Naked eye detection of cyanide in water with Co^{II} bis(terpyridine) complexes

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Graphical abstract:

Abstract: Herein, we first time report Co^{II} bis(terpyridine) complexes as instant 'naked eye' colorimetric detectors of cyanide (CN⁻) in micromolar concentration in polar solvents, including water, following formation of the corresponding Co^{III} tricyanide complex. The new Co^{III} tricyanide complex [Co^{III}(4-pyridyl-terpyridine)(CN)₃] is characterized by single crystal XRD diffraction. The quantitative detection of cyanide is monitored by UV-Vis spectroscopic method and the selectivity of Co^{II} bis(terpyridine) complexes to the cyanide anion is shown in presence of other anions.

Keywords: Cyanide sensing in water, Cobalt(II)-bis-terpyridine complex, naked eye detection

1. Introduction:

Cyanide (CN⁻) is known to be one of the most toxic anions for physiological systems because of its ability to inhibit many heme-containing enzymes. [1] Industrial wastewater contains significant amounts of cyanide, and represents a threat to mammalian and aquatic

life; thus an important worldwide research effort has been devoted to develop cyanide detectors with better selectivity and sensitivity, especially in aqueous media. [2-5,8,10] The United States Environmental Protection Agency (EPA) has set the maximum safe concentration for cyanide in drinking water at 0.2 ppm ($\sim 7.6 \mu\text{M}$). [11] The limit recommended by WHO International Standards for drinking-water is 0.07 mg/L ($\sim 2.5 \mu\text{M}$). [12] In the last 40 years, optical sensors for cyanide have been widely studied, in order to provide simple, inexpensive, and rapid detection. [2b,d] Although most reported cyanide sensing species are made of organic materials, [3] their design and syntheses can be quite tedious. Only a few self-assembled metal complexes have been used for cyanide detection, [4-6] indicating an opportunity to explore and improve coordination complex-based cyanide detectors. [5-6,8,10]

The use of 3d metal based complexes as sensor is expected to be more cost efficient and environmental friendly. As a use of 3d metal complexes for cyanide sensing, besides Cu^{II} , Zn^{II} and a recently reported one Ni^{II} compounds, [4,5,4f] only a few cobalt-based compounds are known where cyanide ions interact directly with the $\text{Co}^{\text{II/III}}$ centre. [6] The Co^{II} ion of vitamin B_{12} [6] can coordinate cyanide, allowing for colorimetric detection of millimolar concentrations of cyanide in water. Similarly, a Co^{III} corrinoid complex has been employed as a colorimetric cyanide sensor, where cyanide replaces the water bound to the Co^{III} center. A Co^{II} salen-based fluorescent cyanide sensor has also been reported to have Co-CN bonding interactions [6c], but none of these have crystallographic support of $\text{Co}^{\text{II/III}}\text{-CN}$ coordination. In the present work, we have utilized the known affinity of cyanide ions towards the Co^{II} ion for the visual ‘naked eye’ colorimetric detection of cyanide (KCN) in water down to 10^{-5} M concentration (Fig. 1 and 3).

Fig. 1. Crystal structures of the cobalt complexes in compounds **1** and **2**, rendered with

50% thermal ellipsoids. Magenta, blue and black ellipsoids represent Co, N and C atoms, respectively; H atoms and anions are omitted for clarity.

2. Results and Discussion:

While screening chelating ligands potentially capable of selective dual cation/anion detection, we prepared a variety of terpy-type ligands and their corresponding first-row transition metal complexes. Among those metal-terpyridine compounds that have been synthesized, 10^{-5} M methanol solutions of $[\text{Co}^{\text{II}}(4\text{-pyridyl-terpy})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**1**) [7, 9†] exhibited visible color changes from red-brown to pale yellow upon addition of three equivalents of KCN (Fig. 1 and 3). The reaction between **1** and KCN in methanol leads to the formation of the new cobalt complex $[\text{Co}^{\text{III}}(4\text{-pyridyl-terpy})(\text{CN})_3]$ (**2**)†, which is characterized by single crystal X-ray diffraction (Fig. 1 and ESI). The crystallographic parameters of **1** and **2** are listed in Table S1. Such crystallographic confirmation of product after cyanide interaction is rare in the literature: only a very few examples has been reported. [8] Here cyanide showed a remarkable anti-chelating property: three cyanide moieties instantly substitute one chelating 4-pyridyl-terpyridine ligand of Co^{II} center with concomitant oxidation to Co^{III} .

Notably, even though **1** is less soluble in water compared to methanol, a 10^{-5} M aqueous solution was made by stirring **1** in water for a few hours. Similar to the behaviour in methanol, this solution exhibits an instant color change when interrogated by cyanide (Fig. 3). In subsequent investigations, we found that $[\text{Co}^{\text{II}}(\text{terpy})_2]\text{Cl}_2$ (**3**) [10, 15†] has better solubility in water than **1**. The 10^{-5} M aqueous solution of the parent cobalt-terpyridine compound **3** exhibits a similar color change from orange to mostly colorless in the presence of three equivalents of KCN. Similar to **1**, the reaction between **3** and KCN in water results in the formation of the tris-cyano complex $[\text{Co}^{\text{III}}(\text{terpy})(\text{CN})_3]$ (**4**).†

The addition of cyanide to the cobalt terpyridine complexes was detected by electronic absorption spectroscopic measurements at Co^{II} concentrations as low as $10 \mu\text{M}$ (Fig. 2 and S8). In the visible region, compound **1** displays charge-transfer bands at 450 and 517 nm; in the UV region peaks are observed at 326 nm, 278 nm, 248 nm and 210 nm, characteristic to 4-pyridyl-terpyridine ligand coordinated to Co^{II} . The intensities of the charge-transfer bands (450 nm and 517 nm) decrease gradually with each addition of cyanide and then disappear when three

equivalents of KCN are added (Fig. 2). This indicates three equivalents of KCN to a solution of **1** transforms all Co^{II} to Co^{III} as the absorption bands in the visible region diminish (Fig. 2 inset). The spectra are almost superimposable when more than three equivalents of cyanides are added, inferring the completion of the reaction. In the ultraviolet region of **1** (Fig. 2) the intensity of the 326 nm peak decreases and shifts to 317 nm gradually with successive additions of KCN (Fig. 2), which is also observed in the UV-visible spectra of the free 4-pyridyl-terpyridine ligand in methanol (Fig. S7). Aqueous solutions of **3** (10^{-5} M) show similar changes in the absorption spectra upon addition of cyanide (Fig. S8).

Fig. 2. Evolution of electronic absorption spectra for a 10^{-5} M methanolic solution of **1** upon titration with a 2×10^{-3} M KCN solution (methanol). Inset: expansion of the visible region exhibiting the vanishing of charge-transfer bands upon addition of methanolic KCN.

Changes in the fluorescence spectra for **1** and **3** upon cyanide addition in both water and methanol are negligible. The addition of KCN generates free ligand, but the weak fluorescence of these ligands overlap with the weak emissions of the parent complexes (Fig. S21 and S22).

In order to probe the selectivity of Co^{II} bis(terpy)-type complexes toward other salts, aqueous solutions of **1** and **3** were allowed to interact with salts containing different anions (Fig. 3). Complexes **1** and **3** appear to be unreactive towards the other anions tested.

Fig. 3. The influence of different anions: KCN showed significant color change in comparison to other salts, (a) in the 10^{-5} M methanolic solution of **1**; (b) in the 10^{-5} M aqueous solution of **1**. (c) in the 10^{-5} M aqueous solution of **3**. Note: the anions are added in little more than 3 equivalent including the case of ‘all+KCN’ condition.

As discussed above, two phenomena are observed upon addition of KCN to **1** or **3**: (i) the Co^{II} centre is oxidized to Co^{III} and (ii) one terpyridine ligand dissociates from its bonding interaction with the cobalt center. The reaction of the cyanide with **1** and **3** is very fast (the color change is observed in 1-2 seconds), thus it is not easy to observe if the two phenomena are occurring simultaneously or consecutively. The generation of free terpyridine and 4-pyridyl-terpyridine is confirmed by $^1\text{H-NMR}$ (Fig. 4 and S9-S16).[†] The $^1\text{H-NMR}$ spectra of **1** and **3** in CD_3OD show the presence of paramagnetic Co^{II} (Fig. 4 and S10 and S14) centres. Upon addition of KCN to **1**, the paramagnetic shifts disappear (Fig. 4 and S12) and compound **2** precipitates; consequently the presence of free 4-pyridyl-terpyridine is observed in the $^1\text{H-NMR}$ (Fig. S11 and S9). In contrast, in the case of **3**, upon addition of KCN along with disappearance of paramagnetic peaks, the spectrum shows two types of terpyridines in the $^1\text{H-NMR}$ spectrum (Fig. S15 and S16); one of which refers to free terpyridine (Fig. S13) while the other is expected to correlate to the chelated terpyridine of **4**, $[\text{Co}^{\text{III}}(\text{terpyridine})(\text{CN})_3]$. Notable here, the same colorimetric change (from **1** to **2** and **3** to **4**, respectively) is observed when KCN is added to a methanolic solution of **1** and **3** under nitrogen atmosphere, which eliminates the possibility of air oxidation (O_2) of the Co^{II} centre to Co^{III} . When an outer-sphere oxidant (NOBF_4) is first added to a CD_3OD solution of **3** (under nitrogen atmosphere), we observe oxidation of $[\text{Co}^{\text{II}}(\text{terpy})_2]^{2+}$ (**3**) to $[\text{Co}^{\text{III}}(\text{terpy})_2]^{3+}$, a color change from orange-brown to yellow, and the absence of free terpyridine (Fig. S17-S20). [10,15, 7] Subsequent addition of KCN to the “**3** + NOBF_4 ” solution in CD_3OD does not change the electronic absorption or $^1\text{H-NMR}$ spectrum (Fig. S19 and S20). This study suggests that once the Co^{II} is oxidized to Co^{III} , the cyanide substitution does not occur.

Fig. 4. (top) ^1H -NMR of **1** in CD_3OD . (Bottom) ^1H -NMR of **1** in CD_3OD in presence of KCN. All paramagnetic peaks disappear which indicates generation of **2**, the low spin Co(III) species.

Based on the NMR data we infer the mechanism of the conversion of **3** to **4** is initiated by substitution of a terpyridine for three cyanide ions, followed by oxidation to Co^{III} . If the cobalt already turns into the oxidation state of +3 state it can not coordinate with cyanide. The reduced by-product associated with this Co^{II} oxidation, i. e., the species being reduced when Co^{II} is being oxidized, has not been detected; however, similar behaviors in both air and inert atmosphere suggest the solvent (water or methanol) as likely the electron acceptor.

3. Conclusion:

The Co^{II} -bis-terpyrine based complexes **1** and **3** are found to be highly selective and sensitive for 'naked eye' colorimetric detection of $10\ \mu\text{M}$ solution of cyanide in water. This results increase the scope of using the simple 3d metal based coordination complexes for cyanide detection. Future efforts are focused on the fabrication of molecular films of **1** and/or related complexes on silica/glass surfaces to translate the present solution-based cyanide detection to hybrid sensor materials. [13-15]

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