

Synthesis and Characterization of Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} complexes with dithiocarbamate and N-donor ligands

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ABSTRACT

New complexes of first series of transition metals with 1-Naphthyl dithiocarbamate of the general formula $[\text{M}(\text{1-Napdtc})_2]$, $[(\text{1-Napdtc})_2\text{nL}]$ $\text{M}=\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$, and $[\text{R}_4\text{N}][\text{M}(\text{1-Napdtc})_3]$. 1-Napdtc=1-Naphthyl dithiocarbamate. $\text{n}=2$ when $\text{L}=\text{Py}$, $\gamma\text{-Pic}$, iso Quinoline, 3,5-lutidine. $\text{n}=1$ when $\text{L}=1,10\text{-phenanthroline}$, ethylenediamine. $\text{R}=\text{ethyl C}_2\text{H}_5$. All prepared complexes have been characterized by Conductance measurement, Magnetic susceptibility, Electronic spectra, Infrared spectrum and metal analysis by atomic absorption. The measurements showed a tetrahedral geometry. Where $[\text{Fe}(\text{II})]$, $[\text{Co}(\text{II})]$, $[\text{Ni}(\text{II})]$, $[\text{Cu}(\text{II})]$, $[\text{Zn}(\text{II})]$ complexes of the type $[\text{M}(\text{1-Napdtc})_2]$, and octahedral geometry for complexes type $[(\text{1-Napdtc})_2\text{nL}]$ and $[\text{R}_4\text{N}][\text{M}(\text{dtc})_3]$. Conductivity measurements showed that complexes type $[\text{M}(\text{1-Napdtc})_2]$ and $[(\text{1-Napdtc})_2\text{nL}]$ non-electrolyte while the complexes $[\text{R}_4\text{N}][\text{M}(\text{dtc})_3]$ showed 1:1 electrolyte.

Key words: Dithiocarbamate, N-donor ligand, tetrahedral geometry, Octahedral geometry.

INTRODUCTION

Transition metal with dithiocarbamate complexes used in many applications such as material science, medicine and agriculture^[1], and possess interesting structural chemistry^[2]. The importance of their complexes makes the study continuously attractive and biological activity (as antibacterile, cytostatic, anti tumor of immunoregulatory) most of these application are based on complication properties of dithiocarbamate ligands with metal ions, especially with transition ions^[3]. Zinc dithiocarbamates are used to modify the cross linking of certain polyolefin's with sulfur, a process called vulcanization. They are used as ligands for chelating metals.^[4]

Dithiocarbamates specifically ethylene bisdithiocarbamates (EBDCs), in the form of complexes with manganese (maneb), zinc (zineb) or a combination of manganese and zinc (mancozeb), have been used extensively as fungicides in agriculture from the 1940s.^[5]

In this work we report the synthesis and characterization of some transition element $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Zn}(\text{II})$ with dithiocarbamate ligand 1-Naphthyl dithiocarbamate to form complexes.

EXPERIMENTAL

All reagents and solvents are analytical grade and used as supplied from Fluka or BDH chemical companies, infrared spectra were recorded on Brucker Tensor 27CO.FTIR spectrophotometer in 400-4000 cm^{-1} range using KBr discs: and CsI discs in the range 400-200.

Conductivity measurements were carried out on 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 a solvent at 25°C using 1cm quartz cell. Metal content were determined using AA670 atomic absorption. Melting point were recorded on an electro chemical 9300 apparatus and uncorrected. The magnetic measurements was carried out in the solids state by Faradays method using Brucker BM₆ instrument.

Preparation of Potassium 1-Naphthyl dithiocarbamate:

The 1-Naphthyl dithiocarbamate ligand (1-Napdtc) was prepared according to the literature method^[6] by adding (0.1mol, 14.31g) of 1-Naphthyl amine dissolved in 15 cm^3 ethanol then added to a solution (0.1mol, 5.61g) of potassium

hydroxide. The resulting mixture cooled in ice and (0.1 mol, 7.6g) carbon disulfide was added dropwise with continuous stirring. The crude product extracted by ether, the precipitate filtered off washed with ether and dried. The chemical suggestion reaction is shown in (Figure 1).

Preparation of complexes $[M(1\text{-NapAdtc})_2]$

$M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$: To a solution containing (0.005 mol) of the required salt FeCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 in a small amount of water/ethanol 50/50 respectively was added to (0.01 mol) of potassium 1-Napdte. The mixture was stirred for about 30 min, then the precipitate was filtered, washed several times with ethanol and finally dried under vacuum. Other complexes were prepared by the same procedure. The reaction is shown in (Figure 2).

Preparation of complexes $[M(1\text{-NapdAdtc})_2(L)_2]$

$L = \text{Py}, \gamma\text{-Pic}, 3,5\text{-lutidine}, \text{Isoquinoline}$: A solution containing (0.01 mol, 2.57g) of K-1-Napdte ligand in 10cm^3 water/ethanol 50/50, added to (0.005 mol) of metal salt dissolved in (0.01 mol, 0.791g) of pyridine. The mixture was continuously stirred for 30 min. The precipitate formed was filtered and washed with ethanol and dried under vacuum. Other complexes of nitrogenous base prepared by the same procedure above. The reaction is shown in (Figure 3).

Preparation of complexes $[M(1\text{-NapAdtc})_2L]$

$M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{and Zn(II)}$, $L = \text{en}, 1,10\text{-phen}$.

The complexes prepared by the same procedure that referred in 1 and 2 and add (0.005 mol, 0.901g) of 1,10-phen. drop wise with continuous stirring for 30 min. The precipitate formed were filtered and washed with ethanol and dried under vacuum. The reaction was shown in (Figure 4).

Preparation of complexes $[R_4N][M(1\text{-Napdte})_3]$, $R = \text{ethyl}$

To a solution of (0.003 mol) of K-1-Napdte dissolved in ethanol was added (0.001 mol) of tetraethyl ammonium chloride dissolved in distilled water to was added. The mixture was stirring (0.001 mol of FeCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 ,) The precipitate filtered off and washed with acetone and dried. The reaction is shown in (Figure 5).

RESULTS AND DISCUSSION

The new ligand was prepared for the reaction of 1-Naphthyl di-amine with potassium hydroxide then added carbon disulfide, the complexes were prepared through direct reaction of the metal salt, FeCl_2 or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or ZnCl_2 hydrous with the above ligand in (1:2) molar ratio. The values of conductivity in dimethyl Formamide solution of the complexes range from (0.6-16.6) $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ which are typical values for non-electrolyte type^[7] while complexes of the type $[R_4N][M(1\text{-Napdte})_3]$ are 1:1 electrolyte.

Infra-red spectral studies

The important IR band of 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^[8]. The $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ were observed in the ranges of (1464-1530) cm^{-1} and (926-1009) cm^{-1} . The presence of only one band in the later region reports the bidentate coordination of the dithio ligand^[9].

IR spectra showed a new band at (410-440) cm^{-1} the evidence for the coordination of metal to sulfur (M-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 (470-522) cm^{-1} region^[10].

Electronic spectral studies

The UV-visible spectra of ligand 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) gave absorption peak at (9876 cm^{-1}), which correspond to ${}^5\text{E} \rightarrow {}^5\text{T}_2$ transition in a tetrahedral geometry^[11]. Complexes (2-8) shows absorption peaks at the range a(9820-11095 cm^{-1}), which were assigned to ${}^5\text{T}_2\text{g} \rightarrow {}^5\text{Eg}$ transition^[12] in Octahedral geometry. The Co(II) complex (9) exhibited an absorption peak at (16077 cm^{-1}) region, which was assigned ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition^[13]. 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 (10-16) showed three absorption peaks at the range ($9321-10537\text{cm}^{-1}$), ($14623-16890\text{cm}^{-1}$, $20711-25250\text{cm}^{-1}$) which were assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{p})$ transition in octahedral configuration^[14] the Ni(II) complex (17) showed two absorption peaks at (8744cm^{-1}) and (14373cm^{-1}) which were assigned to ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$ and ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition in a tetrahedral geometry^[11] respectively, the complexes (18-24) shows three absorption peaks in the range ($9461-10245\text{cm}^{-1}$), ($13098-16432$), ($21413-25793\text{cm}^{-1}$), which were assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{p})$ ^[15]. The Cu(II) complex (25) gave an absorption peak at (9827cm^{-1}), which correspond to (${}^2\text{T}_2 \rightarrow {}^2\text{E}$) transition in a tetrahedral geometry^[16,17], the complexes (26-32) shows abroad peaks in the region ($10224-12297\text{cm}^{-1}$), which was assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition which may be formed from the combination of three transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$.

Magnetic susceptibility measurements

The magnetic moments of the complexes (Table1) were measured at (25°C). The magnetic moments for Fe(II), Co(II), Ni(II) and Cu(II) complexes (1,9,17,25) are (1.91-4.98B.M) suggesting a tetrahedral geometry^[11]. The magnetic moments values of the other complexes (2-8,10-16,18-24,24-32) were in the rang (1.72-5.29B.M) in octahedral geometry^[11].

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

No	Compound	Color	M.P ($^\circ\text{C}$)	Molar conductivity $\Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$	%M	% yield	M_{eff} B.M
L	$\text{C}_{11}\text{H}_8\text{NS}_2\text{K}$	White	184	-----	-----	83	-----
1	$[\text{Fe}(\text{1-Napdte})_2]$	brown	>300	7.3	(10.92) 11.35	88	4.98
2	$[\text{Fe}(\text{1-Napdte})_2(\text{py})_2]$	Reddish brown	230*	3.7	(8.31) (8.59)	65	5.17
3	$[\text{Fe}(\text{1-Napdte})_2(\text{isoQui})_2]$	Reddish brown	132-135	13.0	(7.22) (7.44)	62	5.28
4	$[\text{Fe}(\text{1-Napdte})_2(\gamma\text{-pico})_2]$	Brown	>300	22.5	(7.83) (8.22)	74	5.02
5	$[\text{Fe}(\text{1-Napdte})_2(3,5\text{-Lut})_2]$	dark brown	198*	6.9	(7.32) (7.90)	83	5.04
6	$[\text{Fe}(\text{1-Napdte})_2(\text{en})]$	Brown	122*	12.5	(9.73) (10.11)	77	4.94
7	$[\text{Fe}(\text{1-Napdte})_2(1,10\text{-phen})]$	Reddish brown	164	7.19	(7.84) (8.31)	82	4.99
8	$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Fe}(\text{1-Napdte})_3]$	Light brown	180*	73.2	(6.24) (6.64)	78	5.29
9	$[\text{Co}(\text{1-Napdte})_2]$	Green olive	118-120	5.2	(11.23) (11.90)	55	3.86
10	$[\text{Co}(\text{1-Napdte})_2(\text{py})_2]$	Green olive	148	6.8	(8.37) (9.02)	72	4.70
11	$[\text{Co}(\text{1-Napdte})_2(\text{isoQui})_2]$	Dark green	230*	2.8	(7.53) (7.82)	65	4.55
12	$[\text{Co}(\text{1-Napdte})_2(\gamma\text{-pico})_2]$	Dark green	135	4.7	(8.31) (8.63)	69	4.41
13	$[\text{Co}(\text{1-Napdte})_2(3,5\text{-Lut})_2]$	Green olive	128	0.6	(7.98) (8.30)	79	4.91
14	$[\text{Co}(\text{1-Napdte})_2(\text{en})]$	brown	110*	1.6	(10.02) (10.61)	73	4.96
15	$[\text{Co}(\text{1-Napdte})_2(1,10\text{-phen})]$	Green olive	285*	1.4	(8.19) (8.73)	76	5.01
16	$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Co}(\text{1-Napdte})_3]$	Dark green	140	87	(6.74) (6.99)	71	4.4
17	$[\text{Ni}(\text{1-Napdte})_2]$	Light brown	136-138	4.6	(11.23) (11.86)	84	3.47
18	$[\text{Ni}(\text{1-Napdte})_2(\text{py})_2]$	Light green	110-112	16.6	(8.33) (8.98)	98	2.91
19	$[\text{Ni}(\text{1-Napdte})_2(\text{isoQui})_2]$	light green	152*	8.37	(7.53) (7.79)	83	2.97

20	[Ni(1-Napdtc) ₂ (γ-pico) ₂]	Light green	135	9.1	(8.24) (8.60)	78	2.83
21	[Ni(1-Napdtc) ₂ (3,5-Lut) ₂]	Green	148-150	10.3	(7.64) (8.27)	86	3.08
22	[Ni(1-Napdtc) ₂ (en)]	Brown green	137*	13.2	(9.89) (10.58)	82	2.78
23	[Ni(1-Napdtc) ₂ (1,10-phen)]	Light green	130-132	4.6	(7.99) (8.69)	79	2.77
24	[(C ₂ H ₅) ₄ N][Ni(1-Napdtc) ₃]	Light green	128	69	(6.73) 6.94)	91	3.05
25	[Cu(1-Napdtc) ₂]	Yellow	214	7.3	(12.20) (12.72)	61	1.91
26	[Cu(1-Napdtc) ₂ (py) ₂]	Yellow	144-146	11.5	(8.97) (9.66)	71	2.06
27	[Cu(1-Napdtc) ₂ (isoQui) ₂]	Yellow	106	9.2	(8.16) (8.38)	62	1.87
28	[Cu(1-Napdtc) ₂ (γ-pico) ₂]	Yellow	132-134	12.4	(8.76) (9.24)	68	1.81
29	[Cu(1-Napdtc) ₂ (3,5-Lut) ₂]	Dark yellow	114-117	7.0	(8.49) (8.90)	72	1.72
30	[Cu(1-Napdtc) ₂ (en)]	Green yellow	138*	11.7	(10.86) 11.35)	83	1.98
31	[Cu(1-Napdtc) ₂ (1,10-phen)]	Yellow	162-164	13.2	(8.74) (9.35)	76	2.1
32	[(C ₂ H ₅) ₄ N][Cu(1-Napdtc) ₃]	Yellow	141	77	(6.78) 7.49)	64	1.88
33	[Zn(1-Napdtc) ₂]	White	132-134	3.6	(12.73) (13.04)	80	Dia
34	[Zn(1-Napdtc) ₂ (py) ₂]	White	118	2.2	(9.35) (9.91)	62	Dia
35	[Zn(1-Napdtc) ₂ (isoQui) ₂]	White	110	3.07	(8.17) (8.60)	77	Dia
36	[Zn(1-Napdtc) ₂ (γ-pico) ₂]	Of-white	156	6.80	(9.03) (9.49)	53	Dia
37	[Zn(1-Napdtc) ₂ (3,5-Lut) ₂]	Of-white	112*	15.3	(8.77) (9.13)	75	Dia
38	[Zn(1-Napdtc) ₂ (en)]	Of-white	234*	4.4	(11.32) (11.64)	56	Dia
39	[Zn(1-Napdtc) ₂ (1,10-phen)]	White	210	9.5	(8.96) (9.59)	66	Dia
40	[(C ₂ H ₅) ₄ N][Zn(1-Napdtc) ₃]	White	126-128	86.3	(7.17) (7.69)	71	Dia

*=Degree of disintegration

Table 2: IR bands (cm⁻¹) and electronic spectral data of ligand and prepared complexes.

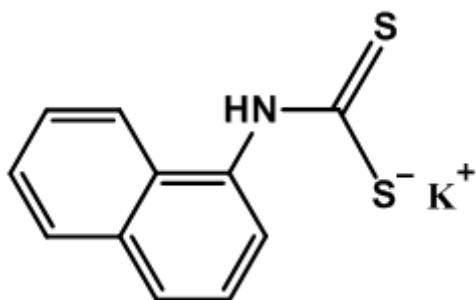
No	Compound	U.V band(cm ⁻¹)	IR Spectra(cm ⁻¹)			
			ν(C-N)	ν(C-S)	ν(M-N)	ν(M-S)
L	C ₁₁ H ₈ NS ₂ K	----	1464	1009	-----	----
1	[Fe(1-Napdtc) ₂]	9876	1500	975	-----	435
2	[Fe(1-Napdtc) ₂ (py) ₂]	10309	1478	983	478	420
3	[Fe(1-Napdtc) ₂ (isoQui) ₂]	10940	1482	991	480	430
4	[Fe(1-Napdtc) ₂ (γ-pico) ₂]	9820	1490	984	482	425
5	[Fe(1-Napdtc) ₂ (3,5-Lut) ₂]	10100	1483	990	470	420
6	[Fe(1-Napdtc) ₂ (en)]	11007	1473	980	476	418
7	[Fe(1-Napdtc) ₂ (1,10-phen)]	10964	1480	986	474	424
8	[(C ₂ H ₅) ₄ N][Fe(1-Napdtc) ₃]	11095	1492	995	522	415
9	[Co(1-Napdtc) ₂]	16077	1528	970	----	430
10	[Co(1-Napdtc) ₂ (py) ₂]	9321, 14652, 21257	1511	992	494	421
11	[Co(1-Napdtc) ₂ (isoQui) ₂]	9814, 15273, 24390	1482	995	488	420

12	[Co(1-Napdte) ₂ (γ-pico) ₂]	10227, 20763	14785, 1500	981	481	418
13	[Co(1-Napdte) ₂ (3,5-Lut) ₂]	10537, 20711	15130, 1492	990	475	424
14	[Co(1-Napdte) ₂ (en)]	9700, 15384, 22173	1496	987	491	419
15	[Co(1-Napdte) ₂ (1,10-phen)]	10020, 24577	14623, 1506	985	511	422
16	[(C ₂ H ₅) ₄ N][Co (1-Napdte) ₃]	10409, 25250	16890, 1489	979	478	410
17	[Ni(1-Napdte) ₂]	8744, 14373	1507	953	-----	440
18	[Ni(1-Napdte) ₂ (py) ₂]	9874, 15290, 24875	1500	990	474	430
19	[Ni(1-Napdte) ₂ (isoQui) ₂]	9654, 16432, 25793	1498	973	480	432
20	[Ni(1-Napdte) ₂ (γ-pico) ₂]	9461, 15290, 25252	1474	969	499	424
21	[Ni(1-Napdte) ₂ (3,5-Lut) ₂]	9803, 13098, 25731	1480	986	474	429
22	[Ni(1-Napdte) ₂ (en)]	10167, 25125	15847, 1496	973	484	430
23	[Ni(1-Napdte) ₂ (1,10-phen)]	10245, 25510	15527, 1488	987	476	431

Continue

No	Compound	U.V band (cm ⁻¹)	IR Spectra (cm ⁻¹)			
			ν(C-N)	ν(C-S)	ν(M-N)	ν(M-S)
24	[(C ₂ H ₅) ₄ N][Ni(1-Napdte) ₃]	9909, 15723, 21413	1483	968	482	435
25	[Cu(1-Napdte) ₂]	9827	1530	973	-----	428
26	[Cu(1-Napdte) ₂ (py) ₂]	10913	1522	982	470	436
27	[Cu(1-Napdte) ₂ (isoQui) ₂]	11792	1506	993	476	418
28	[Cu(1-Napdte) ₂ (γ-pico) ₂]	10482	1491	988	492	427
29	[Cu(1-Napdte) ₂ (3,5-Lut) ₂]	10224	1510	995	520	422
30	[Cu(1-Napdte) ₂ (en)]	12626	1493	983	488	420
31	[Cu(1-Napdte) ₂ (1,10-phen)]	12297	1519	999	484	447
32	[(C ₂ H ₅) ₄ N][Cu(1-Napdte) ₃]	11652	1488	985	494	440
33	[Zn(1-Napdte) ₂]	----	1500	926	-----	326
34	[Zn(1-Napdte) ₂ (py) ₂]	----	1485	945	482	430
35	[Zn(1-Napdte) ₂ (isoQui) ₂]	----	1470	960	478	429
36	[Zn(1-Napdte) ₂ (γ-pico) ₂]	----	1491	953	494	419
37	[Zn(1-Napdte) ₂ (3,5-Lut) ₂]	----	1489	973	505	428
38	[Zn(1-Napdte) ₂ (en)]	----	1473	987	480	423
39	[Zn(1-Napdte) ₂ (1,10-phen)]	----	1492	967	482	433
40	[(C ₂ H ₅) ₄ N][Zn (1-Napdte) ₃]	----	1478	989	486	420

Suggest complexes structures



Potassium 1-Naphthyldithiocarbamate (1-Napdte)

Fig. 1: The predicate structure of the ligand

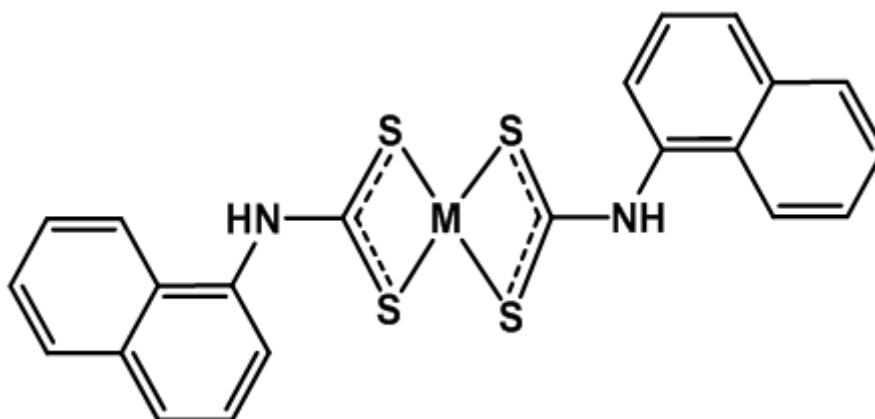


Fig. 2 : The predicate structure of the complex (1,9,17,25,33) M= Fe(II), Co(II),Ni(II),Cu(II),Zn(II)

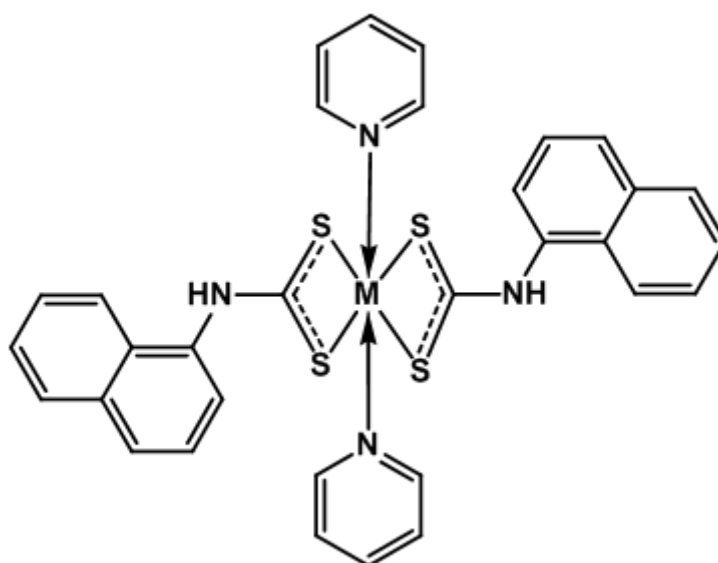


Fig. 3: The predicate structure of the complex (2-5, 10-13,18-21, 26-29, 34- 37) M= Fe(II), Co(II), Ni(II), Cu(II), Zn(II)

n= Number of nitrogen bases =2 when X= Py,γ-Pic,iso Quinoline, 3,5-lutidine

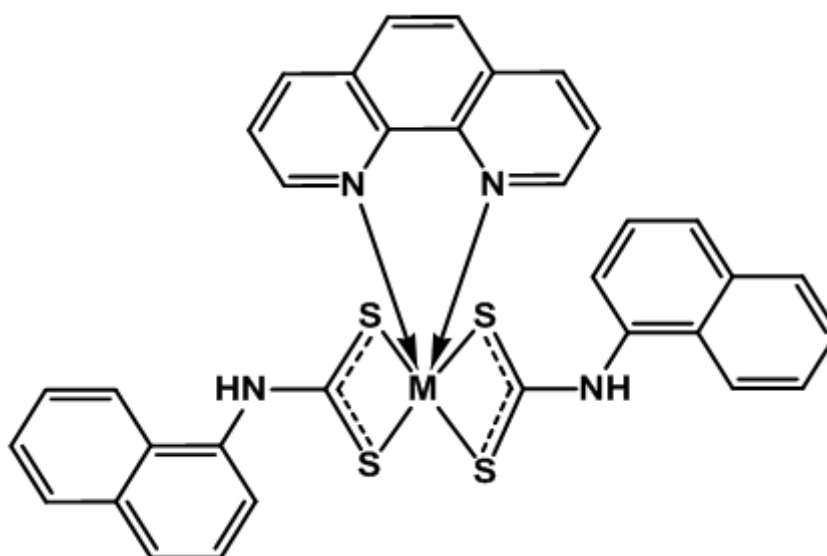


Fig. 4: The predicate structure of the complex (6,7,14,15,22,23,30,31,38,39)

M=Fe(II), Co(II), Ni(II), Cu(II), Zn(II) n= Number of nitrogen bases =1 when x=1,10-phenanthroline, en.

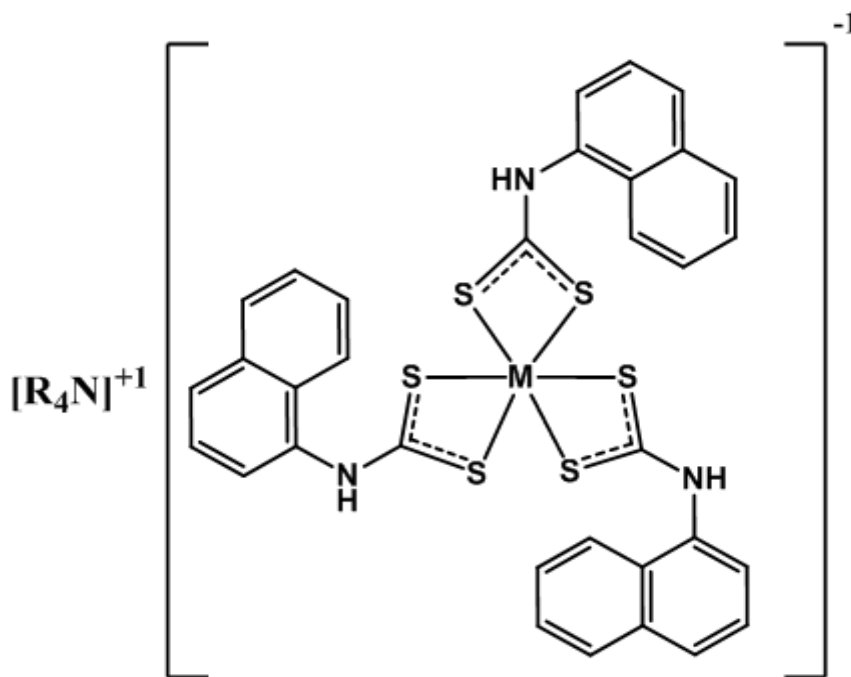


Fig. 5: The predicate structure of the complex of type $R_4N [Ni (PABdtc)_3]$ R= ethyl

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