



# Phosphorus, Sulfur, and Silicon and the Related Elements

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# Tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')cobalt(III) for anion sensing and preparation of cobalt-iron sulfide nanoparticles: A new photocatalyst for the degradation of dyes

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#### ABSTRACT

Tris(N-(pyrrol-2-ylmethyl)-N-butyldithiocarbamato-S,S')cobalt(III) (1) and tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')cobalt(III) (2) have been synthesized and characterized by elemental analysis and spectroscopy (IR, UV-vis and NMR). The elemental analysis and IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the formation of the cobalt(III) complexes with dithiocarbamate ligands. The anion binding properties of 1 and 2 based on host-guest interaction have been examined with the use of cyclic voltammetry.This study showed that both complexes preferred to bind with 1 compared to other halides. 2 has been used as precursors for the preparation of cobalt-iron sulfide nanoparticles. TEM image of cobalt-iron sulfide nanoparticles showed that the particles are spherical. The elemental compositions of the nanoparticles were confirmed by energy dispersive X-ray spectroscopy. IR spectral studies on nanoparticles confirm the presence of capping agent (triethylenetetramine). The nanoparticles were explored as photocatalysts to study the degradation of dyes using methylene blue and rhodamine-B in aqueous solution under UV irradiation. The cobalt-iron sulfide works as an efficient photocatalyst for degradation of rhodamine-B.

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Anion sensing; cobalt(III) dithiocarbamate; cobalt-iron sulfide; nanoparticles; single source precursors

#### **GRAPHICAL ABSTRACT**



#### Introduction

A wide range of metal-dithiocarbamate complexes is known with examples finding use in applications as diverse as industry, agriculture, medicine and material science.<sup>[1–7]</sup> Metal sulfide nanoparticles have shown vital applications in many fields such as IR detectors,<sup>[6]</sup> photocapacitors for energy conversion and storage,<sup>[7]</sup> sensors,<sup>[8]</sup> photonic materials<sup>[9]</sup> and advanced optoelectronic devices.<sup>[10]</sup> In recent years, transition metal dithiocarbamate complexes have received a great deal of attention because of their importance as single source precursors for the preparation of metal sulfide nanoparticles.<sup>[11,12]</sup> The N-bound organic moieties in dithiocarbamate ligands in metal complexes affect the morphology and size of the metal sulfide

nanoparticles.<sup>[13,14]</sup> These nanoparticles have been used for the photocatalytic degradation of various organic pollutants such as dyes and p-nitrophenol.<sup>[15,16]</sup> The photocatalytic activity of the metal sulfide nanoparticles depends on the morphology and size of the nanoparticles.<sup>[17]</sup> Furthermore, transition metal dithiocarbamates containing redox active ferrocene moiety are used as sensors for anions.<sup>[18,19]</sup> Particularly, cobalt(III) dithiocarbamate complexes have been used as catalysts for the synthesis of  $\beta$ -enaminoesters and  $\beta$ -enaminones from 1,3-diketones and  $\beta$ - ketoesters,<sup>[20]</sup> sensor for ions<sup>[21,22]</sup> and single source precursors for the preparation of metal sulfide nanoparticles.<sup>[23]</sup> Our aim is to prepare cobalt(III) dithiocarbamate complexes for the sensing of anions and preparation of cobalt

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Scheme 1. Preparation of the complexes 1 and 2.

sulfide and cobalt-iron sulfide nanoparticles. In this paper we report, synthesis and characterization of tris(N-(pyrrol-2-ylmethyl)-N-butyldithiocarbamato-S,S')cobalt(III) (1) and tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-

S,S')cobalt(III) (2) and their utilization for anion sensing and in addition, preparation of cobalt-iron sulfide nanoparticles from complex 2 and photocatalytic behavior of as-prepared nanoparticles for dye degradation are presented.

#### **Results and discussion**

Complexes 1 and 2 were prepared according to the synthetic procedure shown in Scheme 1. Butylamine and 2-phenylethylamine were condensed with pyrrole-2-carboxaldehyde and ferrocenecarbaldehyde, respectively, to form the imines. The imines were reduced with NaBH<sub>4</sub> to yield the secondary amines. 1 and 2 were prepared from the secondary amine by reaction with  $CS_2$ and  $CoCl_2$ . The complexes are quite stable at ambient conditions. They are soluble in chloroform, dichloromethane and acetonitrile and insoluble in ethanol and methanol.

#### **Spectral studies**

IR, UV-vis and NMR (<sup>1</sup>H and <sup>13</sup>C) spectra of complexes 1 and 2 are shown in Figures S 1 to S 8 (Supplemental Materials).

#### **IR spectral studies**

The IR spectra of the metal dithiocarbamate complexes are used to find the coordination mode (monodentate or bidentate) of the dithiocarbamate ligands.<sup>[24]</sup> In the case of a bidentate coordinating mode, a solitary band is observed in the region of 950–1050  $\text{cm}^{-1}$  while the splitting of this band within a narrow range of 20  $\text{cm}^{-1}$  is due to the monodentate coordination of dithiocarbamate ligand. Only one band associated with the C-S stretching is observed around 1027  $cm^{-1}$  for 1 and 2 in the IR spectra confirming the bidentate coordination mode of the ligands. The spectral region from 1450-1500 cm<sup>-1</sup> is associated with the  $\nu_{\text{C-N}}$  (thioureide) vibrational mode. For complexes 1 and 2, the ( $\nu_{C-N}$ ) (thioureide) were found around 1485 cm<sup>-1</sup>, indicating the partial double bond character. The vN-H value exhibited by 1 (3380 cm<sup>-1</sup>) indicates the non-involvement of pyrrole nitrogen in the coordination.

#### NMR spectral studies

#### <sup>1</sup>H NMR spectral studies

The protons of methylene group attached to pyrrole group in complex 1 appear around 4.75 ppm. The remaining three signals in the aliphatic region are due to the butyl group; that shifted to lower field being nitrogen bound. NH protons of pyrrole rings are observed at 9.04 ppm. The methylene protons of ferrocenyl methyl, NCH<sub>2</sub> protons of NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and ferrocene ring protons are appeared in the region 3.65-4.80 ppm for complex **2**. The aromatic proton signals of both complexes are appeared in the region 6.15-7.30 ppm.

### <sup>13</sup>C NMR spectral studies

For complex **1**, the signals for methylene carbon attached to pyrrole and NCH<sub>2</sub> (butyl) carbons are observed at 48.1 and 44.7 ppm, respectively. The other signals that appeared in the aliphatic region of **1** are assigned to the remaining carbons of methylene and methyl of butyl group. In the case of complex **2**, the signals observed at 33.4, 47.9 and 49.2 ppm are due to methylene carbon of N-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, ferrocenyl methyl group and N-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, respectively. Ferrocene ring carbons resonate in the region 68.5-77.2. The important <sup>13</sup>C NMR chemical shift value of the thioureide carbon (N<sup>13</sup>CS<sub>2</sub>) was observed at 205.6 and 205.0 ppm for **1** and **2**, respectively due to the partial double bond character of N-CS<sub>2</sub> bond in the dithiocarbamate ligands.

#### **Electronic spectral studies**

UV-vis spectra of metal-dithiocarbamate complexes usually show three absorption bands in the ultraviolet region due to  $\pi$ - $\pi^*$  transition of NCS and SCS moiety and n- $\pi^*$  transition (i.e. transfer of a electron of the lone pair on the S to an antibonding  $\pi$ -orbital).<sup>[25]</sup> In the present study, these three bands are observed around 250, 275 and 325 nm. The band which appeared around 400 nm may be due to either metal- $\rightarrow$ ligand or ligand $\rightarrow$  metal charge transfer. Complexes 1 and 2 show two bands in the visible region (488 and 642 nm for 1 and 472 and 632 nm for 2) due to d-d transitions. The absorption pattern suggests an octahedral coordination around Co(III).<sup>[26]</sup>

#### Preliminary anion binding studies

The anion sensing studies of complexes 1 and 2 with biologically important anions like  $F^-,\ Cl^-,\ Br^-$  and  $I^-$  were performed using cyclic voltammetry and cyclic voltammograms are displayed in Figure 1. Both the complexes were examined for their anion sensing ability by cyclic voltammetry in 1  $\times$  10  $^{-4}$  M CH\_3CN solution containing 0.01 M of tetrabutylammonium fluoroborate as supporting electrolyte. The cyclic voltammogram of complex 1 shows reduction at -1.1555V. This is one electron reduction and similar reduction was observed in cobalt (III) dithiocarbamate complexes.<sup>[27]</sup> Upon the addition of halide ions, complex 1 exclusively response to I, with the reduction potential of the complex 1 shift from -1.1555 V to -1.5568 V ( $\Delta E =$ 0.4013 V) however, the addition of F<sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup> shows very less change in reduction potential of the complex 1 (0.025-0.063 V). The tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')cobalt(III) (2) containing three ferrocenyl groups exhibits a single oxidation wave at 0.8816 V which suggests that three ferrocene moieties are oxidized in a single step and are electrochemically independent of one another.<sup>[18]</sup> The addition of  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  anions to electrochemical solution of the complex **2** resulted in significant cathodic shifts of ferrocene redox couple.  $I^-$  induced larger magnitudes of cathodic shift in the ferrocene redox couple compared to  $F^-$ ,  $Cl^-$  and  $Br^-$  (Table 1). This suggests a preferential binding interaction with the  $I^-$  anion. No detectable shifts were observed for Co(III) dithiocarbamate imidazolinium cryptand receptor.<sup>[28]</sup> Tris(N-furfuryl-N-methylferrocenyldithiocarbamato-S,S)cobalt(III) preferred to bind with  $Br^-$  compared to those of benzoate,  $F^-$  and  $I^$ ions.<sup>[22]</sup> These studies indicates that anion sensing property of complexes depends on N-bound organic moiety of dithiocarbamate ligand.

#### Characterization of metal sulfide nanoparticles

The morphological characterization of cobalt-iron sulfide nanoparticles was carried out using TEM and is shown in Figure 2. TEM image demonstrated that cobalt-iron sulfide are perfect spherical and quasispherical in shape and the particles diameter are in the range 11–35 nm. Synthesis and characterization of cobalt iron sulfide nanoparticles from tris(N-furfuryl-N-methylferrocenyldithiocarbamato-S,S)cobalt(III) were reported.<sup>[22]</sup> This nanoparticles are cuboid. Hence, the shape of nanoparticles are influenced by the N-bound organic moiety of dithiocarbamate ligand.

To confirm the chemical composition of the product, cobalt-iron sulfide are analyzed using Energy dispersive X-ray spectroscopy (EDS). Energy dispersive X-ray spectrum of cobalt-iron sulfide nanoparticles are displayed in **Figure S 9** and the EDS data shows that the ratio of Co:Fe:S in cobalt iron sulfide is 1:1.7:2.5. This confirms the formation of cobalt-iron sulfide

The optical properties of cobalt-iron sulfide were studied by the UV-vis absorption and photoluminescence (PL) spectroscopic techniques and are shown in **Figures S 10** and **S 11**. The room temperature absorption and emission spectra were recorded by dispersing the samples in ethanol. Optical absorption spectra of cobalt sulfide exhibit a band at 264 nm, which is blue shifted from the absorption edge of the bulk cobalt sulfide<sup>[29]</sup> and iron sulfide.<sup>[30]</sup> The increase in band gap energy of cobalt-iron sulfide nanoparticles indicates the quantum confinement effect due to the decrease in size. The PL spectrum of cobalt-iron sulfide shows a broad peak at 422 nm. This is due to the radiative transition of electrons from shallow trap states near the conduction band to sulfur vacancies residing near the valence band.

The FT-IR spectrum of cobalt-iron sulfide nanoparticles is shown in **Figure S 12**. In IR spectrum, the bands in the region 2850–2960 cm<sup>-1</sup> are assigned to C-H vibrations of the sample. A broad peak observed around 3400 cm<sup>-1</sup> can be assigned to the N-H stretching mode. These observations suggest the presence of capping agent triethylenetetramine. The absence of bands around 1480 cm<sup>-1</sup> and 3060–3150 cm<sup>-1</sup> due to C-N (thioureide) and C-H (aromatic) stretching modes confirm that dithiocarbamate ligands are not present with the cobalt-iron sulfide.



Figure 1. Changes in the cyclic voltammograms of complexes (a) 1 and (b) 2 on the additions of anions.

#### Photocatalytic activity

The photocatalytic activity performance of as-prepared cobaltiron sulfide was evaluated by photocatalytic degradation of methylene blue and rhodamine-B in aqueous solutions. It should be noted that the experiment in the absence of catalyst exhibited negligible amount of methylene blue and rhodamine-B photodegradation, indicating that self photolysis of methylene blue and rhodamine-B is negligible under ultraviolet irradiation. The degradation of methylene blue and rhodamine-B dyes under ultraviolet light irradiation was followed by spectrophotometric monitoring. The experimental results are expressed by the change in relative concentration of dyes with irradiation time and are shown in Figure 3. This shows the continuous decrease in concentration of aqueous solution of

Table 1. Electrochemical anion recognition data of complexes 1 and	12.
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Anions complex	Complex (1)		Complex (2)	
	Complex	-1.1555	_	0.8955
TBA Fluoride	-1.0960	0.0595	0.9051	0.0096
TBA Chloride	-1.2187	0.0632	1.3115	0.4160
TBA Bromide	-1.1307	0.0248	1.1893	0.2938
TBA lodide	-1.5568	0.4013	1.4587	0.5632

<sup>a</sup>shift of Co(III) /Co(II) reduction potential produced by the anions. <sup>b</sup>shift of Fc/Fc+ oxidation potential produced by the anions.

dyes in presence of catalyst (cobalt-iron sulfide) with UV light irradiation. After irradiation of 180 min, the spectra suggest the 95% and 97% of degradation of methylene blue and rhodamine-B, respectively in presence of cobalt-iron sulfide. Cobalt



Figure 2. TEM image of cobalt-iron sulfide.

sulfide (Co<sub>3</sub>S<sub>4</sub>) nanoparticles prepared from tris(N,N-difurfuryldithiocarbamato-S,S')cobalt(III) were used as catalyst for the degradation of rhodamine-B under ultraviolet irradiation. Co<sub>3</sub>S<sub>4</sub> degraded 85% of rhodamine-B in 180 min.<sup>[22]</sup> This study indicates that as-prepared cobalt-iron sulfide acts as good catalyst for dye degradation.

#### Mechanism of photodegradation process

In the presence of air, the irradiated semiconductor nanoparticles are capable of destroying many organic pollutants. The activation of metal sulfide by UV irradiation produces electron-hole pairs which are powerful oxidizing and reducing agents, respectively.

CoFeS + 
$$h\gamma \rightarrow h^+ + e^-$$

The oxidative and reductive reactions are expressed as:

$$OH^{-}+ h^{+} \rightarrow OH \text{ and } O_{2} + e^{-} \rightarrow O_{2}^{-}$$

These hydroxyl radicals degraded the dye molecule and hence the decolourisation of the solution occurred.

#### **Experimental**

#### Materials and instrumentation

All reagents and solvents were commercially available highgrade materials (Merck/Sd fine/Sigma Aldrich) and used as received. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range: 4000–400 cm<sup>-1</sup>) as KBr pellets. A Shimadzu UV-1650 PC double-beam UVvis spectrophotometer was used for recording the electronic spectra. The spectra of complexes were recorded in CHCl<sub>3</sub> and the pure solvent was used as the reference. The NMR spectra were recorded on Bruker 500 MHz NMR spectrometer at room temperature in DMSO- $d_6$ , using TMS as internal reference. TEM images were recorded using TECNAI T2 G2 make-FEI. EDS were performed by SUPRA 55VP CARL. Photoluminescence spectra were recorded using Perkin Elmer 1555 fluorescence spectrophotometer at room temperature.

#### Cyclic voltammetric studies

Cyclic voltammetry was performed using a conventional three electrode system. A glassy carbon (GC) was used as a working electrode. The counter electrode was a platinum wire, and reference electrode was Ag/AgCl. The HPLC grade of dichloromethane was used as the solvent and tetrabuty-lammonium fluoroborate (0.01 M) as the supporting electrolyte. The scan rate was 100 mVs<sup>-1</sup>. Complexes **1** and **2** were investigated at 25 °C in an oxygen-free atmosphere, provided by bubbling purified nitrogen through the solution. The concentration of the compounds was  $1 \times 10^{-4}$  M and electrochemical solution of (n-Bu<sub>4</sub>N) X (X = I, Br, Cl, F; 5  $\times 10^{-4}$  M) in CH<sub>2</sub>Cl<sub>2</sub>. Cyclic voltammograms were recorded on a CHI604C Electrochemical Analyser.

#### Photocatalytic experiments

The photocatalytic activity of cobalt-iron sulfide was evaluated by degradation of aqueous solution of methylene blue and rhodamine-B. All the solutions were prepared using double distilled water. A typical photocatalytic experiments, Catalyst (0.1 g) was added to an aqueous solution of dye (50 mL) in the concentration of  $1.0 \times 10^{-4}$  M. The solution was maintained under darkness for 30 min to reach dye



Figure 3. Time-dependent UV-Vis absorption spectra for decolourization of (a) methylene blue and (b) rhodamine-B using cobalt-iron sulfide under ultraviolet light.

solution adsorption-desorption equilibrium. The solution with the suspended nano-photocatalyst was irradiated by UV light from mercury vapour lamp. At given time intervals, 3 mL of aliquots was withdrawn and centrifuged to remove catalyst, concentration of both dye solution was determined with the help of UV-vis spectrophotometer.

#### **Preparation of amines**

N-(pyrrol-2-ylmethyl)-N-butylamine and N-methylferrocenyl-N-(2-phenylethyl)amine were prepared by general methods reported earlier.<sup>[12]</sup>

## Preparation of tris(N-(pyrrol-2-ylmethyl)-Nbutyldithiocarbamato-S,S')cobalt(III) (1)

N-(pyrrol-2-ylmethyl)-N-butylamine (3.0 mmol) in ethanol (20 mL) was mixed with carbon disulfide (3.0 mmol, 0.2 mL) under ice cold condition (5 °C). The solution was stirred for 30 min. This produced the (N-(pyrrol-2-ylmethyl)-N-butyldi-thiocarbamic acid solution.<sup>[12]</sup> An aqueous solution of  $CoCl_2 \cdot 6H_2O$  (1.0 mmol, 10 mL) was added to the dithiocarbamic acid solution resulting in the formation of a green precipitate. The precipitate obtained was filtered, washed several times with cold water and then air dried (Scheme 1). It was observed that Co(II) is converted to Co(III) by aerial oxidation in the

presence of dithiocarbamate ligands, forming Co(III) tris(dithiocarbamate) complexes.<sup>[26]</sup> Yield: 78%, mp: 155-156 °C. IR (KBr, cm<sup>-1</sup>):  $\nu = 3380 \ (\nu_{\text{N-H}})$ , 1488  $(\nu_{\text{C-N}})$ , 1027  $(\nu_{\text{C-S}})$ . UV-Vis (CHCl<sub>3</sub>, nm):  $\lambda$  ( $\epsilon$ ,dm<sup>3</sup> mol<sup>-1</sup>·cm<sup>-1</sup>) = 250, 277, 327, 400, 488 (52), 642: <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  0.98 (broad, 9H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.38 (broad, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C CH<sub>3</sub>), 1.68 (broad, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 3.65 (6H, N-CH2-CH2-CH2-CH3) 4.67- 5.02 (m, 6H, N-CH2 (pyrrole)), 6.15 (s, 3H, H-3(pyrrole)), 6.20 (s, 3H, H-4, (pyrrole)), 6.81 (s, 3H, H-5(pyrrole)), 9.04 (3H, NH-pyrrole). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  13.7 (N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.1 (N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 28.9 (N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 44.7 (N-CH<sub>2</sub>-CH<sub>2</sub>-CH2-CH3), 48.1 (N-CH2 (pyrrole)), 107.8, 109.4, 119.1, 125.6 (pyrrole ring carbons), 205.6 (NCS<sub>2</sub>). Anal. Calcd. for C30H45CoN6S6, (%): C, 48.62; H, 6.12; N, 11.34; found (%): C, 48.49; H, 6.08; N, 11.24 .

## Preparation of tris(N-methylferrocenyl-N-(2phenylethyl)dithiocarbamato-S,S')cobalt(III) (2)

A method similar to that described for the synthesis of **1** was adopted; however, N-methylferrocenyl-N-(2-phenyle-thyl)amine was used instead of N-(pyrrol-2-ylmethyl)-N-butylamine (Scheme 1) Yield: 84%, mp: 165-166 °C. IR (KBr, cm<sup>-1</sup>):  $\nu = 1485 \ (\nu_{C-N})$ , 1025 ( $\nu_{C-S}$ ). UV-Vis (CHCl<sub>3</sub>, nm):  $\lambda$  ( $\varepsilon$ ,dm<sup>3</sup> mol<sup>-1</sup>cm<sup>-1</sup>) = 249, 274, 323, 401, 472 (59), 632: <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.91 (N-CH<sub>2</sub>-CH<sub>2</sub>-

C<sub>6</sub>H<sub>5</sub>), 3.65–4.80 (NCH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, N-CH<sub>2</sub> ferrocenyl and cyclopentene), 7.24 (broad, 15H, phenyl ring protons) <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  33.4 (N-CH<sub>2</sub>-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 47.9 (N-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), 49.2 (N-CH<sub>2</sub>-ferrocenyl), 68.6, 68.8, 70.1, 80.1 (C-C (ferrocenyl ring carbons) 126.5, 128.6, 128.8, 138.3 (phenyl ring carbons), 205.0 (NCS<sub>2</sub>). Anal. Calcd. for C<sub>60</sub>H<sub>60</sub>CoFe<sub>3</sub>N<sub>3</sub>S<sub>6</sub> (%): C, 58.02; H, 4.87; N, 3.38; found (%): C, 58.00; H,4.84; N,3.37.

#### Preparation of cobalt-iron sulfide

2 (0.5 g) was mixed with triethylenetetraamine (15 mL) in a round bottom flask and then the content of the flask was refluxed for 15 min. The black precipitate obtained was filtered off and washed with methanol.

#### Conclusions

In this contribution two new cobalt(III) dithiocarbamates containing pyrrole (1) and ferrocenyl (2) units were synthesized and characterized by elemental analysis and spectroscopic techniques. UV-vis spectral data are consistent with the formation of octahedral cobalt(III) complexes. Both the complexes were evaluated for their ability to sense halide ions using cyclic voltammetric techniques. Both the complexes prefer to bind with I<sup>-</sup>. Complex 2 contains redox active ferrocene moiety is a better sensor compared to those of 1. Bimetallic sulfide (cobalt-iron sulfide) nanoparticles were successfully prepared from 2 and characterized by EDS, TEM, UV-vis, photoluminescence and FT-IR spectroscopy. Photocatalytic activity of as prepared nanoparticles was evaluated by degradation of methylene blue and rhodamine-B in aqueous solution under ultraviolet irradiation. It was found that the as prepared cobalt-iron sulfide is an efficient photocatalyst for the degradation of rhodamine-B. This study indicates that cobalt(III) dithiocarbamate complexes can be used for sensing anions and synthesis of bimetallic sulfide nanoparticles.

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### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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