

## Synthesis, characterization and biological activity of some nickel(II) mixed ligands complexes of dithiocarbamate and 1,10-phenanthroline

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## ARTICLE INFORMATION



DOI: 10.5155/eurjchem.8.4.367-370.1636

Received: 11 August 2017  
 Received in revised form: 23 September 2017  
 Accepted: 07 October 2017  
 Published online: 31 December 2017  
 Printed: 31 December 2017

## KEYWORDS

Sulfur ligands  
 Bidentate nitrogen ligands  
 Heterocyclicdithiocarbamate  
 Tetramethylenedithiocarbamate  
 Pentamethylenedithiocarbamate  
 Nickel(II) mixed ligand complexes

## ABSTRACT

Two ligands; pyrrolidine-1-carbodithioate sodium salt ( $L^1$ ) and piperidine-1-carbodithioate sodium salt ( $L^2$ ) and their nickel(II) mixed ligands complexes with 1,10-phenanthroline ( $L^3$ ) have been synthesized and characterized by FT-IR, UV-visible,  $^1H$  NMR spectra. The biological activities of these complexes were also evaluated. The spectral data indicated that the 1,10-phenanthroline and dithiocarbamate ligands are considered as a bidentate nitrogen and sulfur ligands, respectively. The study suggested that the above ligands formed complexes of general formula  $[Ni(L^x)_2(L^3)_1]$  and  $[Ni(L^x)_1(L^3)_2]Cl$  ( $x=1$  or  $2$ ) mononuclear (monomer) complexes. The complexes show moderate and selective activity against tested microorganisms.

Cite this: *Eur. J. Chem.* 2017, 8(4), 367-370

## 1. Introduction

Dithiocarbamates (DTCs) are the half amides of dithiocarbonic acids belong to a class of compounds known as the 1,1-dithiolates [1,2], they are also include dithiophosphates, dithiophosphinates and other related compounds, which can function either as unidentate or bidentate chelating ligands [3-5]. Dithiolates are formed when nucleophiles attack carbon disulphide [1]. There are some reports for synthesis of DTC derivatives in the literature [6-9], also there is a substantial interest in developing efficient one-pot-three component reaction from a simple starting materials (amines, carbon disulfide and epoxides) in novel reaction media such as water and ionic liquid [10-13]. These 1,1-dithiolate systems are of current interest due to their potential biological activity and practical application in the field of rubber technology and agriculture in addition to general consideration of metal-sulfate bonding and electron delocalization in transition of metal complexes [14,15].

In this report, we synthesized two bidentate sulfur donor ligands, tetramethylene- or pentamethylene-dithiocarbamate sodium salt ( $L^1$  and  $L^2$ , respectively) and their nickel(II) mixed ligands complexes with 1,10-phenanthroline ( $L^3$ ). The prepared compounds have been characterized by elemental analysis, FT-IR, UV-Visible,  $^1H$  NMR and anti-bacterial activity.

## 2. Experimental

## 2.1. Materials

All starting materials were purchased from Fluka Chemicals Comp. and they were used without further purification.

## 2.2. Instrumentation

The FT-IR spectra by KBr pellets were recorded by using a FT-IR 8400S spectrophotometer model 2000 from Shimadzu Japan. The  $^1H$  NMR spectral data were recorded at room temperature by using a Bruker NMR spectrometer (300 MHz). The electronic spectra were recorded in the UV-visible range 200-800 nm by using a UV-9200 Biotech Engineering Management Co. LTD. (UK.) UV spectrophotometer.

## 2.3. Synthesis of dithiocarbamate ligands

A general method for the preparation of DTC ligands is the nucleophilic addition reaction of N-nucleophiles with carbon disulphide ( $CS_2$ ) as in below.



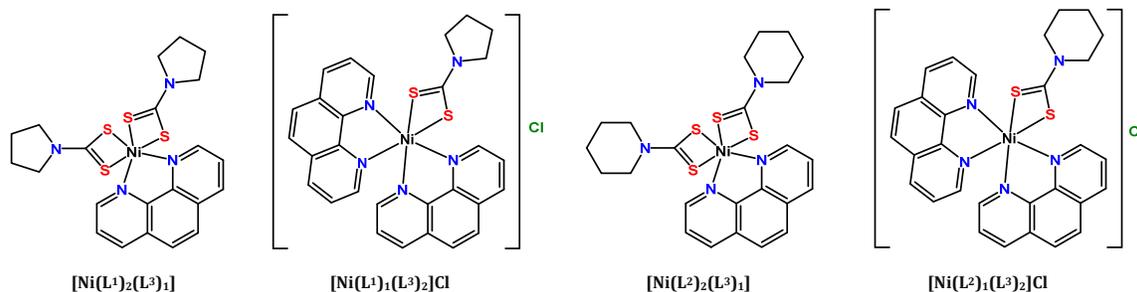


Figure 1. Molecular structure of the prepared compounds.

Dithiocarbamate ligands have been prepared according to literature [16-18] by treating a solution of secondary amine (80 mmol) in 70 mL of ethanol with sodium hydroxide (80 mmol) in 10 mL of distilled water whilst cooling and stirring carbon disulphide (8 mmol) then added gradually with continuous cooling over 30 min and maintained the temperature below 10 °C. The white product of dithiocarbamate was filtered, washed with methanol and dried in vacuum.

**Sodium tetramethylenedithiocarbamate (L¹):** Color: Yellowish-white solid. Yield: 67%. M.p.: 150-152 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1423  $\nu$ (C-N), 999  $\nu$ (C-S), 1326  $\nu$ (N-C), 864  $\nu$ (C-S).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 3.62-3.67 (s, 4H,  $\text{CH}_2$ -N), 1.79-1.83 (m, 4H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 241, 257, 308. Anal. calcd. for  $\text{C}_5\text{H}_8\text{NNaS}_2$ : C, 35.48; H, 4.76; N, 8.28. Found: C, 34.3; H, 4.53; N, 8.2%.

**Sodium pentamethylenedithiocarbamate (L²):** Color: White solid. Yield: 70%. M.p.: 160-162 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1467  $\nu$ (C-N), 1008  $\nu$ (C-S), 1226  $\nu$ (N-C), 889  $\nu$ (C-S).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 4.23-4.29 (s, 6H,  $\text{CH}_2$ -N), 1.51-1.56 (m, 4H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 240, 270, 284. Anal. calcd. for  $\text{C}_6\text{H}_{10}\text{NNaS}_2$ : C, 39.32; H, 5.50; N, 7.64. Found: C, 40.70; H, 5.31; N, 8.90%.

#### 2.4. Synthesis of complexes

L¹ or L² ligands (2 mmol, individually in  $\text{H}_2\text{O}$ -ethanol mixed solvent) were added dropwise with vigorous stirring to an aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) and an aqueous solution of 1,10-phenanthroline (L³) (1 mmol) with gentle heating for 1 h. The obtained green complexes were separated out, filtered, washed thoroughly with water, recrystallized from chloromethane and dried in vacuum over  $\text{P}_2\text{O}_5$  (Figure 1) [19].

**[Ni(L¹)₂(L³)₁]:** Color: Greenish Yellow. Yield: 75%. M.p.: 122-124 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1508  $\nu$ (C-N), 946  $\nu$ (C-S), 1336  $\nu$ (N-C), 887  $\nu$ (C-S), 453  $\nu$ (M-S), 444  $\nu$ (M-N).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 4.08-4.10 (m, 8H,  $\text{CH}_2$ -N), 1.94-1.97 (m, 8H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 234, 286, 384. Anal. calcd. for  $\text{C}_{22}\text{H}_{24}\text{N}_4\text{NiS}_4$ : C, 49.73; H, 4.55; N, 10.54. Found: C, 49.34; H, 4.80; N, 10.00%.

**[Ni(L¹)₁(L³)₂]Cl:** Color: Reddish Brown. Yield: 77%. M.p.: 115-117 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1458  $\nu$ (C-N), 950  $\nu$ (C-S), 1238  $\nu$ (N-C), 846  $\nu$ (C-S).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 4.09-4.37 (m, 4H,  $\text{CH}_2$ -N), 1.39-1.77 (m, 4H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 245, 266, 324. Anal. calcd. for  $\text{C}_{29}\text{H}_{24}\text{ClN}_5\text{NiS}_2$ : C, 57.97; H, 4.03; N, 11.66. Found: C, 58.10; H, 4.44; N, 12.13%.

**[Ni(L²)₂(L³)₁]:** Color: Reddish Brown. Yield: 83%. M.p.: 132-134 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1509  $\nu$ (C-N), 998  $\nu$ (C-S), 1236  $\nu$ (N-C), 883  $\nu$ (C-S), 384  $\nu$ (M-S), 470  $\nu$ (M-N).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 3.07-3.18 (m, 8H,  $\text{CH}_2$ -N), 1.03-1.12 (m, 12H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 232, 270, 324. Anal. calcd. for  $\text{C}_{24}\text{H}_{28}\text{N}_4\text{NiS}_4$ : C, 51.53; H, 5.04; N, 10.01. Found: C, 51.30; H, 5.36; N, 9.88%.

**[Ni(L²)₁(L³)₂]Cl:** Color: Yellow. Yield: 79%. M.p.: 128-130 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1440  $\nu$ (C-N), 1111  $\nu$ (C-S), 1238  $\nu$ (N-C), 884  $\nu$ (C-S).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 4.28-4.35 (m, 4H,  $\text{CH}_2$ -N), 1.06-1.51 (m, 6H,  $\text{CH}_2$ ). UV/Vis ( $\text{CH}_3\text{CHOH}$ ,  $\lambda_{\text{max}}$ , nm): 246, 326, 390. Anal. calcd. for  $\text{C}_{30}\text{H}_{26}\text{ClN}_5\text{NiS}_2$ : C, 58.61; H, 4.26; N, 11.39. Found: C, 58.12; H, 4.70; N, 12.10%.

#### 2.5. Antibacterial activity

The antibacterial activity of the ligands and their nickel complexes were assessed against some bacterial species: *Staphylococcus aureus* and *Escherichia coli*. Overnight cultures were used after 24 h of incubation; bacterial suspension (inoculums) was diluted with sterile physiological solution for the diffusion test, to  $1 \times 10^8$  CFU/mL; (CFU = Colony forming unit). (Turbidity = McFarland barium sulfate standard 0.5).

The bacterial inoculums was uniformly spread using sterile cotton swab on a sterile Petri dish Mueller Hinton agar. 50  $\mu\text{L}$  of each concentration of the ligands and complexes were added to each well (7 mm diameter holes cut in the agar gel, 20 mm apart from one another). The plates were incubated for 24 h at  $36 \pm 1$  °C, under aerobic condition. After incubation, confluent bacterial growth was observed. Inhibition of the bacterial growth was measured in mm [20,21].

### 3. Result and discussion

#### 3.1. Synthesis

The elemental analysis gives satisfactory agreement between observed and calculated values for carbon, hydrogen and nitrogen. The prepared ligands are generally soluble in water, ethanol, methanol, DMF, DMSO and THF.

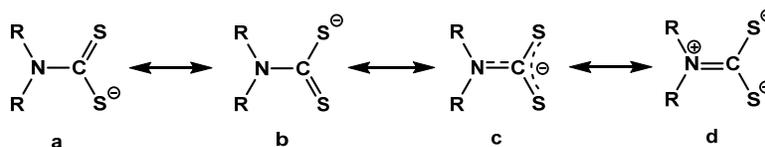
#### 3.2. Infrared spectroscopy

The structure of dithiocarbamates can be illustrated in the terms of four resonance structures (Scheme 1), where the ligands can coordinate to a metal center via sulfur atom in a monodentate (structures a and b) or in a bidentate (structures c and d) [22]. The contribution of structure was shown to be very important in the overall electronic structure, which was achieved by the assignment of the polar bond at  $1450$ - $1550$   $\text{cm}^{-1}$  [17].

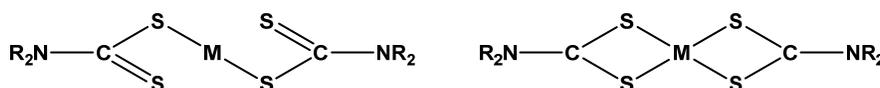
The ligands and complexes show a sharp bands between  $1423$  and  $1509$   $\text{cm}^{-1}$  which attributed to the  $\nu(\text{C} \cdots \text{N})$  stretching vibration [22]. The high vibrational frequency of this band in mixed ligand complexes indicate a partial double bond character, of  $\text{C} \cdots \text{N}$  group arising from mesomeric drift of electrons from the dithiocarbamate moiety toward the nickel(II) ion center [23].

**Table 1.** Antibacterial activity at concentration 100mg/mL of ligands and complexes.

No	Compound	Inhibition diameters (mm)	
		<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>
I	L <sup>1</sup>	4	4
II	Ni(L <sup>1</sup> ) <sub>2</sub> (L <sup>2</sup> ) <sub>1</sub>	No activity	No activity
III	[Ni(L <sup>1</sup> ) <sub>1</sub> (L <sup>2</sup> ) <sub>2</sub> ]Cl	3	3
IV	L <sup>2</sup>	4.1	4.3
V	Ni(L <sup>2</sup> ) <sub>2</sub> (L <sup>3</sup> ) <sub>1</sub>	No activity	No activity
VI	[Ni(L <sup>2</sup> ) <sub>1</sub> (L <sup>3</sup> ) <sub>2</sub> ]Cl	1.5	2



Scheme 1



Scheme 2

All complexes show  $\nu(\text{C}=\text{N})$  bands in the range 1440-1509  $\text{cm}^{-1}$  which lie between  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{N})$  in the 1640-1690  $\text{cm}^{-1}$  and 1250-1350  $\text{cm}^{-1}$  ranges, respectively [24]. In metal dithiocarbamate complexes the region 950-1050  $\text{cm}^{-1}$  is considered characteristic of the nature of binding of the dithiocarbamate moiety. The presence of a solitary band in the above region is due to symmetrical bidentate coordination of the dithiocarbamate group while the splitting of this band within a narrow range of 20  $\text{cm}^{-1}$  is due to the unsymmetrical monodentate nature of the dithiocarbamate group as shown in Scheme 2 [25].

In the present study, a single sharp band of high intensity has been observed in the two complexes in 946-1111  $\text{cm}^{-1}$  range, indicating symmetrical bidentate binding of the dithiocarbamate moiety. However, the ring frequencies associated with 1,10-phenanthroline have been observed in the range 1650 and 1000  $\text{cm}^{-1}$ . In the present study, the complexes (II and V) show small band at 1624 and 1631  $\text{cm}^{-1}$ , respectively. Other bands are masked by those of dithiocarbamate ligand [26]. A new band appears in spectra of compounds (II and V) at 444 and 470  $\text{cm}^{-1}$ , respectively, due to  $\nu(\text{M}-\text{N})$  stretching mode, which matches well with the literature values [27]. A new band of weak to medium intensity was observed in the region 453-384  $\text{cm}^{-1}$ , which may be assigned to  $\nu(\text{M}-\text{S})$  [28].

Thus the FT-IR spectral results provide strong evidences for the complexation of dithiocarbamate ligands with metal ions in a bidentate mode.

### 3.3. <sup>1</sup>H NMR Spectra

<sup>1</sup>H NMR spectroscopy provides more information beside the identification of functional groups present in the structure of dithiocarbamate ligands and their complexes. The <sup>1</sup>H NMR spectral data for the dithiocarbamate ligands and the nickel(II) complexes were recorded at room temperature. The expected protons ratio are agree well with pervious work [23,29].

The <sup>1</sup>H NMR spectra displayed the chemical shift of methylene (-CH<sub>2</sub>) protons as multiplets at  $\delta$  1.79-1.83 ppm and  $\delta$  1.51-1.56 ppm for the ligands (L<sup>1</sup> and L<sup>2</sup> ligands), respectively, and  $\delta(-\text{HC}-\text{N})$  are observed in the deshielded region at about  $\delta$  3.62-3.67 and 4.23-4.29 ppm for these ligands, respectively. This deshielding was caused by the high electron density around the sulphur or metal atom via the

thioureide  $\pi$ -system [30]. This deshielding confirmed the coordination of the dithiocarbamate to the metal atom and was attributed to the mesomeric drift of electrons from heterocyclic ring towards the metal atom. On complexation there was an only slight chemical shift. The <sup>1</sup>H NMR spectra of the complexes showed that resonance of aromatic rings in the region  $\delta$  7.77-9.11 ppm, which was agreed with literature [31].

### 3.4. Electronic spectra

The electronic spectra for the dithiocarbamate ligands and the nickel(II) complexes were recorded in the UV-Visible range 200-800 nm. Dithiocarbamate ligands generally show three bands in the UV region, which are related to an intramolecular charge transfer. Band I corresponding to  $\pi-\pi^*$  transitions of the N-C=S system [24]. Band II is attributed to  $\pi-\pi^*$  transitions of S-C=S group [25]. Band III with low intensity is assigned to an n- $\pi^*$  transitions, i.e. transition of an electron of the lone pair on the sulphur atom to an antibonding  $\pi$ -orbital [32]. When metal complexes absorb radiation, the transition obtained is attributed to excitation of the metal ion, excitation of the ligand or charge transfer transition. Therefore, two types of transitions are expected. While the transition on the ligand can be  $\pi-\pi^*$  and n- $\pi^*$  transitions, but  $\pi-\pi^*$  transitions are stronger than n- $\pi^*$  transitions. Transitions due to the excitation of the metal ions are known as d-d transitions and these are normally weak [33]. Charge transfer transition is very intense and is as a result of the excitation of an electron from the metal ion to the ligand and vice versa.

### 3.5. Antibacterial activity

The general screening of the pathogenic bacteria was obtained for the prepared compounds. In the screening, it was clear that most of these compounds possess a selective antibacterial activity against Gram negative bacteria; *Escherichia coli* and Gram positive; *Staphylococcus aureus* except the complexes (II and V) as shown in Table 1.

### 4. Conclusion

New mixed ligands and their ternary nickel(II) complexes of dithiocarbamate with 1,10-phenanthroline have been synthesized and characterized. Based on analytical, FT-IR and electronic spectral data, they adopt octahedral geometry

around nickel(II). The two ligands moieties display a bidentate coordination mode in the complexes. Most of the prepared compounds possess a selective antibacterial activity against Gram negative bacteria; *Escherichia coli* and Gram positive; *Staphylococcus aureus* except the complexes (II and V).

### Acknowledgments

I am grateful to Prof. Hayat Hamza Abbas and two final year project's students; Radhwan Salman Abdhussien and Zaynab Ali Mhayer for their help.

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