

## Synthesis and Characterization of 3-Methoxypropyldithiocarbamate Complexes with Iron(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) and Their Adducts with Nitrogen Base Ligands

Saad E. Al-Mukhtar

Marwa Th. Aghwan

*Department of Chemistry*

*College of Science*

*University of Mosul*

(Received 13 / 9 / 2012 ; Accepted 17 / 12 / 2012)

### ABSTRACT

New complexes of dithiocarbamate of the general formula  $[M(3\text{-MeoPrdtc})_2]$  and  $[M(3\text{-MeoPrdtc})_2.nL]$  Where  $M = \text{Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)}$ , and (3-Meoprdtc) = 3-Methoxypropyldithiocarbamate, and  $n=2$  when  $L = \text{pyridine, Isoquinoline, } \gamma\text{-picoline, 3,5-lutidine}$ ,  $n=1$  when  $L = \text{ethylenediamine, (1,10)-phenanthroline}$ , have been prepared and characterized by metal analyses, infrared, conductance measurements, electronic absorption spectra and susceptibility measurements. Magnetic moment and electronic spectra, indicate that the complexes of the type  $[M(3\text{-meoprdtc})_2]$  are of tetrahedral geometry while the complexes of the type  $[M(3\text{-meoprdtc})_2.nL]$  have octahedral geometry.

**Keywords:** Dithiocarbamate, Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II), Complexes.

(II)

-3

(II)

(II)

(II)

(II)

=K(3-Meoprdtc)

$[M(3\text{-MeoPrdtc})_2]$

-3

[ Zn(II),Cu(II),Ni(II),Co(II),Fe(II) =M]

= L  $[M(3\text{-MeoPrdtc})_2.nL]$

=L 1=n . - $\gamma$  -5,3

=L 2=n

. -10,1

$[M(3\text{-MeoPrdtc})_2]$

$[M(3\text{-MeoPrdtc})_2.nL]$

## INTRODUCTION

The bis-(dithiocarbamate) complexes  $[M(S_2CNR_2)_2]$ , where R = alkyl group, are the most common among other ligand and complexes. Many studies and reviews have been published on transition and non-transition metals (Onwudiwe and Ajibade, 2010) which indicate that there are a wide variety of compounds of anions such as dithiocarbamate, dithiocarbonate, dithiocarboxylate, trithiocarbonate, xanthate, thioxanthate, dithiophosphinate and dialkyldithiophosphinate (Rathore *et al.*, 2007).

Dithiocarbamate and dithiophosphinate complexes have important uses. Dithiocarbamates derived from secondary amines are the most studied ones because they are stable and possess interesting electrochemical and optical properties (Cotero-Villegas *et al.*, 2010). Most of aliphatic and aromatic dithiocarbamates synthesized until now may coordinate only through the dithio-group, behaving as uninegative bidentate ligands in reactions with metal ions (Leka *et al.*, 2006).

Transition metal dithiocarbamate complexes find use in diverse applications such as material science, medicine and agriculture (Shaheen *et al.*, 2007) and possess interesting structural chemistry (Onwudiwe and Ajibade, 2011) that make their study continuously attractive, and biological activity (as antibacterial, cytostatic, antifungal and immunoregulatory) most of these applications are based on the complexation properties of dithiocarbamate ligands with metal ions, especially with transition metal ions (Golcu, 2006).

In view of these interesting results, we have prepared a new dithiocarbamate ligand and its complexes with different metal ions and their nitrogeneous adducts.

## EXPERIMENTAL

### Materials and Methods

All reagents and solvents were of analytical grade and used as supplied from Fluka or BDH chemical companies. Infrared spectra were recorded on a Bruker Tensor 27co. FTIR spectrophotometer in the 400-4000  $\text{cm}^{-1}$  range using KBr discs. Conductivity measurements were carried out on a  $10^{-3}$  M solution of the complexes in DMF using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer UV-160 for  $10^{-3}$ M solution of complexes in DMF as solvent at 25°C using 1cm quartz cells Metals content were determined using AA670 atomic absorption. Melting points were recorded on an Electrothermal 9300 apparatus and were uncorrected. The magnetic measurement was carried out at 25°C on the solids by Faraday's method using Bruker BM6 instrument.

### Synthesis of potassium 3-Methoxypropyldithiocarbamate

To (8.90 g, 0.10 mol) of 3-Methoxypropylamine was added to aqueous solution (5.61g, 0.10 mol) of potassium hydroxide with stirring. The mixture was cooled in an ice bath, to this mixture (7.60  $\text{cm}^3$ , 0.10 mol) of carbon disulfide was added dropwise with continuous stirring for 30 min in ice bath. The precipitate formed was extracted with (100 ml) diethylether filtered off, washed with diethylether and dried under vacuum. A white precipitate formed.

**I.A. Synthesis of complex [M (3-MeoPrdtc)<sub>2</sub>]****M=Fe(II), Co(II), Ni(II), Cu(II), Zn(II)**

Ethanol solution of FeCl<sub>2</sub>.XH<sub>2</sub>O (1.26 g, 0.01 mol) or CoCl<sub>2</sub>.6H<sub>2</sub>O (2.37g, 0.01 mol) or NiCl<sub>2</sub>.6H<sub>2</sub>O (2.37 g, 0.01 mol) or CuCl<sub>2</sub>.2H<sub>2</sub>O (1.70g, 0.01 mol) or ZnCl<sub>2</sub> (1.36 g, 0.01 mol) was added dropwise to ethanolic solution of potassium 3-methoxypropyldithiocarbamate (4.06 g, 0.02 mol) with stirring for 30 min until complete precipitation. The precipitate was filtered off, washed with ethanol. Then with diethylether and dried under vacuum.

**I.B. Synthesis of complex [M (3-MeoPrdtc)<sub>2</sub>(L)<sub>2</sub>]****L= pyridine, isoquinoline,  $\gamma$ -picoline, 3, 5-lutidine**

It was prepared similarly as in (I.A.). The precipitate formed was treated with (0.02 mol) of (pyridine, isoquinoline,  $\gamma$ -picoline, 3,5-lutidine) dropwise with continuous stirring for 30 min, the precipitate formed, was filtered and washed with ethanol then dried under vacuum.

**I.C. Synthesis of complex [M (3-MeoPrdtc)<sub>2</sub>(L)]****L=1,10-phenanthroline, ethylenediamine**

It was prepared similarly as in (I.A.) and the precipitate formed was treated with (0.01 mol) of (1,10-phenanthroline, ethylenediamine) dropwise with continuous stirring for 30 min, the precipitate formed was, filtered, washed with ethanol, then dried under vacuum.

**RESULTS AND DISCUSSTION**

The new ligand was prepared by the reaction of 3-methoxypropylamine with potassium hydroxide and then added carbon disulphide: the complexes were prepared through direct reaction of the metal chlorides, FeCl<sub>2</sub>.XH<sub>2</sub>O or CoCl<sub>2</sub>.6H<sub>2</sub>O or NiCl<sub>2</sub>.6H<sub>2</sub>O or CuCl<sub>2</sub>. 2H<sub>2</sub>O and ZnCl<sub>2</sub>.unhydrous with the above ligand in (1:2) molar ratio. The values of conductivity in dimethylformamide solution of the complexes range from (0.40-25.10)  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , which are typical values for non electrolyte type (Geary, 1971).

**Infra-red spectral studies**

The important IR bands of the ligand and its complexes are listed in Table (2). The stretching frequency of the  $\nu(\text{C} = \text{N})$  band for the dithiocarbamates was intermediate between the stretching frequencies associated with typical single and double-bonded carbon and nitrogen atoms (Srinivasan *et al.*, 2010). The  $\nu(\text{C} - \text{N})$  and  $\nu(\text{C} - \text{S})$  were observed in the ranges of (1500-1550)  $\text{cm}^{-1}$  and (968-1038)  $\text{cm}^{-1}$ . The presence of only one band in the later region reports the bidentate coordination of the dithio ligand (Serrano, 2003).

IR spectra showed a new band at (418-445)  $\text{cm}^{-1}$  which is the evidence for the coordination of metal to sulfur  $\nu(\text{M}-\text{S})$ . This behavior may be attributed to the electron-releasing of the amines, which forces high electron density towards the sulfur atoms, the  $\nu(\text{M}-\text{N})$  was observed in the (465-523)  $\text{cm}^{-1}$  region (Raya *et al.*, 2006). In the adduct, the band corresponding to  $\nu(\text{N}-\text{H})$  of the ethylenediamine (6, 13, 21 and 27) was observed at lower frequency (3211-3270)  $\text{cm}^{-1}$  (Montagner *et al.*, 2011). This indicates that it was shown in coordination with metal ions, as well as the band  $\nu(\text{C}=\text{N})$  ring which was

observed as (1441-1522)  $\text{cm}^{-1}$  which means the coordination of the donor atoms with the metal ions (Geraldo *et al.*, 2011).

### Electronic spectral studies

The UV-Visible spectra of the ligands and their complexes of  $10^{-3}$  M solution in DMF were recorded; the results were listed in Table (2). The UV-Visible spectrum of the Fe(II) complex (1) gives an absorption band at (11180  $\text{cm}^{-1}$ ), which corresponds to ( ${}^5\text{E} \rightarrow {}^5\text{T}_2$ ) transition in a tetrahedral geometry (Nicholls, 1973). Complexes (2-7) show absorption bands at the range (9803-11095  $\text{cm}^{-1}$ ), which were assigned to ( ${}^5\text{T}_2\text{g} \rightarrow {}^5\text{Eg}$ ) transition (Cocouvanis and Fackler, 1967).

The Co(II) complex (8) exhibited an absorption band at (15673  $\text{cm}^{-1}$ ) region, which was assigned ( ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ ) transition (Siddiqi and Nishat.; 2000), in tetrahedral configuration of this complex and the absence of ( ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ ) and ( ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ ), are due to the sensitivity of the instrument used. Complexes (9-14) show three absorption bands at the range (9700-9842  $\text{cm}^{-1}$ ), (15243-16891  $\text{cm}^{-1}$ ) and (20716-25252  $\text{cm}^{-1}$ ), which were assigned to ( ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{F})$ ), ( ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{A}_2\text{g}(\text{F})$ ) and ( ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{P})$ ) transition in octahedral configuration (Martel, 1971).

The Ni(II) complex (15) shows two absorption bands at (10066  $\text{cm}^{-1}$ ) and (13022  $\text{cm}^{-1}$ ) which were assigned to ( ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$ ) and ( ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ ) transitions in a tetrahedral geometry (Nicholls, 1973), respectively, the complexes (16-21) show three absorption bands in the range (9872-10355  $\text{cm}^{-1}$ ), (14517-18161  $\text{cm}^{-1}$ ) and (24509-26315  $\text{cm}^{-1}$ ), which were assigned ( ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_2\text{g}(\text{F})$ ), ( ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{F})$ ) and ( ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{P})$ ) (Singh *et al.*, 1989).

The Cu(II) complex (22) gives an absorption band at (10073  $\text{cm}^{-1}$ ), which corresponds to ( ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ ) transition in an tetrahedral geometry (Cookson *et al.*, 2010), the complexes (23-28) show a broad band in the region (9823-12444  $\text{cm}^{-1}$ ), which was assigned to ( ${}^2\text{Eg} \rightarrow {}^2\text{T}_2\text{g}$ ) transition which may be formed from the combination of three transitions ( ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{A}_1\text{g}$ ), ( ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{B}_2\text{g}$ ) and ( ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{Eg}$ ) (Lever *et al.*, 1984).

### Magnetic susceptibility measurements

The magnetic moments of the complexes Table (1) were measured at (25 °C). The magnetic moments for Fe(II) Co(II) and Ni(II) and Cu(II) complexes (1,8,15 and 22) are (1.83-4.99 B.M) suggesting a tetrahedral geometry (Nicholls, 1973). The low values of magnetic moments for complexes (15 and 22) are due to the antiferromagnetic interaction. The magnetic moments values of the other complexes (2-7,9-14,16-21,23-28) were in the range (1.68-5.70 B.M.) in an octahedral geometry (Nicholls, 1973).

**Table 1: Analytical and some physical properties of the prepared complexes**

No.	Compound	Color	m.p (°c)	Molar conductivity $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	%M	%yield	$\mu_{\text{eff}}$ B.M
L	C <sub>5</sub> H <sub>10</sub> NOS <sub>2</sub> K	White	134-136	----	---	---	---
1	[Fe(3-Meoprdtc) <sub>2</sub> ]	Orange	285*	13.98	13.70 (14.54)	49	4.99
2	[Fe(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	Orange	280*	22.90	9.92 (10.30)	70	5.09
3	[Fe(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	Light brown	270*	5.33	8.48 (9.08)	52	5.35
4	[Fe(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	Orange	290*	20.20	9.10 (9.80)	68	5.33
5	[Fe(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	Orange	240*	12.02 <sup>***</sup>	8.79 (9.34)	61	4.96
6	[Fe(3-Meoprdtc) <sub>2</sub> (en)]	Brown	200*	15.72	11.99 (12.58)	78	5.16
7	[Fe(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	Light purple	105-107	10.50	8.93 (9.02)	60	5.70
8	[Co(3-Meoprdtc) <sub>2</sub> ]	Dark green	146-149	10.90	14.73 (15.22)	55	4.10
9	[Co(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	Dark brown	109-112	15.40	9.29 (10.28)	54	5.1
10	[Co(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	Dark brown	90*	6.20	8.44 (9.13)	62	4.69
11	[Co(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	Dark brown	123-127	3.30	8.84 (10.81)	60	4.34
12	[Co(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	Dark brown	228-231	7.30	8.03 (9.80)	50	4.71
13	[Co(3-Meoprdtc) <sub>2</sub> (en)]	Black	200*	12.40	12.83 (13.18)	85	1.93
14	[Co(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	Dark brown	97-100	14.87	8.38 (9.48)	67	1.77
15	[Ni(3-Meoprdtc) <sub>2</sub> ]	Dark green	142-145	0.90	14.14 (15.18)	82	3.20
16	[Ni(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	Orange	143-146	6.10	10.45 (10.77)	50	2.73
17	[Ni(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	Dark green	132-135	0.40	8.60 (9.10)	54	2.99
18	[Ni(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	Dark green	133-138	10.00	10.08 (10.25)	77	2.77
19	[Ni(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	Dark green	119-121	14.90	9.48 (9.77)	91	3.05
20	[Ni(3-Meoprdtc) <sub>2</sub> (en)]	Light purple	230*	12.40	12.46 (13.13)	62	2.98
21	[Ni(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	Dark green	142-147	0.40	9.05 (9.44)	42	2.36
22	[Cu(3-Meoprdtc) <sub>2</sub> ]	Dark brown	109-112	3.30	15.11 (16.22)	73	1.83
23	[Cu(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	Light yellow	290*	1.70	10.93 (11.56)	76	2.06
24	[Cu(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	Green yellow	98-102	16.80	9.46 (9.78)	55	1.77
25	[Cu(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	Brown	110-113	2.30	10.39 (11.00)	72	1.68

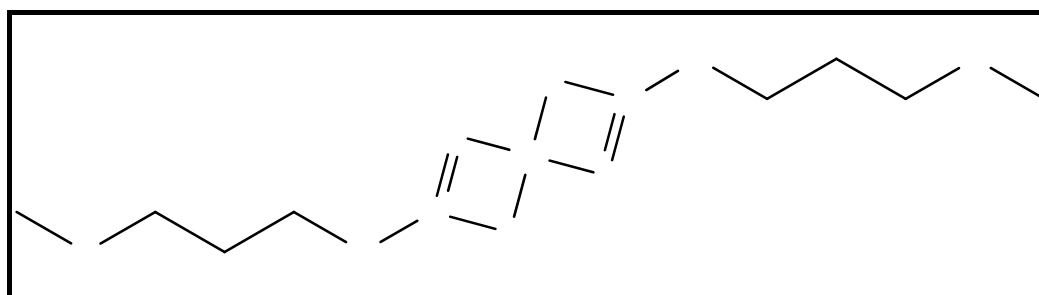
No.	Compound	Color	m.p (°C)	Molar conductivity $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	%M	%yield	$\mu_{\text{eff}}$ B.M
26	[Cu(3-MeoPrdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	Brown	104-107	11.86	9.72 (10.49)	65	1.96
27	[Cu(3-MeoPrdtc) <sub>2</sub> (en)]	Light brown	96-99	18.60	13.23 (14.07)	66	1.69
28	[Cu(3-MeoPrdtc) <sub>2</sub> (1,10-phen)]	Yellow	99-102	24.60	9.39 (10.14)	68	2.02
29	[Zn(3-MeoPrdtc) <sub>2</sub> ]	White	98-100	1.10	16.09 (16.61)	58	Dia
30	[Zn(3-MeoPrdtc) <sub>2</sub> (Py) <sub>2</sub> ]	White	101-104	9.10	11.44 (11.85)	52	Dia
31	[Zn(3-MeoPrdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	Light yellow	210*	20.60	8.90 (10.03)	53	Dia
32	[Zn(3-MeoPrdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	White	116-119	14.08	10.86 (11.28)	69	Dia
33	[Zn(3-MeoPrdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	Light yellow	101-104	18.00	9.83 (10.76)	63	Dia
34	[Zn(3-MeoPrdtc) <sub>2</sub> (en)]	Yellow	124-127	24.90	13.96 (14.41)	88	Dia
35	[Zn(3-MeoPrdtc) <sub>2</sub> (1,10-phen)]	Light yellow	235*	25.10	9.14 (10.41)	66	Dia

\*decomposition

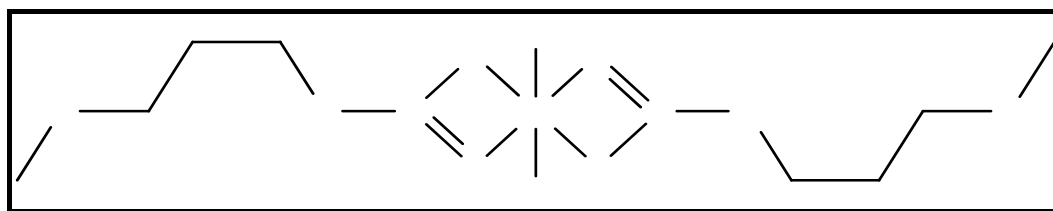
**Table 2: IR bands ( $\text{cm}^{-1}$ ) and electronic spectral data of ligand and prepared complexes**

No.	Compound	UV bands ( $\text{cm}^{-1}$ )	IR spectra ( $\text{cm}^{-1}$ )				
			$\nu(\text{C} \cdots \text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{C}=\text{N})$ ring	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
L	C <sub>5</sub> H <sub>10</sub> NOS <sub>2</sub> K	---	1487	1045	---	---	---
1	[Fe(3-MeoPrdtc) <sub>2</sub> ]	11180, 36231	1540	983	---	---	430
2	[Fe(3-MeoPrdtc) <sub>2</sub> (Py) <sub>2</sub> ]	10910, 34695	1531	991	1522	478	440
3	[Fe(3-MeoPrdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	10100, 32679	1509	1038	1498	480	434
4	[Fe(3-MeoPrdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	10490, 34965	1516	1020	1480	465	430
5	[Fe(3-MeoPrdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	10514, 35971	1513	1020	1450	466	445
6	[Fe(3-MeoPrdtc) <sub>2</sub> (en)]	10641, 22935, 37037	1518	997	1504	476	445
7	[Fe(3-MeoPrdtc) <sub>2</sub> (1,10-phen)]	10309, 32679	1527	999	1493	474	435
8	[Co(3-MeoPrdtc) <sub>2</sub> ]	15673, 32467	1550	978	---	---	436
9	[Co(3-MeoPrdtc) <sub>2</sub> (Py) <sub>2</sub> ]	9803, 15243, 24390, 27777	1523	988	1483	523	432
10	[Co(3-MeoPrdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	15576, 20746, 32258, 46296	1529	1016	1511	494	420
11	[Co(3-MeoPrdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	15625, 25252, 28910, 32467	1512	1028	1474	488	426
12	[Co(3-MeoPrdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	15384, 24390, 27777, 31645	1512	1008	1444	481	423
13	[Co(3-MeoPrdtc) <sub>2</sub> (en)]	9700, 16891, 25000, 29761, 32894	1535	991	1490	475	428
14	[Co(3-MeoPrdtc) <sub>2</sub> (1,10-phen)]	9842, 15243, 24039, 30120	1533	996	1489	491	426
15	[Ni(3-MeoPrdtc) <sub>2</sub> ]	10066, 13022, 20661, 25510	1545	966	---	---	440

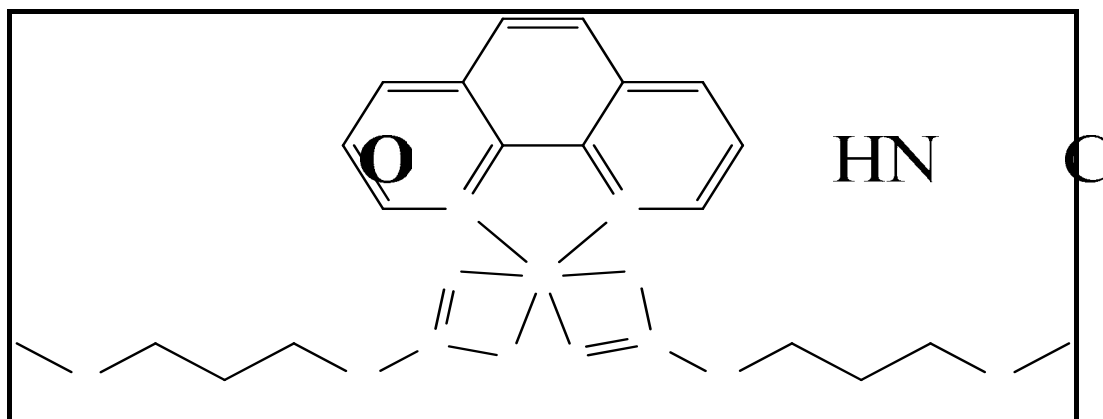
No.	Compound	UV bands (cm <sup>-1</sup> )	IR spectra (cm <sup>-1</sup> )				
			$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{C}=\text{N})$ ring	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
16	[Ni(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	10163, 16078, 25510, 29585	1500	968	1441	478	430
17	[Ni(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	10355, 18161, 24509, 30303	1507	1030	1473	476	433
18	[Ni(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	9872, 16049, 24752, 49019	1501	976	1490	474	425
19	[Ni(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	9957, 18118, 25125, 29585	1528	968	1487	480	429
20	[Ni(3-Meoprdtc) <sub>2</sub> (en)]	10163, 14517, 26315, 29339	1511	995	1458	499	441
21	[Ni(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	9990, 15886, 25125, 29339	1545	966	1490	474	439
22	[Cu(3-Meoprdtc) <sub>2</sub> ]	10073, 33333	1500	939	---	---	439
23	[Cu(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	12444, 17985, 36764	1493	951	1478	476	426
24	[Cu(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	10917, 28409	1500	943	1450	482	436
25	[Cu(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	9823, 23474, 27472	1498	984	1444	465	422
26	[Cu(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	9842, 26595, 31055	1490	941	1450	465	438
27	[Cu(3-Meoprdtc) <sub>2</sub> (en)]	12297, 31645, 35211	1492	1007	1462	476	439
28	[Cu(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	24038, 32894	1498	945	1465	492	438
29	[Zn(3-Meoprdtc) <sub>2</sub> ]	---	1516	964	---	---	431
30	[Zn(3-Meoprdtc) <sub>2</sub> (Py) <sub>2</sub> ]	---	1510	1036	1452	488	430
31	[Zn(3-Meoprdtc) <sub>2</sub> (IsoQ) <sub>2</sub> ]	---	1496	1017	1486	484	418
32	[Zn(3-Meoprdtc) <sub>2</sub> ( $\gamma$ -Pico) <sub>2</sub> ]	---	1509	1009	1477	494	424
33	[Zn(3-Meoprdtc) <sub>2</sub> (3,5-lut) <sub>2</sub> ]	---	1511	991	1446	489	420
34	[Zn(3-Meoprdtc) <sub>2</sub> (en)]	---	1506	973	1473	482	418
35	[Zn(3-Meoprdtc) <sub>2</sub> (1,10-phen)]	---	1508	997	1489	478	419



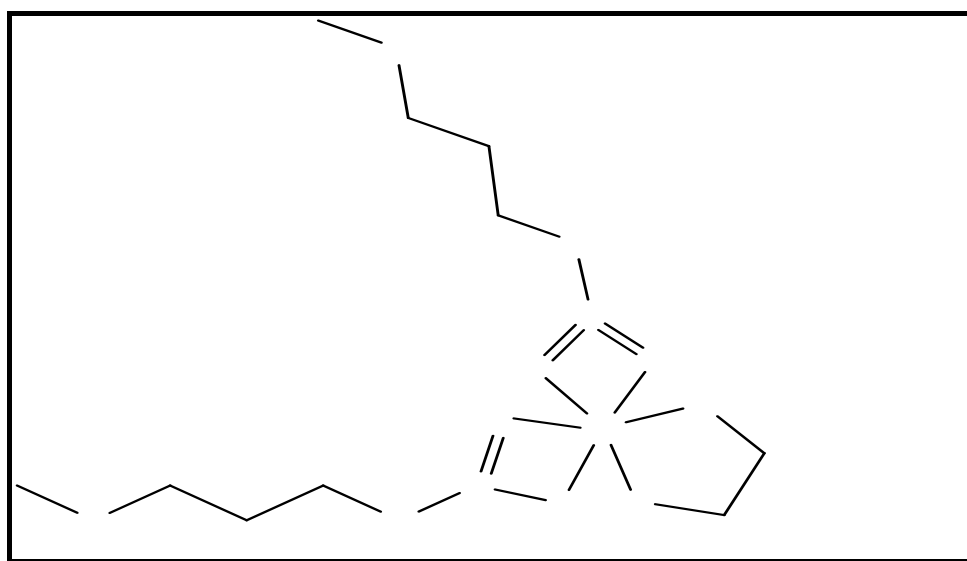
(a)



(b)



(c)



(d)

**Fig. 1: Suggest structures (a) complexes [1, 8, 15, 22, 29], (b) complexes [2-5, 9-12, 16-19, 23-26, 30-33], (c) complexes [6,13,20,27,34], (d) complexes [7, 14, 21, 28, 35]**

## REFERENCES

- Cookson, J.; Emma, A.L.E.; John, P.M.; Christopher, J.S.; Rowena, L.P.; Andrew, R.C.; Michael, G.B.D.; Paul, D. (2010). Metal directed assembly of large dinuclear copper(II) dithiocarbamate Macrocyclic complexes. *Inorg. Chem. Acta.*, **363**, 1195-1203.
- Cotero-Villegas, A.M.; García, P.G.; Höplf-Bachner, H.; Pérez-Redondo, M.C.; Martínez-Salas, P.; López-Cardoso, M.; Olivares, R. C. (2010). Synthesis and spectroscopic characterization of six new monosubstituted dithiocarbamate compounds containing



- organotellurium(IV) heterocycles: Single-crystal structures of  $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$ ,  $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$ ,  $4H_8OTeI[S_2CN(CH_2CH_2)_2]$  and  $C_5H_{10}TeI[S_2CN(CH_2CH_2)_2]$ . *J. Organometallic Chem.* **695**, 1246–1252.
- Coucouvani, D.; Fackler, J.P. (1967). Square-planar sulfur complexes.VI. reactions of bases with xanthate, dithiocarbamates, and dithiolates of nickel(II). *J. Inorg. Chem.*, **6**, 2047-2053.
- De Lima, G.M.; Menezes, D.C.; Cavalcanti, C.A.; Dos Santos, J.A.F.; Ferreira, I.P.; Paniago, E.B.; Wardell, J.L.; Wardell, S. M.S.V.; Krambrock, K.; Mendes, I.C.; Beraldo, H. (2011). Synthesis, characterisation and biological aspects of copper(II) dithiocarbamate complexes,  $[Cu\{S_2CNR(CH_2CH_2OH)\}_2]$ , (R = Me, Et, Pr and  $CH_2CH_2OH$ ). *J. Molecular Struct.*, **988**, 1–8.
- Geary, W.J. (1971). The use of conductivity measurements in organic solvents for characterization of coordination compounds. *Coord. Chem. Rev.* **7**, 8-122.
- Golcu, A. (2006). Transition metal complexes of propranolol dithiocarbamate: synthesis, characterization, analytical properties and biological activity. *Trans. Metal. Chem.* **31**, 405–412.
- Holah, D.G.; Murphy, C.N. (1972). Transition metal complexes involving ionic xanthates, *Inorg. Nucl. Chem.*, **8**, 1069-1072.
- Leka, Z.B.; Leovac, V.M.; Luki, S.; Sabo, T.J.; Trifunovi, S.R. ; Szécsényi, K.M. (2006). Synthesis and physico-chemical characterization of new dithiocarbamate ligand L and its complexes copper(II), nickel(II) and palladium(II). *J. Therm. Anal. Calor.*, **83**(3), 687–691.
- Lever, A.B.P. (1984). "Inorganic Electronic Spectroscopy". 2nd ed., Elsevier, Amsterdam, 357 p.
- Martell, A.E. (1971). "Coordination Chemistry". Van Nostrand Reinhold, New York., 1 p.
- Montagner, D.; Marzano, C.; Gandin, V. (2011). Synthesis, characterization and cytotoxic activity of palladium (II)dithiocarbamate complexes with a x-diamines. *Inorg. Chem. Acta.*, **376** , 574–580.
- Nicholls, D. (1973). "The Chemistry of Iron, Cobalt and Nickel". Pergamon press, Oxford, 1st ed., pp.1037, 1087, 1088, 1090, 1091, 1093, 1151, 1154.
- Onwudiwe, D.C.; Ajibade, P.A. (2010). Synthesis and characterization of metal complexes of N-alkyl-N-phenyl dithiocarbamates. *Polyhedron.*, **29**, 1431-1436.
- Onwudiwe, D.C.; Ajibade, P.A. (2011). Synthesis and Crystal Structure of Bis (N-alkyl-N-phenyl dithiocarbamate) mercury(II). *J. Chem. Crystallogr.*, **41**, 980–985.
- Sarwar, M.; Ahmad, S.; Ahmad, S.; Ali, S.; Ahmed, S.A. (2007). Copper(II) complexes of pyrrolidine dithiocarbamate. *Trans. Met. Chem.*, **32**, 199–203.
- Serrano, J.L.; Garcí'a, L.; Pe' rez, J.; Pe' rez, E.; Sa' nchez, G.; Garcí'a, J.; Lo' pez, G.; Garcí'a, G.; Molins, E. (2003). New dithiocarbamate and xanthate complexes of nickel(II)with iminophosphines. *Inorg. Chem. Acta.*, **355**, 33-40.
- Shaheen, F.; Badshah, A.; Gielen, M.; Dusek, M.; Fejfarova, K.; De Vos, D.; Mirza, B. (2007). Synthesis, characterization, antibacterial and cytotoxic activity of new palladium(II) complexes with dithiocarbamate ligands: X-ray structure of bis(dibenzyl-1-S: S'-dithiocarbamate) Pd(II). *J. Organomet. Chem.* **692**, 3019–3026.

- Siddiqi, K.S.; Nishat, N. (2000). Synthesis and characterization of succinimide and phthalimide dithiocarbamate and their complexes with some transition metal ions. *Synth. React. Inorg. Met-Org. Chem.*, **30**(8), 1505 -1518.
- Singh, N.; Singh, N.K.; Kaw, C. (1989). Synthetic and spectroscopic studies of xanthate-bridged heterobimetallic complexes containing diamagnetic and paramagnetic metal ions. *Bull. Chem. Soc. (Jpn.)*, **62**, 3328-3333.
- Srinivasan, N.; Valarmathi, P.; Thirumaran, S.; Ciattini, S. (2010). Synthesis and spectral studies on NiS<sub>4</sub>, NiS<sub>2</sub>PN, NiS<sub>2</sub>P<sub>2</sub> chromophores: Single-crystal X-ray structure of [Ni(dbpdtc)<sub>2</sub>] (dbpdtc=benzyl(4-(benzylamino)phenyl)dithiocarbamate). *Trans Met Chem.*, **35**, 815-819.
- Rathore, H.S.; Varshney, G.; Mojumdar, S.C.; Saleh, M.T. (2007). Synthesis, characterization and fungicidal activity of zinc diethyldithiocarbamate and phosphate. *Ther. Anal. Calorim*, **90** (3), 681–686.
- Raya, I.; Baba, I. ; Yamin, B.M. (2006). New mixed ligands complexes of samarium(III) with dithiocarbamates and 1,10-phenanthroline. *Malaysia. J. Anal. Sci.*, **10**(1), 93-98.