



A novel development of dithizone as a dual-analyte colorimetric chemosensor: Detection and determination of cyanide and cobalt (II) ions in dimethyl sulfoxide/water media with biological applications



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ABSTRACT

The behavior of dithizone (DTZ), an easily available dye has been studied for the first time in chromogenic sensing of CN^- as an anionic species and for Co^{2+} as a cationic species in DMSO/ H_2O media. So employing DTZ an efficient colorimetric chemosensor was afforded with a chromogenic selectivity for Co^{2+} over other cations with detection limit of $0.04 \mu\text{mol L}^{-1}$. The complex of Co^{2+} with DTZ also displayed ability to detect up to $0.43 \mu\text{mol L}^{-1} \text{CN}^-$ (K^+ salts) among other competing anions through a fast response time of less than 30 s which is much lower than most recently reported chromogenic probes. The linear dynamic ranges for the determination of Co^{2+} and CN^- were 0.3–4.4 and 3.3–58.6 $\mu\text{mol L}^{-1}$ respectively. This method could have potential application in a variety of cases requiring rapid and accurate analysis of Co^{2+} and CN^- for human serum and water samples.

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1. Introduction

There is an increasing interest in the development of a new generation of molecules for the sensing of target chemical species of environmental or biological interest. Among them, chromogenic receptors are especially attractive because the recognition process is accomplished with an easy-to-detect perceptible color evolution. Significant efforts have been carried out in the last years for understanding the theoretical basis of the chromogenic guest recognition and a number of selective chemosensors for anions, cations, and neutral species have been designed and synthesized [1,2].

The determination of trace amounts of cobalt in water is of great interest because cobalt is important for living species as complexed Vitamin B₁₂. The deficiency of cobalt in humans and animals results in anemia [3], while large amounts of cobalt lead to toxic effects (vasodilatation, flushing and cardiomyopathy), usually after occupational exposure to cobalt dusts (cobalturia, cobalt-emia) [4]. Since one of routes of incorporation of cobalt into the human body is by ingestion, therefore its determination in drinking water becomes very important. Because the cobalt concentration levels are very low in water samples, sensitive analytical techniques are required to obtain low detection limits.

Anions play important role in chemical, biological and environmental processes. An important aspect of modern chemistry is the

utilization of hydrogen bonding in the development of receptors for recognition of anions [5]. Although cation receptors have been studied for more than four decades but the development of anion receptors received less attention. Several reasons why reliable sensing of anions is a particularly challenging area of research are: (i) anions are larger than isoelectronic cations and, therefore, have lower charge-to-radius (surface) ratio, a feature that makes the electrostatic binding of anions to the receptors less effective [6], (ii) anions have a wide range of geometries and are often present in delocalized forms, which results in higher complexity in design and synthesis of receptors and (iii) pH sensitivity. Therefore, to achieve the desired selectivity, the combination of electrostatic attraction, hydrogen bonding and a suitable framework onto which these structural components can be assembled needs to be taken into consideration when designing artificial anionic hosts [7].

Among various anions, cyanide is one of the most concerned anions because it is being widely used in synthetic fibers, resins, herbicide, and the gold-extraction process [8]. Unfortunately, cyanide anion is extremely detrimental, and could be absorbed through lungs, gastrointestinal track, and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death [9]. According to the World Health Organization (WHO), only water with cyanide concentration lower than 1.9 μM is drinkable [10]. Thus, there exists a need for an efficient sensing system for cyanide to monitor its concentration from contaminant sources.

As a result, the detection of cyanide has attracted considerable attention in recent years, and many cyanide sensors have been

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developed [11–15]. Several strategies for detecting cyanide have been developed based on fluorogenic and chromogenic organic dyes [11], semiconductor nanoparticles [12], chromatography [13], electrochemical sensors [14] and polymers [15]. Colorimetric chemosensors are particularly attractive because they can be read by the naked eye, and in some cases at the point of use.

To date, many of the reported cyanide anion receptors have relied on hydrogen-bonding motifs and, as a consequence, have displayed poor selectivity in aqueous media [16]. To overcome this limitation, reaction-based receptors have been developed recently [17,18]. This reaction-based recognition mode takes advantage of the particular feature of the cyanide ion: its good nucleophilic character and little competition from the aqueous media. However, many receptors for cyanide reported [16–18] so far, they have several limitations such as poor selectivity over F^- or AcO^- , or utilization of expensive instruments, complicated synthesis, and many of receptors are reported to work only in organic media. According to the literature, there are a few methods able to detect the cyanide anions in pure water [19–25] using water soluble polymers [20], glycoconjugation [21,22], glycerilation [23], surface functional modification of nanocrystalline TiO_2 films or membrane anchored with an azo dye [24] and the biosourced plastic film starting from starch [25].

During last thirty years, these receptors and other many organic based synthetic anion receptors that have been reported [26,27], are rather difficult to synthesize or require expensive instruments for detections. Taking this dilemma into consideration recently, we have undertaken an extensive research program to explore bromo pyrogallol red (BPR) as an easily available dye demonstrated a high chromogenic receptor for cations and anions [28–30]. In this work, we report new applications of dithizone (DTZ). DTZ is considered as a selective and sensitive ligand to prepare specific sorbents for heavy metal removal and preconcentration. Polymeric supports loaded with dithizone were used for preconcentration of mercury from seawater but with little success [31].

This dye demonstrates a high chromogenic sensing ability for cobalt (II) in DMSO/ H_2O (75:25 v/v) media and in continuation, we wish to report a new probe molecule ($[Co(DTZ)_2]^{2+}$ complex) for highly selective cyanide detection in the same media. This chemodosimeter has shown a selective and sensitive response to cyanide anion over other various anions through a nucleophilic addition reaction of the cyanide to the probe molecule. The strong nucleophilicity of cyanide will make the described cyanide-probe more feasible working as a reaction-based chemodosimeter. The mode of interaction of cyanide was also studied by UV–Vis, 1H NMR and IR spectroscopy to be via the nucleophilic attack to the N atom (azo group) on the chemosensor. According to our knowledge, DTZ has not still been used for determination of anionic species.

2. Experimental

2.1. Reagents

Reagents with analytical grades and demineralized water were used for preparing the solutions. DTZ (dithizone; (E)-1, 5-diphenylthiocarbazon) was purchased from Merck, and used without further purification. Stock solutions ($1.0 \times 10^{-1} \text{ mol L}^{-1}$) of Na^+ , K^+ , Co^{2+} , Rb^+ , Ba^{2+} , Mn^{2+} , Cl^{3+} , Al^{3+} , Zr^{4+} , Ce^{3+} , Mg^{2+} , Cd^{2+} , W^{6+} , Bi^{3+} , Ag^+ , Hg^+ , Cu^{2+} and Sn^{2+} were prepared by direct dissolution of proper amounts of nitrate salts of Na^+ , K^+ , Ba^{2+} , Mn^{2+} , Cr^{3+} , Ce^{3+} , Cd^{2+} , Mg^{2+} , Bi^{3+} , Ag^+ , Hg^+ and Cu^{2+} chloride salts of Co^{2+} , Sn^{2+} and Rb^+ , zirconium oxychloride and phosphotungstic acid (were purchased from Merck) in deionized water. Stock solutions ($1.0 \times 10^{-1} \text{ mol L}^{-1}$) of anions were prepared by direct dissolution of proper amounts of potassium salts of anions. Working standards

were prepared daily by serial dilutions from the $1.0 \times 10^{-1} \text{ mol L}^{-1}$. DMSO was dried with CaH_2 and then distilled in reduced pressure.

2.2. Apparatus

A Shimadzu 1601 PC UV–Vis spectrophotometer with a quartz cuvette (path length = 1 cm) was used for recording all spectra and absorbance measurements are in the wavelength range of 200–700 nm. FT-IR spectra were recorded on a Bruker Vector 22 Fourier Transmission Infrared spectrometer with wave numbers in the range of 400–4000 cm^{-1} . Elemental analyses were performed by a VARIO EL-III (German) element analytical instrument. ICP-AES Varian, Vista-pro (Salt lake city, Australia) was used for measuring the concentration of Co (II). 1H NMR spectra were measured with Varian unity plus 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. A Jenway 3510 pH-meter which calibrated against two standard buffer solutions at pH 4.0 and 10.0 was used to measure the pH of the solutions. A Hamilton syringe (10 μL) was used to deliver small volumes of reagent into the cell. DMSO/ H_2O (75:25 v/v) was used as the solvent in the reference cell. All measurements were made in the absorbance mode.

2.3. pH measurement procedure

The pH was measured in aqueous organic solvents, taking into account the reference pH values of primary standard buffer solutions, pH_S , for the standardization of potentiometric sensors in organic–water mixtures. The knowledge of pHs values allows one to perform pH measurements in a mixed solvent as easily as in water taking into account the operational definition of pH [32]:

$$pH_X = pH_S + (E_S - E_X)/K_g \quad (1)$$

where the unknown pH of solution X, pH_X , is related to the pH of a standard reference solution, pH_S , and the emf values of the potentiometric cell contain the standard, E_S , and the unknown solution, E_X . K_g must be used for practical measurements ($K_g = (\ln 10) RT/F$), usually carried out in cells with glass electrodes, and corresponds to the practical slope of the E versus pH function. Thus, the availability of standard buffer solutions of known pH (Phosphate buffer: KH_2PO_4 (0.025 mol L^{-1}) + NaH_2PO_4 (0.025 mol L^{-1}) in DMSO/ H_2O media), in the desired solvent mixture, is the key to pH measurements in these media [32].

2.4. General methods

All titration experiments were carried out at 298.2 K, unless otherwise mentioned. 2.5 mL solution of DTZ ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) in DMSO/ H_2O (75:25 v/v) was transferred to the quartz cuvette and the absorption spectra was recorded immediately. Changes in the UV–Vis absorption spectrum of DTZ upon addition of 2.0×10^{-7} – $7.8 \times 10^{-5} \text{ mol L}^{-1}$ of chloride salt of Co(II) ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) were used for complexation studies.

The presence of Co^{2+} resulted in the red shift in wavelength of maximum absorption from 475 to 482 nm and reduced the absorbance intensity in both 475 and 610 nm (Fig. 1a), which resulted in a color change of the solution from green to red (Fig. 1b). The $[Co(DTZ)_2]^{2+}$ has been proved to be suitable chromogenic chemosensor for anion sensing. Thus, changes in the visible spectrum were recorded in DMSO/ H_2O (75:25 v/v) solution of this receptor upon addition of $1.0 \times 10^{-2} \text{ M}$ of F^- , Cl^- , Br^- , I^- , HSO_4^- , CH_3COO^- (AcO^-), $C_6H_5COO^-$ (BzO^-), NO_3^- , $H_2PO_4^-$, CN^- , and SCN^- anions as their potassium salts in water solutions. Titration of $[Co(DTZ)_2]^{2+}$ complex with CN^- resulted in the blue shift in wavelength of maximum absorption from 482 to 475 nm and reduced the absorbance

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