

## SPECTRAL AND STRUCTURAL STUDIES ON NICKEL(II) DITHIOCARBAMATE COMPLEXES AND THEIR UTILITY FOR SENSING ANIONS

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### Abstract

Bis(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')nickel(II) (1) and bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamate-S,S')nickel(II) (2) have been prepared and characterized by IR, and UV-visible absorption spectra. The electrochemical anion sensing ability of bis(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')nickel(II) (1) and bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamate-S,S')nickel(II) (2) toward  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  was investigated. Cyclic voltammogram of 1 shows a peak at -0.8416 V which corresponds to the normally observed and well documented Ni(II)/Ni(I) reduction (one electron addition). The addition of  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  anions to electrochemical solutions of the complex 1 resulted in a significant shift in the Ni(II)/Ni(I) reduction potential

**Key words:** Nickel (II) dithiocarbamate, Spectral Studies, Anion Sensing

### Introduction

Dithiocarbamates are widely used as reagent in organic synthesis, medicine, biology and other field of science [2, 11]. The most widespread use of dithiocarbamates is found in the rubber industry where they are used as vulcanization accelerators. At the same time, they have good antioxidant properties which makes them even more valuable. These antioxidant properties are also put to good use in greases and oils. Dithiocarbamates are used as fungicides.

Dithiocarbamates and their complexes have been widely used as antibacterial agents [12]. Dithiocarbamates containing piperazine [13], piperidine [14], saccharin [15], imidazoles [16], propanol and pyrrolidine [17] have been tested for their antibacterial potency. Transition metal dithiocarbamate complexes generally exhibit higher antibacterial activities than the parent ligands. Cis-platin is still the most predominately used and effective drug for the cancer treatment [18]. The search for new anticancer drugs has been necessitated by the fact that cis-platin had a lot side effects such as nausea and vomiting [18]. Dithiocarbamates especially those of palladium and platinum uses for the treatment of cancer have shown reduced side effects [18]. In addition, diethyldithiocarbamate is effective chemoprotective agent and is the only chemoprotective when administrate after cis-platin [19]. Dithiocarbamates are used in a variety of house hold applications as herbicide, anthelmintics and pest repellent [20]. The uses of dithiocarbamates are also therapeutic agents for alcoholism and metal intoxication. The dithiocarbamates effect acquired immune depressive syndrome. Dithiocarbamates have been used in conjunction with polymers in water treatment for the removal of heavy metal ion [21-23].

## 2 Experimental

### 1.1. Materials and instrumentation

Reagent grade chemicals were procured from commercial sources and used as such. The synthesis of the compounds was carried out under an inert-gas atmosphere of nitrogen. Solvents were purified according to standard procedures and dried before use whenever required. IR spectra were recorded on a thermo NICOLET AVATAR 330 FT-IR spectrophotometer. The  $^1H/^{13}C$  NMR spectra were recorded on BRUKER 400/100 MHz NMR spectrometer at room temperature in  $CDCl_3$  solvent. SHIMADZU UV-1650 PC double beam UV-visible spectrophotometer was used for recording the electronic spectra of the complexes.

## 1.2. Cyclic voltammetric studies

Cyclic voltammograms were recorded on a CHI604C Electrochemical Analyser. The working electrode was glassy carbon. The counter electrode was a platinum wire, and reference electrode was Ag/AgCl. Pure dichloromethane was used as the solvent and tetrabutylammonium fluoroborate (0.01 M) as the supporting electrolyte. The scan rate was  $100 \text{ mVs}^{-1}$ . All the measurements were recorded at room temperature ( $27^\circ\text{C}$ ) in an oxygen-free atmosphere, provided by bubbling purified nitrogen through the solution. The concentration of the compounds was  $1 \times 10^{-4} \text{ M}$  and electro chemical solution of (n-Bu<sub>4</sub>N) I, (n-Bu<sub>4</sub>N) Br, (n-Bu<sub>4</sub>N) F and sodium benzoate ( $5 \times 10^{-4} \text{ M}$ ) in  $\text{CH}_2\text{Cl}_2$ .

## 1.3. Preparation of complexes

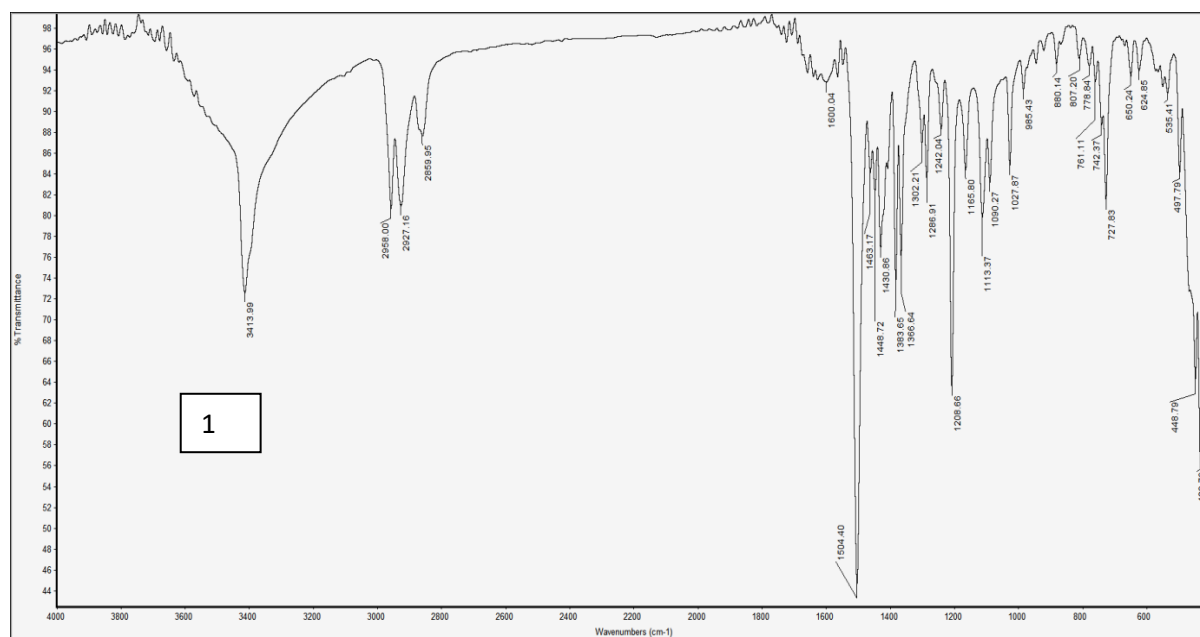
N-(pyrrol-2-ylmethyl)-N-butylamine and N-methylferrocenyl-N-(2-phenylethyl)amine of nickel (II) dithiocarbamate complexes were prepared by general methods reported earlier [24].

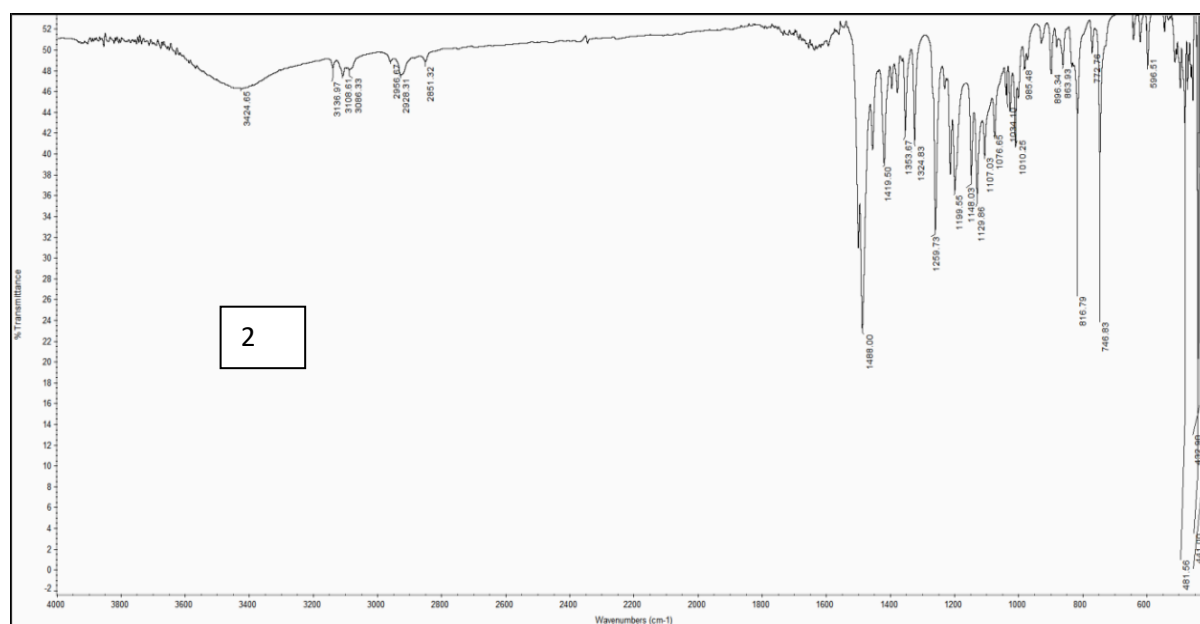
## 3. Result And Discussion

### 3.1. Spectral studies

#### 3.1.1. Infrared spectral studies

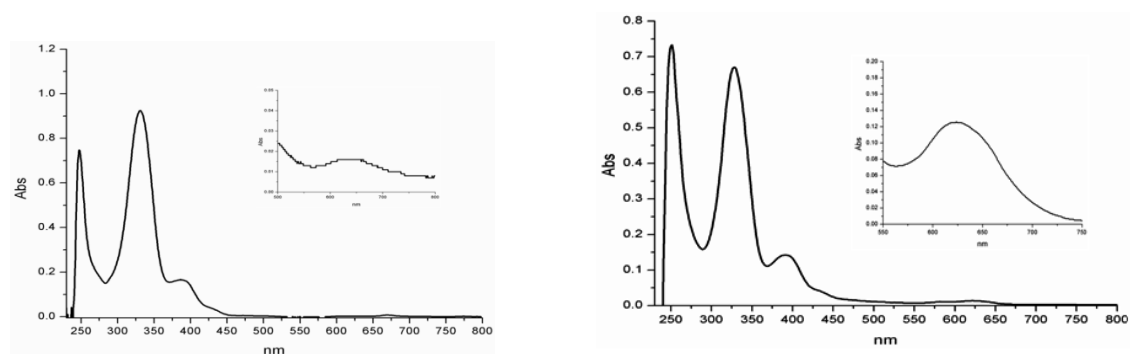
IR spectra of complexes **1** and **2** display a  $\nu_{\text{C-N}}$  (thioureide) band in the region  $1478\text{--}1527 \text{ cm}^{-1}$ , indicating the partial double bond character of  $\text{S}_2\text{C-N}$  bond in dithiocarbamate ligand. The presence of a single sharp band in the region of  $1010\text{--}1029 \text{ cm}^{-1}$  for complexes **1** and **2** is indicative of bidentate coordination of dithiocarbamate ligand via its two sulfur atoms [25, 26].



Fig. 1. IR spectra of complexes **1** and **2**

### 3.1.2. Electronic spectral studies

Electronic spectra of complexes **1** and **2** apparently show a high intensity band around 250 nm is attributed to the  $\pi \rightarrow \pi^*$  of N=C=S system and a band *ca.* 330 nm is assigned to the  $n \rightarrow \pi^*$  located on sulfur [4]. A band observed around 390 nm for homoleptic complex **1** and **2** is assigned to the ligand to metal (LMCT) or metal to ligand (MLCT) charge transfer transitions. These are characteristic feature of coordinated dithiocarbamate ligands. Electronic spectra of homoleptic complexes **1** and **2** reveal two absorptions around 463-479 nm and 620 – 668 nm assignable to  $d_z^2 \rightarrow d_{x^2-y^2}$  and  $d_{xy} \rightarrow d_{x^2-y^2}$  transitions, respectively. In previously described nickel(II) bis(dithiocarbamate) complexes, similar bands were reported and ascribed to transitions from the lower filled d-orbitals to the unoccupied  $d_{x^2-y^2}$  orbitals [6].

Fig.2. Electronic spectrum of complexes **1** and **2**

## 4. Anion binding studies

The electrochemical anion sensing ability of bis(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')nickel(II) (**1**) and bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamate-S,S')nickel(II) (**2**) toward  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  was investigated. Cyclic voltammogram of **1** shows a peak at -0.8416 V which corresponds to the normally observed and well documented Ni(II)/Ni(I) reduction (one electron addition). The addition of  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  anions to electrochemical solutions of the complex **1** resulted in a significant shift in the Ni(II)/Ni(I) reduction potential (Table 1 and Fig. 3). Table 1 shows that the anion induced magnitudes of shift in the respect of

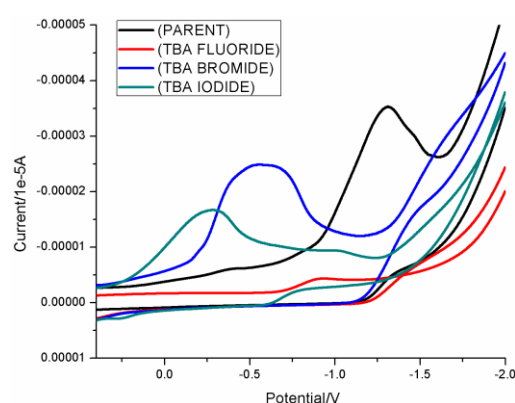
Ni(II)/Ni(I) reduction potential. Table 1 suggests that complex **1** show a preferential binding interaction with  $I^-$ . Fig. 3 revealed that **2** shows moderate electrochemical sensing to  $Br^-$  with the  $\Delta E=0.3328$  V, respectively. However, the addition of other anions to **2** in  $CH_3CN$  solution exhibits a little or almost no change in its electrochemical potential.

Table.1. Electrochemical anion recognition data of complexes **1** and **2**

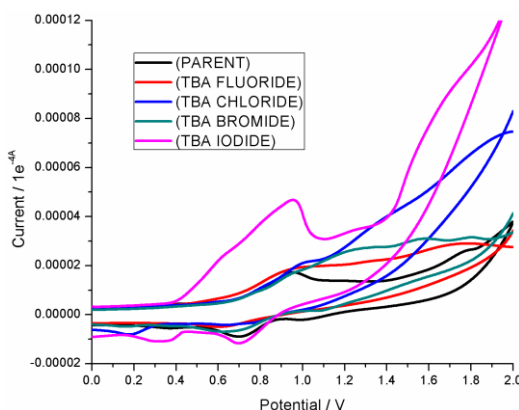
Anions Complex	Complex (1)		Complex (2)	
	E <sub>pc</sub> (V)	$\Delta E_{1/2}$ (V) <sup>a</sup>	E <sub>pc</sub> (V)	$\Delta E_{1/2}$ (V) <sup>b</sup>
Complex	-0.8416		0.9541	
TBA Fluoride	-0.8786	0.037	0.9835	0.0294
TBA Chloride	-0.5306	0.311	0.9984	0.0443
TBA Bromide	-0.5766	0.265	1.2869	0.3328
TBA Iodide	-0.2776	0.564	0.9691	0.015

<sup>a</sup>-shift of Ni(II)/Ni(I) reduction potential produced by the anions

<sup>b</sup>-shift of Fc/Fc<sup>+</sup> oxidation potential produced by the anions



Complex **1**



Complex **2**

Fig. 3. Changes in the cyclic voltammograms of complexes (a) **1** and (b) **2** on the addition of anions.

## 5. Conclusions

Complexes **1** and **2** were prepared and characterized by elemental analysis, IR, NMR and UV-visible spectroscopy. Cyclic voltammogram of **1** shows a peak at -0.8416 V which corresponds to the normally observed and well documented Ni(II)/Ni(I) reduction (one electron addition). The addition of  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  anions to electrochemical solutions of the complex **1** and **2** resulted in a significant shift in the Ni(II)/Ni(I) reduction potential.

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