the stock solutions. The pH of the metal salt solution was adjusted by 1.5 mM HNO₃ solution.

Apparatus

The UV–vis spectroscopy measurements were carried out on a spectrophotometer (Model HP Agilent 8453). The pH values were measured using a pH meter of model PHS-3C (Shanghai Honggai Instrument Factory) with a combined glass–calomel electrode of sensitivity (± 0.01) pH units. The conductivity of each sample was measured with a conductivity meter (Model 145A+, Thermo Orion), using a conductivity cell

(Model 011510, Thermo Orion). The conductivity cell was equipped with a water circulating jacket, and the temperature was controlled within ± 0.02 K with a low temperature thermostat (Model DC-2006, Shanghai Hengping Instrument Factory). IR spectra were performed using a Nicolet NEXUS-470 Fourier transform infrared (FT-IR) spectrometer.

General procedure for UV–vis titrations

The UV–vis absorbance study was performed as per the following procedure (Jia *et al.* 2014; Yan *et al.* 2017). (i) Mixture solutions of appropriate amounts of 1×10^{-4} M Cr³⁺ and 0.8 mL 1×10^{-3} M ligand solution were added to a 10 mL volumetric flask and completed to the mark with C₂H₅OH/H₂O. The pH of the solution was adjusted as a proper value. (ii) The mixture solutions were put in an ultrasonic bath for 10 min, and then placed in room temperature for 4 h to reach coordination equilibrium. (iii) The adsorption spectrum scanning (190–350 nm) of mixture solutions was measured by UV–vis spectrometer.

Conductometric measurements

The conductance of the metal ions was measured as a function of ligand concentration in solution. The experimental procedure was as follows: a solution of the metal ion (about 3×10^{-5} M, 25 mL) was placed in the cell (volume 100 mL) and the conductance of the solution was measured. A ligand solution was added into the solution of the metal ion step by step until the total concentration of the ligand was approximately five times as large as that of the metal

ions. The concentration of ligand increased from 1.5×10^{-5} to 1.5×10^{-4} M.

Determination of Cr³⁺ in real samples

The proposed method was applied to determine trace amounts of Cr³⁺ in water samples (tap water and pond water) and in the alloy. Water samples were collected without adding any preservative in polyethylene bottles and analyzed within 6 h. Water samples were filtered through filter paper before use. The alloy sample was prepared as follows: 0.5–1.0 g alloy was completely dissolved in 20–40 mL of hydrochloric acid (1 + 1) by water-bath heating, and then 2–3 mL of 30% hydrogen peroxide was added. The excess of peroxide was decomposed by heating and the mixture was cooled and filtered. The filtered mixture was diluted to 500 mL with distilled water in a calibrated flask.

An amount of 0.1 mL stock solution of ligand was mixed with 5 mL sample solution in a volumetric flask and then the solution was spiked with different known concentrations of Cr³⁺. The solution was analyzed via a UV–vis spectrometer. The measured absorbance values were calculated for the Cr³⁺ concentrations using the standard addition method.

RESULTS AND DISCUSSION

Selectivity of two ligands towards different metal ions

The UV–vis absorption spectra of the two ligands in C₂H₅OH/H₂O at 1.0×10^{-5} M concentration are shown in Figure 2. The ligands are characterized by a strong band at

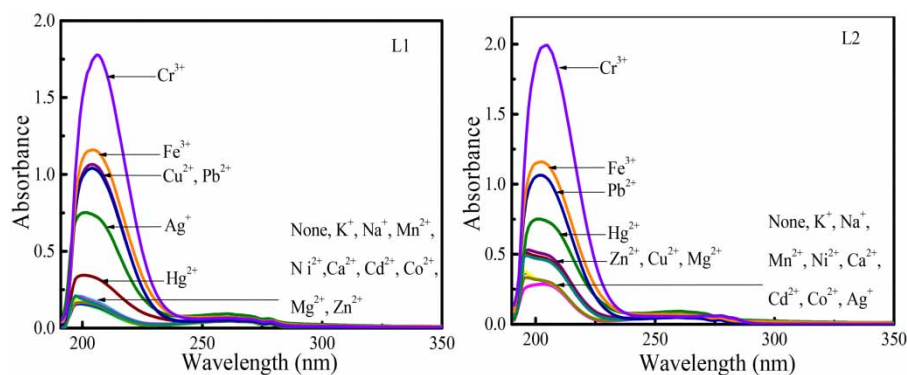


Figure 2 | UV–vis absorption spectra of L1 and L2 (1.0×10^{-5} M) upon addition of different metal ions (1.0×10^{-5} M) in C₂H₅OH/H₂O solution.

197 nm. The UV-vis absorption behaviour of the ligand/metal ions was investigated with the addition of 1.0×10^{-5} M of various metal ions such as K⁺, Mn²⁺, Ca²⁺, Co²⁺, Ag⁺, Cu²⁺, Hg²⁺, Fe³⁺, Cr³⁺, etc. The observed changes in UV-vis absorption spectra are also shown in Figure 2. Figure 2 indicates that the addition of equal moles of Cr³⁺ into the ligand solutions caused a significant increase of the absorbance at 197 nm, accompanied by a 10 nm red shift. The different maximum absorbance of the Cr³⁺-L complex may be attributed to changes in the conjugated system of ligand molecules. A trivalent chromium ion was connected with the nitrogen atoms that have a lone pair of electrons and formed a coordination bond. Therefore, as the conjugated system increased, the maximum absorbance of the Cr³⁺-L complex was shifted to longer wavelengths. This finding suggests a binding of the ligand with the Cr³⁺ ion.

In order to further illuminate the interaction between the ligands and metal ions, the relative reduction in the absorbance $((A-A_0)/A_0)$ was calculated. As shown in Figure 3, among the examined metal ions, Cr³⁺ addition caused the largest relative reduction in the absorbance. Therefore, it can be concluded that the two ligands possess excellent selectivity in binding with Cr³⁺ and can be used for detection of Cr³⁺.

Conductometric titration

According to the method in the literature (Takeda *et al.* 1980), the complex formation constants (K_f) of the two ligands with many metal ions were calculated using the measured conductivity data at 298.15 K. The results in

Table 1 show that among the obtained complex formation constants, the K_f values for the two ligands with Cr³⁺ ions are the largest ones. It indicates that L1 and L2 have high binding selectivity towards Cr³⁺ ions and are expected to act as suitable ligands for the recognition of Cr³⁺ ions.

Using the obtained formation constants at 293.15, 298.15, 303.15 and 308.15 K, the thermodynamic function of complex formation was evaluated from Equation (1):

$$\Delta_f G = -RT \ln K_f = \Delta_f H - T\Delta_f S \quad (1)$$

where $\Delta_f G$, $\Delta_f H$ and $\Delta_f S$ are the standard free energy, enthalpy and entropy of complex formation, respectively. The obtained values are presented in Table 2. The negative $\Delta_f G$ value in all cases indicates that complex formation is a thermodynamically favourable process. The negative enthalpy $\Delta_f H$ of coordination reactions suggests that the process is exothermic.

The binding ratios and constants of the two ligands with Cr³⁺

In order to study the sensitivity and binding mechanism of the two ligands, quantitative spectrometric titration was conducted in the presence of Cr³⁺. It can be seen from Figure 4 that upon addition of 0–5 equiv. of Cr³⁺, the intensity of the absorption band of the ligands at 197 nm increased accompanied with a continuous red shift from 197 nm to 207 nm. The binding ratios and constants of the ligands with Cr³⁺ were calculated using the Benesi–Hildebrand (B-H) equation. The Benesi–Hildebrand method (Benesi & Hildebrand 1949) is a widely used approach for determining the

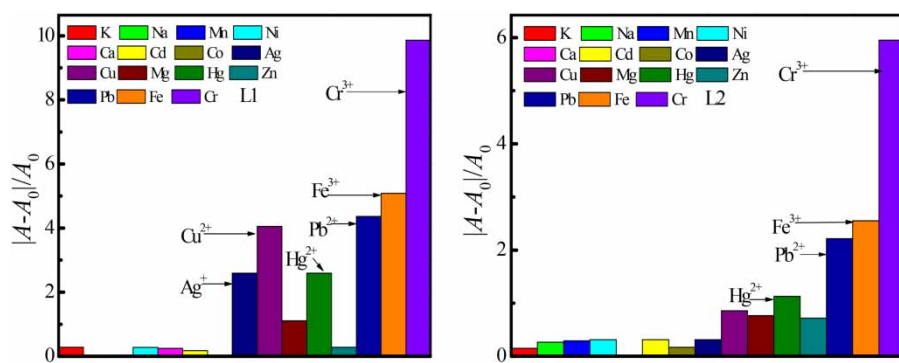


Figure 3 | Relative reduction in UV-vis absorbance at λ_{max} of L1 and L2 upon addition of different metal ions.

Table 1 | Complex formation constants (log *K_f*) of two ligands with metal ions

Ligand	Cr ³⁺	Pb ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Co ²⁺	Hg ²⁺	Ag ⁺	Na ⁺	K ⁺	Mn ²⁺	Ca ²⁺	Fe ³⁺	Mg ²⁺
L1	3.85	3.13	2.91	3.15	2.78	2.84	2.86	3.00	3.09	2.83	2.82	2.74	2.83	3.18	2.87
L2	3.68	3.02	2.70	2.96	2.92	2.73	2.69	2.99	2.89	2.68	2.64	2.73	2.80	3.07	2.95

Table 2 | Thermodynamic parameters of the two ligands coordinating with Cr³⁺

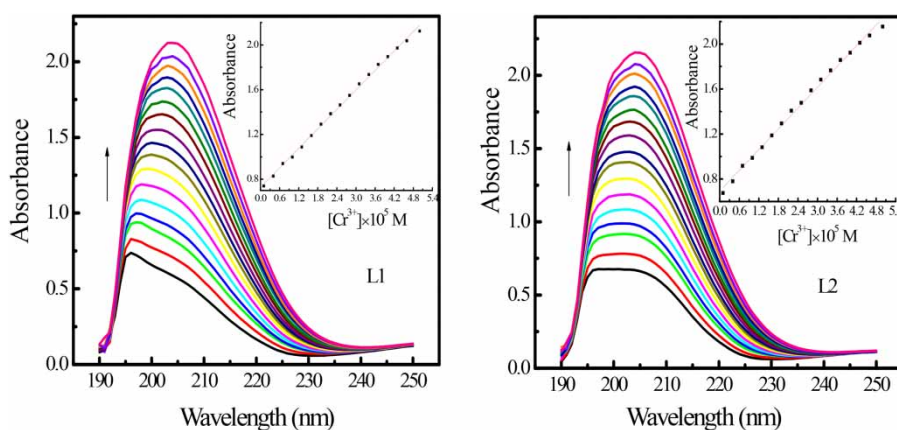
	$\Delta_r G$ (kJ/mol)				$\Delta_r H$ (kJ/mol)	$\Delta_r S$ (J/mol·K)
	293.15 K	298.15 K	303.15 K	308.15 K		
Cr ³⁺ -L1	-21.85	-21.98	-22.13	-22.29	-12.86	30.60
Cr ³⁺ -L2	-20.21	-20.63	-21.00	-21.16	-1.40	64.40

binding stoichiometry and equilibrium constants of non-covalent binding interactions, particularly for 1:1 and 1:2 binding stoichiometry. The association constant K_a was evaluated graphically by plotting $1/\Delta A$ vs $1/[M^{Z+}]^n$ according to the B-H equation:

$$\frac{1}{A - A_0} = \frac{1}{K_a(A_{\max} - A_0)[M^{Z+}]^n} + \frac{1}{A_{\max} - A_0} \quad (2)$$

where A_0 is the absorbance before metal ion addition; A is the absorbance after metal ion addition; A_{\max} is the absorbance after adding an excess amount of metal ions. When there is a linear relationship between $1/\Delta A$ and $1/[M^{Z+}]$, the binding stoichiometry is 1:1, and the B-H equation is given as below:

$$\frac{1}{A - A_0} = \frac{1}{K_a(A_{\max} - A_0)[M^{Z+}]} + \frac{1}{A_{\max} - A_0} \quad (3)$$

**Figure 4** | UV-vis spectra of ligand (1.0×10^{-5} M) with gradual addition of Cr³⁺ ion. Insert: Beer's law plot.

It can be seen from Figure 5 that there is a linear relationship between $1/\Delta A$ and $1/[Cr^{3+}]$ with the linear correlation coefficients of 0.9992 and 0.9999 for Cr³⁺-L1 and Cr³⁺-L2, respectively. The excellent linear relationship indicates a 1:1 stoichiometric binding between ligand and Cr³⁺. From the slope and the intercept values, the K_a values were determined to be 1.45×10^4 and 8.36×10^5 L·mol⁻¹ for Cr³⁺-L1 and Cr³⁺-L2, respectively.

Effect of pH

As pH is an important factor in influencing the coordination process, the addition of 1.5 mM nitric acid in 10 ml mixed solution was studied. Since chromium (III) tends to form hydrate precipitate in basic and weak acidic environments, the effect of pH on the interaction between the two ligands and Cr³⁺ was scrutinized in the pH range of 3.4–4.8. The results are shown in Figure 6. From the results, it is observed that the complex exhibits maximum absorbance in the pH range of 3.4–3.7. The reason was possibly that complete chelation required a proper acidity. In more alkaline media the absorbance reduced because of complex hydrolysis and hydroxide formation. Thus, all samples discussed in the following section were prepared around pH 3.5.

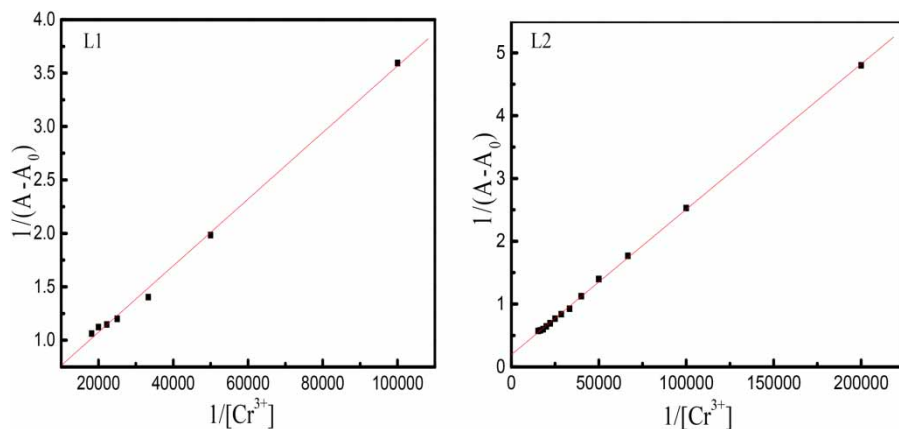


Figure 5 | Changes in UV-vis spectrum with addition of different amounts of Cr³⁺ in C₂H₅OH/H₂O.

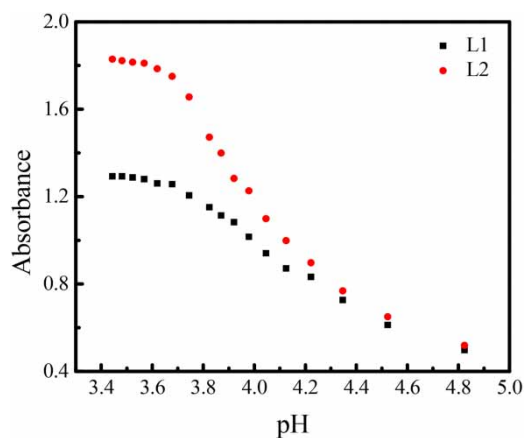


Figure 6 | The variation of the absorbance of the Cr³⁺-L complex vs pH at 207 nm. [Cr³⁺] = 1.0 × 10⁻⁵ M, [L] = 1.0 × 10⁻⁵ M, blank reagent.

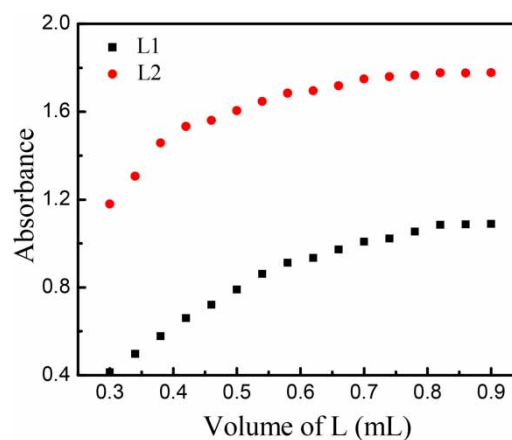


Figure 7 | Effect of the volume of 1.0 × 10⁻⁵ M ligand on the complex with Cr³⁺ (1.0 × 10⁻⁵ M).

Effect of reagent concentration

The effect of reagent concentration on the absorbance of the complex was investigated by varying the reagent concentration at constant Cr³⁺ concentration (1.0 × 10⁻⁵ M). It is clear from Figure 7 that the maximum absorbance was attained with 0.8 mL of 1.0 × 10⁻⁵ M ligand; above this volume up to 0.9 mL the absorbance remained unchanged. Therefore, 0.8 mL of 1.0 × 10⁻⁵ M ligand was used in all further measurements.

Analytical data

A working curve was constructed at optimum conditions by conducting a set of similar experiments at various

concentrations of Cr³⁺, and the respective results are depicted in the inset of Figure 4. The ranges of linearity of absorbance as a function of Cr³⁺ concentration, i.e. obeying Beer's law, provide a satisfactory measure of the sensitivity of the method. Under the optimum conditions, the absorbance of both Cr³⁺-L complexes obeys Beer's law in the Cr³⁺ concentration range of 0.05–2.60 µg/mL. The limit of detection (LOD) was estimated using the normalized response of the UV-vis absorbance calibration value $(A_{\min} - A)/(A_{\min} - A_{\max})$ as a function of $\log[\text{Cr}^{3+}]$ (Shortreed *et al.* 1996; Kim *et al.* 2009). As shown in Figure 8, the lowest detectable limits (LOD) for Cr³⁺ using this method were 0.026 and 0.034 µg/mL, respectively. This is comparable to previously reported methods. The obtained optical parameters are given in Table 3.

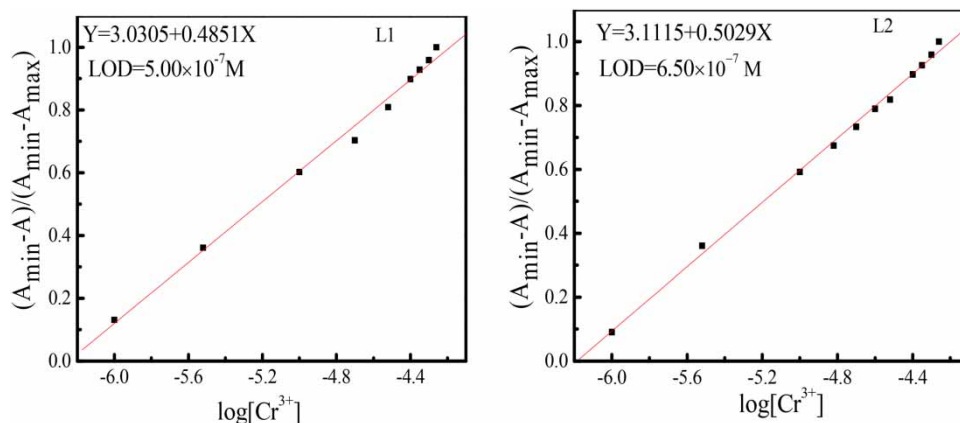


Figure 8 | Normalized response of UV-vis absorbance calibration value as a function of Cr³⁺ concentration in C₂H₅OH/H₂O solutions.

Table 3 | Optical parameters for the determination of Cr³⁺ with two ligands

Parameters	Characteristic (L1)	Characteristic (L2)
Beer's law range (μg/mL)	0.05–2.60	0.05–2.60
Molar absorptivity (L/(mol·cm))	7.11×10^4	1.03×10^5
LOD (μg/mL)	0.026	0.034
Regression equation ^a	$y = 0.728 + 0.2896x$	$y = 0.6924 + 0.3077x$
Correlation coefficient	0.997	0.995
Standard deviation ^b	0.0063	0.0067
Relative standard deviation (%) ^b	0.206	0.115

^ax is the concentration of Cr³⁺ and y is the absorbance.

^bSix replicate measurements.

In addition, an exhaustive comparison is made in Table 4 for some important characteristics like linearity range and detection limit with previous reports by other researchers (Lu *et al.* 2005; Zhao *et al.* 2013; Bao *et al.* 2015; Sharif *et al.* 2015). We can get the result that the proposed method is superior to those sensors in a number of literature sources in some cases, such as low detection limits and wider linear ranges.

Interference effect

In order to investigate the selectivity of the proposed method, the effects of foreign species on the determination of Cr³⁺ were investigated. The interference study was

Table 4 | Analytical features of some spectrophotometric methods employed for Cr³⁺ determination based on different ligands

Reagent	pH	LOD (μg/mL)	Beer's law range (μg/mL)
Azocalixarene derivative (Lu <i>et al.</i> 2005)	3.0	–	48.6–231.4
Rhodamine spirolactam derivative (Bao <i>et al.</i> 2015)	7.2	0.378	2.6–10.4
Glutamine with dansyl groups (Zhao <i>et al.</i> 2013)	5.5	–	0–10.4
Branched polyethyleneimine (Jia <i>et al.</i> 2014)	5.0–6.0	–	0.50–20.0
Silver nanoparticles (Sharif <i>et al.</i> 2015)	6.0	0.023	0.05–2.60
Present work L1	3.5	0.026	0.05–2.60
Present work L2	3.5	0.034	0.05–2.60

performed by using 5.0×10^{-5} M of Cr³⁺ ions and variable concentrations of the interfering cations at pH 3.5. The tolerance limit was defined as the amount of added ions that caused less than 5% relative error in the determination of Cr³⁺. The results are depicted in Table 5. Table 5 shows that the concentration of the target ions can be selectively determined using the proposed method in the presence of excess amounts of the potential interferences examined.

IR spectral studies

The interaction can also be qualitatively grasped by FT-IR spectra (Zhang *et al.* 2015). Figure 9 shows FT-IR spectra of the free

Table 5 | Effect of diverse species on the spectrophotometric determination of Cr³⁺ (5.0 × 10⁻⁵ M)

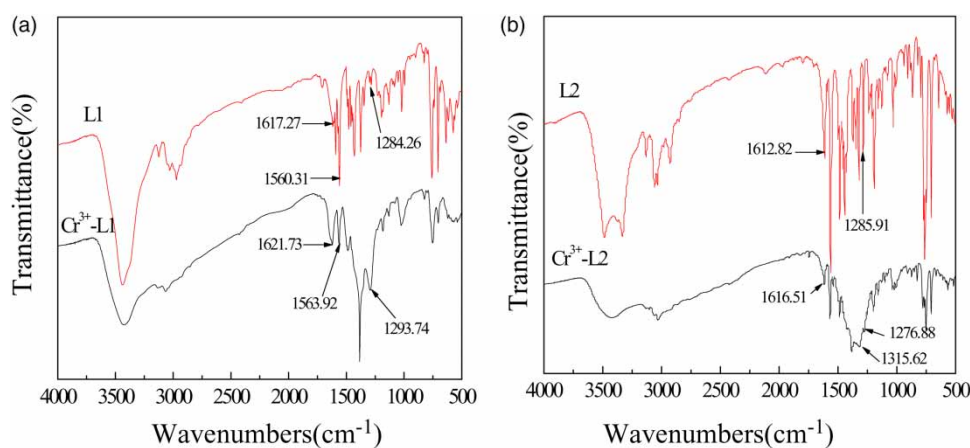
Foreign ions	L1		L2	
	Tolerance limit (M)	Relative error (%) $ \Delta A /A_0 \times 100$	Tolerance limit (M)	Relative error (%) $ \Delta A /A_0 \times 100$
K ⁺	5.0 × 10 ⁻³	4.81	5.0 × 10 ⁻³	0.72
Na ⁺	5.0 × 10 ⁻³	4.10	5.0 × 10 ⁻³	4.13
Mn ²⁺	5.0 × 10 ⁻³	2.79	5.0 × 10 ⁻³	1.39
Ni ²⁺	5.0 × 10 ⁻³	2.03	5.0 × 10 ⁻³	1.30
Co ²⁺	5.0 × 10 ⁻³	2.00	5.0 × 10 ⁻⁵	0.91
Ca ²⁺	1.0 × 10 ⁻³	0.76	1.0 × 10 ⁻³	4.75
Cd ²⁺	1.0 × 10 ⁻⁴	1.54	5.0 × 10 ⁻⁴	0.84
Ag ⁺	5.0 × 10 ⁻⁵	0.29	5.0 × 10 ⁻⁵	4.30
Cu ²⁺	1.0 × 10 ⁻⁵	1.78	1.0 × 10 ⁻⁵	4.96
Mg ²⁺	5.0 × 10 ⁻⁴	1.58	5.0 × 10 ⁻⁴	4.36
Hg ²⁺	5.0 × 10 ⁻⁵	2.39	5.0 × 10 ⁻⁵	0.06
Zn ²⁺	5.0 × 10 ⁻⁵	1.35	5.0 × 10 ⁻⁵	4.13
Pb ²⁺	1.0 × 10 ⁻⁵	2.36	1.0 × 10 ⁻⁵	4.17
Fe ³⁺	5.0 × 10 ⁻⁶	2.53	5.0 × 10 ⁻⁶	4.35

ligand and the mixtures of ligand and Cr³⁺. As shown in Figure 9(a), the IR spectrum of ligand L1 exhibited three characteristic IR peaks at 1,617.27, 1,284.26, and 1,560.31 cm⁻¹ corresponding to the stretch vibrations of -C=N, -C-N in the pyridine ring, and -C=N in the imidazole ring, respectively. Comparing the IR spectra of L1-Cr³⁺ with that of the free receptor, the above three characteristic IR peaks exhibit upward shifts to 1,621.73, 1,293.74 and

1,563.92 cm⁻¹. These differences suggest that the carbon atom of the imidazole ring and the nitrogen atom in the pyridine ring took part in coordination with Cr³⁺ ions. For the free receptor L2 (Figure 9(b)), the peaks located at 1,612.82 and 1,285.91 cm⁻¹ are assigned to -C=N and -C-N stretching in the benzimidazole ring. Comparing the IR spectra of L2-Cr³⁺ with that of L2, the stretch vibration of $\nu(-C=N)$ at 1,612.82 cm⁻¹ exhibited an upward shift to 1,616.51 cm⁻¹ and $\nu(-C-N)$ at 1,285.91 cm⁻¹ was divided into two peaks at 1,315.62 and 1,276.88 cm⁻¹. These results indicate that the carbon atom of one benzimidazole ring and the nitrogen atom in the other benzimidazole ring took part in complexation with Cr³⁺ ions.

DFT calculations

The two ligands have similar structures. However, the sensor based on L1 gives a low detection limit. To illustrate the difference of the interaction strength between the two ligands and Cr³⁺, the charge distribution and orbital energies of the HOMO and LUMO of the two ligands were calculated by quantum-chemical calculation by GaussView 5.0.8. The calculations were performed using the density functional theory (DFT) method and the three-dimensional molecular geometry optimizations were performed using the B3LYP and 6-31G basic sets. The results showed that the more negatively charged area of L1 is located at the nitrogen atom in the pyridine ring, the carbon atom in the imidazole ring and the Cl⁻ atom. The obtained atomic partial charges for these

**Figure 9** | FT-IR spectra of the two ligands and L-Cr³⁺ mixtures, (a) for L1 and (b) for L2.

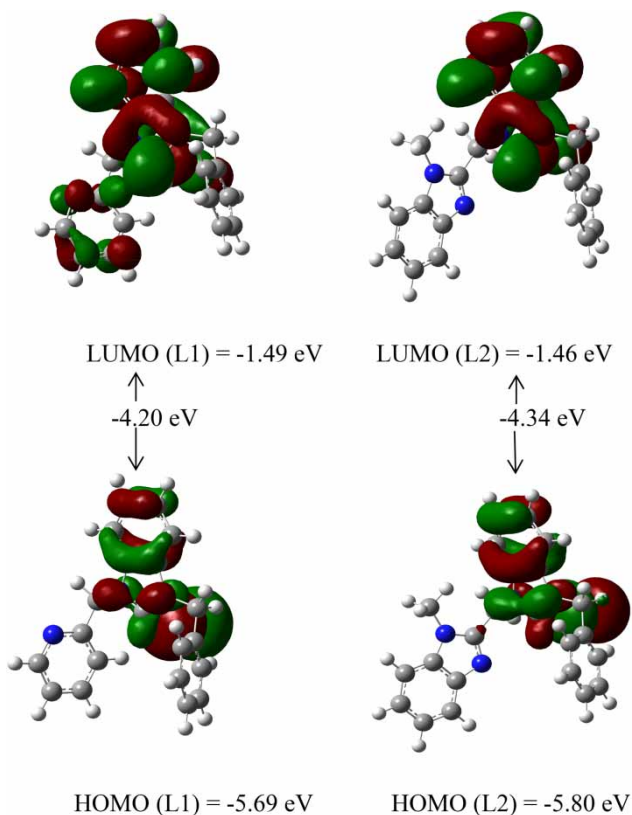


Figure 10 | Computational analysis of the HOMO and LUMO levels of L1 and L2.

atoms are about -0.077 , -1.38 and -0.570 . For L2, the more negatively charged area is located at the nitrogen atom in the benzimidazole ring, the carbon atom in the middle

benzimidazole ring and the Cl⁻ atom. The atomic partial charges for the three atoms are about -0.070 , -0.730 and -0.525 . The more negative charges is favourable for the complexation of L1 to Cr³⁺. The frontier molecular orbitals of the two ligands were also calculated (Figure 10). The calculated total energies and energy gaps for L1 and L2 are -3.80×10^4 , -4.20×10^4 and -4.20 , -4.34 eV, respectively. From these results, we can conclude that L1 has higher selectivity for Cr³⁺. The calculation is in good agreement with the results of UV, IR and conductometric titration.

Application of the method for determination of Cr³⁺ in water samples and alloy samples

To assess the feasibility of the proposed method, an attempt was made to determine Cr³⁺ ion content in real samples. As Cr³⁺ or its compounds are widely used in industry and industrial sewage enters into the environment and drinking water, water and alloy samples were chosen. An excess amount of Cr³⁺ in these samples has a great influence on our lives.

To ensure that the method is valid and has reasonable accuracy and precision, recovery of Cr³⁺ in these samples was determined. The pH of the sample solution was adjusted to 3.5. The results shown in Table 6 indicate good recoveries in the range of 92.3%–103%. The relative standard deviations (RSD) were found to be <5%. The calculated *t*-values listed in Table 6 were less than the

Table 6 | Analytic results of Cr³⁺ in water samples and alloy samples^a

Sample	L1					L2				
	Cr ³⁺ amount (μg/mL)	Added (μg/mL)	Found (μg/mL)	Recovery (%)	<i>t</i> values	Cr ³⁺ amount (μg/mL)	Added (μg/mL)	Found (μg/mL)	Recovery (%)	<i>t</i> values
Tap water	0.14	0.26	0.38	92.3	3.91	0.13	0.26	0.39	99.1	1.18
		0.52	0.67	101	1.29		0.52	0.66	101	1.70
		1.04	1.18	100	0.66		1.04	1.17	99.7	1.74
		1.30	1.44	100	0.38		1.30	1.44	100	3.06
		1.56	1.71	101	1.57		1.56	1.69	100	1.84
Pond water	0.17	0.26	0.43	100	0.10	0.16	0.26	0.41	98	2.68
		0.52	0.69	99.9	0.77		0.52	0.69	101	3.25
		1.04	1.21	100	0.77		1.04	1.20	100	0.81
		1.30	1.47	99.8	3.06		1.30	1.46	100	0.05
		1.56	1.73	100	3.06		1.56	1.72	99.8	1.29
Alloy	1.20	0	1.20	–	1.59	1.14	0	1.14	–	0.67
		0.26	1.46	100	0.45		0.26	1.41	103	1.98
		0.52	1.72	99.8	1.81		0.52	1.65	98.9	1.28

^aNumber of replicate measurements = 3; tabulated *t* value = 4.30 (at 95% confidence level with two degrees of freedom).

critical (tabulated) one. Thus, there is no significant difference between averages and variances of results for the 95% level of significance. This indicates that the developed method was not affected by the matrices of the two types of water samples. The other constituents (Mn, Ni, Cu) in the alloy sample do not interfere significantly with the detection of Cr³⁺. These results suggest the capability of the method in the determination of Cr³⁺ in real samples.

CONCLUSIONS

Due to chromium's extensive applications, the chromium ion is considered to be an environmental pollutant. Therefore, the development of an accurate and reliable method for determination of chromium ions is very important. This work presents a simple, sensitive and selective UV-vis spectrophotometric method for determining trace amounts of Cr³⁺ ions using two benzyl-functionalized benzimidazolylidene ligands (L1 and L2) as receptors. The results of experiments showed Cr³⁺ ions can be qualitatively distinguished and accurately quantified. The stoichiometric ratio was 1:1. Beer's law was found to be obeyed in the concentration range of 0.05–2.60 µg/mL. The detection limits of L1 and L2 for Cr³⁺ were 0.026 and 0.034 µg/mL. The obtained results showed the proposed method is efficient for recognizing Cr³⁺ ions with possible analytical applications.

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