A novel colorimetric chemosensor for the sequential detection of Ni²⁺ and CN⁻ in aqueous solution

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ABSTRACT

A new colorimetric chemosensor **1** for the sequential detection of Ni²⁺ and CN⁻ was designed and synthesized. The presence of Ni²⁺ led to a distinct naked-eye color change from colorless to yellow in a near-perfect aqueous solution. To examine the binding mechanism of **1** with Ni²⁺, UV3–vis spectroscopy, ESI-mass spectrometry analysis and DFT calculations were conducted. The detection limit of **1** for Ni²⁺ was down to nanomolar concentration (57 nM). Also, the sensing ability of **1** for Ni²⁺ was successfully carried out in real water samples (tap, drinking and sewage water). Moreover, the resulting **1**-Ni²⁺ complex acted as an efficient colorimetric chemosensor for CN⁻ via a color change from yellow to colorless. Therefore, chemosensor **1** can be employed as a practical colorimetric chemosensor for detecting of both Ni²⁺ and CN⁻.

1. Introduction

Nickel compounds have many industrial and commercial uses such as Ni-Cd batteries, machinery, painting pigments, welding, electroplating, tools, and a precursor for a catalyst [1,2]. Nickel is also an important metal nutrient in biological system, which is related to biosynthesis and metabolism in certain microorganisms and plants [3]. Apart from its industrial and biological roles, higher uptake of nickel ion can cause a variety of diseases such as asthma, dermatitis, pneumonitis, disorders of central nervous system and cancer of the nasal cavity and lungs [4,5]. Based on these reports, the International Agency for Research on Cancer (IARC) classified nickel compounds as group 1 carcinogenic to human in 1990 [3]. Therefore, practical monitoring of nickel ion in environmental conditions is highly in demand [2,6–16].

Cyanide is extensively used in many industrial processes, such as electroplating, gold mining, plastic manufacturing, herbicide, synthetic fibers and resin industry [17,18]. Therefore, the wide use of cyanide is unavoidable and many industries produce nearly 140,000 tons of cyanide per year worldwide [19,20]. However, cyanide is well known as a highly toxic poison. Cyanide binds efficiently the active site of cytochrome oxidase, and as

a result, interfering with electron transport chain in mitochondria [21,22]. In addition, cyanide leads to vomiting, convulsions, loss of consciousness, and eventually death [23,24]. Thus, there is considerable interest in developing sensitive, selective and quick detection methods for the toxic cyanide.

In order to detect nickel ion and cyanide, a number of analytical techniques such as atomic absorption spectroscopy (AAS), flame atomic absorption spectrometry-electro thermal atomization (AAS-ETA), ICP-AES, flame photometry and microwave-induced plasma have been used [25–32]. However, most of these methods require sophisticated equipment, tedious sample preparation procedures, and trained operators. For simplicity and low costs, optical signal methods are needed [33–37].

A number of chemosensors for the sequential recognition of various cations and anions have been recently reported such as Cu²⁺/CN⁻ [38], Cu²⁺/H₂S [39], Hg²⁺/I⁻ [40], Zn²⁺/H₂S [41], Al³⁺/F⁻ [42], Cr³⁺/F⁻ [43] and La³⁺/F⁻ [44]. Sequential recognition with a single sensor has some advantages, such as cost reduction and more efficient analysis. Nevertheless, the sequential recognition of Ni²⁺ and CN⁻ by using a single chemosensor was not reported, to date.

Pyridine is water-soluble and the lone pair electrons at its nitrogen offer a good chance for chelation with metal ions [45–52]. On the other hand, Schiff bases with π electrons in the C=N group are an important class of ligands in metal coordination chemistry [53–56], and form stable metal complexes [57–59]. Therefore, we expected that the combination of a pyridine and Schiff base would

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show the good chelation to metal ions and endow a unique photo-physical properties and water solubility.

Herein, we report on a colorimetric chemosensor **1** for the sequential detection of Ni^{2+} and CN^-, which was synthesized by the combination of 5(4)-amino-4(5)-(aminocarbonyl)-imidazole hydrochloride and 2-pyridine-carboxaldehyde. **1** could detect Ni^{2+} by colorimetric response in a near-perfect aqueous solution. More-over, sensor **1** could be used as a practical chemosensor to determine the quantitative nickel level in real water samples. Sub-sequently, the resulting **1**-Ni^{2+} complex exhibited highly selective recognition to CN^- through color change from yellow to colorless.

2. Experimental

2.1. Materials and equipment

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^1H NMR and ^{13}C NMR measurements were performed on a Var-ian 400 MHz and 100 MHz spectrometer, and chemical shifts were recorded in ppm. Electrospray ionization mass spectra (ESI–MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Elemental anal-ysis for carbon, nitrogen, and hydrogen was carried out by using a Flash EA 1112 elemental analyzer (thermo) in Organic Chemistry Research Center of Sogang University, Korea. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 25 UV/Vis spectrometer. FT-IR spectra were collected on an Agilent Cary 670 FTIR spectrometer. ICP-spectroscopy analysis for Ni was performed using ICAP-Q (Thermo Fisher Scientific).

2.2. Synthesis of sensor **1**

5(4)-Amino-4(5)-(aminocarbonyl)-imidazole hydrochloride (0.16 g, 1 mmol) was dissolved in 5 mL methanol (MeOH) at the room temperature, and the same equivalent of sodium hydroxide (NaOH) solution was added into the mixture over 15 min. Then, 2-pyridine-carboxaldehyde (155.5 μL, 1.2 mmol) was added into the reaction solution, which was stirred for 30 min. The white product was filtered and washed with ethyl acetate. Yield: 0.13 g (63%). IR (KBr): ν (cm^{-1}) = 3377 (m), 3119 (s), 1653 (s), 1592 (s), 1431 (s), 1291 (m), 1212 (s), 1086 (m). The ^1H NMR spectra were recorded in DMSO-d_6, and the descriptions of the signals include: s = singlet, d = doublet and t = triplet (400 MHz, 25 °C): δ = 12.01 (s, 1H), 9.12 (s, 1H), 8.73 (d, 1H), 8.25 (d, 1H), 7.96 (t, 1H), 7.76 (s, 2H), 7.69 (s, 1H), 7.52 (t, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 160.97, 158.46, 154.11, 150.40, 146.61, 137.54, 136.83, 126.12, 122.16, 120.08. Anal. calcd for $C_{10}H_9N_5O$: C, 55.81; H, 4.22; N, 32.54%. Found: C, 55.47.; H, 4.18; N, 32.73%.

2.3. UV–vis titrations

For Ni^{2+}, a stock solution (5 mM) of the sensor **1** was prepared in MeOH and 24 μL of the sensor **1** (5 mM) was diluted to 2.976 mL bis-tris buffer solution (10 mM, pH 7) to make final concentration of 40 μM. Then, 0.6-6.0 μL of $Ni(NO_3)_2$ solution (20 mM) was added to 3 mL of **1** solution (40 μM). After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

For CN^-, a stock solution (5 mM) of the sensor **1** was prepared in MeOH and 24 μL of the sensor **1** (5 mM) was diluted to 2.976 mL bis-tris buffer solution (10 mM, pH 7) to make final concentration of 40 μM, and 6.0 μL of $Ni(NO_3)_2$ solution (20 mM) was added to 3 mL of **1** solution (40 μM). Then, 3.6-46.8 μL of tetraethylammonium cyanide (TEACN) solution (20 mM) was added to **1**-Ni^{2+} complex

solution. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

2.4. Job plot measurements

For Ni^{2+}, a series of solutions containing sensor **1** (100 μM) and $Ni(NO_3)_2$ (100 μM) were prepared in such a manner that the total sum of sensor **1** and metal ion remained constant (3 mL), and bis-tris buffer was used as a solvent. After mixing them for a few seconds, UV–vis spectra were taken at room temperature. Job plot was drawn by plotted against the molar fraction of sensor **1** under the constant total concentration ($A-A_0$) [A is the absorbance of sen-sor **1** after addition of Ni^{2+}, and A_0 is the absorbance of the free sensor **1** at 400 nm].

For CN^-, a series of solutions containing sensor **1**-Ni^{2+} complex (100 μM) and TEACN (100 μM) were prepared in such a manner that the total sum of **1**-Ni^{2+} complex and anion remained constant (3 mL), and bis-tris buffer was used as a solvent. After mixing them for a few seconds, UV–vis spectra were taken at room temperature. Job plot was drawn by plotted against the molar fraction of **1**-Ni^{2+} complex under the constant total concentration ($A-A_0$) [A is the absorbance of **1**-Ni^{2+} complex after addition of CN^-, and A_0 is the absorbance of the free sensor **1**-Ni^{2+} complex at 400 nm].

2.5. Competition experiments

For Ni^{2+}, a stock solution of the sensor **1** (5 mM) was prepared in MeOH and 24 μL of this solution was diluted to 2.976 mL of bis-tris buffer solution to make final concentration of 40 μM. Stock solu-tions (20 mM) of various metal ions such as Al^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Na^+, K^+, Ca^{2+}, Mn^{2+} and Pb^{2+} were prepared and 6.0 μL of each metal solution was taken and added to 3 mL of the solution of sensor **1** (40 μM) to give 1.0 equiv of metal ions. Then, 6.0 μL of Ni^{2+} solution was added into the mixed solution of each metal ion and **1** to make 1.0 equiv. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

For CN^-, a stock solution (5 mM) of the sensor **1** was prepared in MeOH and 24 μL of this solution was diluted to 2.976 mL of bis-tris buffer solution to make final concentration of 40 μM and 6.0 μL of $Ni(NO_3)_2$ solution (20 mM) was added to 3 mL of **1** solution (40 μM). Stock solutions (100 mM) of various anions such as OAc^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, BzO^-, N_3^-, SCN^-, NO_2^- and HS^- were prepared and 39.6 μL of each anion solution was taken and added to 3 mL of the solution of **1**-Ni^{2+} complex (40 μM) to give 33 equiv of anions. Then, 39.6 μL of CN^- solution was added into the mixed solution of each anion and **1**-Ni^{2+} complex to make 33 equiv. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

2.6. pH effect test

For Ni^{2+}, a series of buffers with pH values ranging from 2 to 12 were prepared by mixing sodium hydroxide solution and hydrochloric acid in bis-tris buffer. After the solution with a desired pH was achieved, a stock solution (5 mM) of the sensor **1** was pre-pared in MeOH and 24 μL of this solution was diluted to 2.976 mL of bis-tris buffer solution to make final concentration of 40 μM. Stock solutions (20 mM) of various concentrations of Ni^{2+} ions were pre-pared and 6.0 μL of each stock solution was taken and added to 3 mL of the solution of sensor **1** (40 μM). After reacting them for a few seconds, UV–vis spectra were taken at room temperature.

For CN^-, a series of buffers with pH values ranging from 2 to 12 were prepared by mixing sodium hydroxide solution and hydrochloric acid in bis-tris buffer. After the solution with a desired pH was achieved, a stock solution (5 mM) of the sensor **1** was pre-pared in MeOH and 24 μL of this solution was diluted to 2.976 mL