

Synthesis and Characterization of 2-Ethoxyethylxanthate Complexes with Manganise (II), Iron (II), Cobalt (II), Nickel (II), Copper (II) and Zinc (II) and their Adducts with Nitrogen Base Ligands

Saad E. AL-Mukhtar¹, Lena N. Mohamed Saleh²

^{1,2}Department of Chemistry, College of Science, University of Mosul, Mosul, IRAQ

ABSTRACT

New complexes and adducts of xanthate of the general formula $[M(2.EthoEtxant)_2]$ and $[M(2.EthoEtxant)_2.nL]$ Where $M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$, and $(2.EthoEtxant) = 2.Ethoxyethylxanthate$, and $n = 2$ where $L = pyridine, Isoquinoline, 4-picoline, 3,5-lutidine$, $n = 1$ where $L = ethylenediamine, (1,10).phenanthroline$, 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 $[M(2.EthoEtxant)_2]$ are of tetrahedral geometry while the complexes of the type $[M(2.EthoEtxant)_2.nL]$ have octahedral geometry.

Keywords: Xanthate, Manganise (II), Iron (II), Cobalt (II), Nickel (II), Copper (II), Zinc (II), Complexes.

INTRODUCTION

Alkyldithiocarbonates, more commonly referred to as xanthates, were first prepared by Semeniuc et al. ⁽¹⁾. Their applications as vulcanizers ⁽²⁾, fungicides ⁽³⁾, and flotation agents ^(4, 5) in metallurgy have been described in the literature. Transition metal dithiolate complexes exhibit a rich and interesting chemistry that have been studied during the last several decades ^(6,7). These form a four membered ring with the metal ion have been extensively investigated and thoroughly reviewed ^(8,9,10). The four membered ring metal complexes expand their coordination number by interaction with a Lewis base. This may take place by adduct formation with order ligands of comparable ligating ability. The resulting complex often are significantly different from those of the complex not having the expand coordination number ^(8,11).

Thus we have described the preparation of some $Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)$ complexes containing 2-Ethoxyethylxanthate ligand and their adducts with nitrogen bases. The nitrogen bases stabilize the binary complexes. The isolated products are stable in air but their stability decreased markedly when dissolved in organic solvents.

Experimental

MATERIALS AND METHODS

All reagent and solvent 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 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 Electro thermal 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 2-Ethoxyethylxanthate

2-Ethoxyethanol (9.01gm,0.1mol) was added to aqueous solution (5.61g,0.10mol) of potassium hydroxide with stirring. The mixture was cooled in an ice bath, to this mixture (6.03cm³,0.10mol) of carbon disulfide was added drop wise with continuous stirring for 30 min. in ice bath, The yellow precipitate formed was filtered off, washed with diethylether and dried under vacuum.

I.A. Synthesis of complex [M(2.EthoEtxant)₂]

M=Mn(II),Fe(II),Co(II),Ni(II),Cu(II),Zn(II)

An ethanolic solution of MnCl₂.4H₂O (1.98g,0.01mol),or FeCl₂.4H₂O(1.98g,0.01mol),or CoCl₂.6H₂O(2.38g,0.01mol),or NiCl₂.6H₂O(2.38g,0.01mol) or CuCl₂.2H₂O(1.70g,0.01mol) or ZnCl₂(1.26g,0.01mol) was added dropwise to an ethanolic solution of potassium 2-Ethoxyethylxanthate(4.08g,0.02) 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(2-EthoEtxant)₂(L)₂]

L=pyridine, isoquinoline,4-picoline,3,5-lutidine

Prepared similarly as in (I.A).The precipitate formed was treated with (0.02mol) of pyridin,isoquinoline,4.picoline,3,5. lutidine)dropwise with continuous stirring for 30 min.the precipitate formed,was filtered off and washed with ethanol then dried under vacuum.

I. C. Synthesis of complex [M(2-EthoEtxant)₂(L)]

L=1,10-Phenanthroline,Ethylenediamine

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

RESULTS AND DISCUSSTION

The new ligand was prepared by the reaction of 2-Ethoxyethanol with potassium hydroxide and then added carbon disulphide: the complexes were prepared through direct reaction of the metal chlorides, MnCl₂.6H₂O or FeCl₂.4H₂O or CoCl₂.6H₂O or NiCl₂.6H₂O or NiCl₂.6H₂O or CuCl₂.2H₂O and unhydrous ZnCl₂ with the ligand in (1:2)molar ratio.The values of conductivity measurement in dimethylformamide solution of the complexes are in the range (3.07-32.44)Ω⁻¹.cm².mol⁻¹ which are typical values for non-electrolyte type⁽¹²⁾

Magnetic susceptibility measurements

The magnetic moments of the complexes Table(1)were measured at (25⁰C).The magnetic moments for Mn(II),Fe(II),Co(II),Ni(II) and Cu(II)complexes(1,8,15,22 and 29)are (1.95-5.99BM.) suggesting a tetrahedral geometry⁽¹³⁾,the magnetic moments values of the other complexes(2-7,9-14,16-21,23-28,29-35) were in the rang(2.05-6.08BM.) in an octahedral geometry. The high values of magnetic moments of some octahedral Co(II)complexes from the spin only value are due to orbital contribution⁽¹³⁾.

Electronic spectra studies

The UV-Visible spectra of ligand and its complexes of 10⁻³ M solution in DMF were recorded; the results were listed in Table(2).

the UV-Visible spectra of the Fe(II) complex (8) gives absorption band at (9090cm⁻¹), which corresponds to (⁵E → ⁵T₂)transition in a tetrahedral geometry⁽¹³⁾,complexes (9-14)show absorption band at the range (9861-11086), which were assigned to (⁵T₂g → ⁵Eg) transition these observation indicating an octahedral geometry around Fe(II) ions⁽¹⁴⁾.

The Co(II) complex (16) exhibited an absorption band at (16556) region, which was assigned to (⁴A₂(F) → ⁴T₁(P)) transition⁽¹⁵⁾, in a tetrahedral configuration of this complex and the absence of the bands (⁴A₂(F) → ⁴T₂(F)) and (⁴A₂(F) → ⁴T₁(F)), are due to the sensitivity of the instrument used.complexes (16-21) show three absorption bands at the range (9606-11905cm⁻¹), (15808-17170cm⁻¹) and (20492-22391cm⁻¹), which were assigned to (⁴T₁g(F) → ⁴T₂g(F)), (⁴T₁g(F) → ⁴A₂g(F)) and (⁴T₁g(F) → ⁴T₁g(p)) transition respectively in an octahedral configuration^(16,17).

The Ni(II) complex (22) show two absorption bands at (9434cm⁻¹) and (13994cm⁻¹) which were assigned to (³T₁(F)→³A₂(F)) and (³T₁(F)→³T₁(P)) transitions respectively in a tetrahedral geometry⁽¹³⁾, the complexes (23-28) show three absorption bands in the range (9294-10352cm⁻¹), (13405-15873cm⁻¹) and (22321-26667cm⁻¹), which were assigned (³A₂g(F)→³T₂g(F)), (³A₂g(F)→³T₁g(F)) and (³A₂g(F)→³T₁g(p)) respectively which is characteristic for an octahedral geometry Ni(II) complexes⁽¹⁸⁾.

The Cu(II) complex (29) gives an absorption band at (9690cm⁻¹), which corresponds to (²T₂→²E) transition in a tetrahedral geometry⁽¹⁹⁾, while the complexes (30-35) show a broad absorption band in the region (9990-14620cm⁻¹) which was assigned to (²Eg→²T₂g) transition which may be formed from the combination of three transitions (²B₁g → ²A₁g), (²B₁g → ²B₂g) and (²B₁g → ²Eg) in an distorted octahedral Cu(II) complexes^(20,21). For all the compounds, the other band appear above (30,000 cm⁻¹) refers to charge transfer band.

Infra-red spectral studies

The important IR bands of the ligand (2-EthoEtXant)K and its complexes are listed in Table (2). The two bonds ν(C-O) and ν(C-S) of the ligand were observed at (1111cm⁻¹) and (1001cm⁻¹), in all complexes these bond shift to appear at the region (1200-1281cm⁻¹) and (899-991cm⁻¹) respectively. The presence of only one band in the later region reports the bidentate coordination of the dithioligand⁽²²⁾.

IR spectra showed a new band at (403-438) cm⁻¹ which is the evidence for the coordination of metal to sulfur ν(M-S). This behavior may be attributed to the electron-releasing of the alcohol, which forces high electron density towards the sulfur atoms⁽²³⁾.

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

N o.	Compound	Color	m.p (°C)	Molar conductivity Ω ⁻¹ .cm ² .mol ⁻¹	%M	%Yield	μ _{eff} B.M
	(2-EthoEtXant)K	Yellow	125	-----	-----	-----	-----
1	[Mn(2.EthoxyEtXant) ₂]	White	*187	23.77	14.26 (14.09)	75	5.99
2	[Mn(2.EthoxyEtXant) ₂ (py) ₂]	White	*240	19.67	10.11 (9.89)	73	5.97
3	[Mn(2.EthoxyEtXant) ₂ (4.pic) ₂]	White	*158	19.17	9.61 (9.16)	69	6.08
4	[Mn(2.EthoxyEtXant) ₂ (3,5-Lu) ₂]	Light brown	*220	15.94	9.16 (8.86)	81	5.91
5	[Mn(2.EthoxyEtXant) ₂ (iso.Q) ₂]	White	*298	21.44	8.54 (8.11)	65	5.94
6	[Mn(2.EthoxyEthxXant) ₂ (en)]	Light brown	*280	13.94	12.32 (11.96)	72	5.97
7	[Mn(2.EthoxyEtXant) ₂ (phen)]	White	*210	12.74	9.72 (8.42)	71	6.02
8	[Fe(2.EthoxyEtXant) ₂]	Light brown	*246	4.67	14.47 (14.28)	75	4.92
9	[Fe(2.EthoxyEtXant) ₂ (py) ₂]	Brown	*250	12.07	10.26 (10.00)	88	4.95
10	[Fe(2.EthoxyEtXant) ₂ (4.pic) ₂]	Brown	*210	8.77	9.76 (9.57)	92	5.09
11	[Fe(2.EthoxyEtXant) ₂ (3,5.Lu) ₂]	Light brown	*200	16.94	9.30 (9.12)	62	5.11
12	[Fe(2.EthoxyEtXant) ₂ (iso.Q) ₂]	Light brown	*212	7.44	8.67 (8.33)	90	5.37
13	[Fe(2.EthoxyEtXant) ₂ (en)]	Brown	*150	7.74	12.50 (12.21)	72	5.03
14	[Fe(2.EthoxyEtXant) ₂ (phen)]	Red	*200	12.74	9.86 (8.78)	97	4.98
15	[Co(2.EthoxyEtXant) ₂]	Dark brown	*155	7.00	15.14 (14.98)	88	3.93

16	$[(\text{Co}(\text{2.EthoxyEtXant})_2(\text{py})_2)]$	Dark brown	*250	2.97	10.77 (10.50)	92	3.99
17	$[\text{Co}(\text{2.EthoxyEtXant})_2(4.\text{pic})_2]$	Dark green	*190	16.77	10.24 (10.01)	97	4.19
18	$[\text{Co}(\text{2.EthoxyEtXant})_2(3,5.\text{Lu})_2]$	Dark green	*210	5.44	9.77 (9.53)	74	4.23
19	$[\text{Co}(\text{2.EthoxyEtXant})_2(\text{iso.Q})_2]$	Dark green	*178	9.84	9.10 (8.82)	73	4.47
20	$[\text{Co}(\text{2.EthoxyEtXant})_2(\text{en})]$	Brown	*240	3.44	13.09 (12.87)	72	4.45
21	$[\text{Co}(\text{2.EthoxyEtXant})_2(\text{phen})]$	Dark green	*150	4.19	10.35 (10.10)	88	4.53
22	$[\text{Ni}(\text{2.EthoxyEtXant})_2]$	Dark green	*78	32.16	15.09 14.93	72	2.92
23	$[\text{Ni}(\text{2.EthoxyEtXant})_2(\text{py})_2]$	Green	*140	25.19	10.73 (10.20)	85	2.97
24	$[\text{Ni}(\text{2.EthoxyEtXant})_2(4.\text{pic})_2]$	Green	*120	28.77	10.21 (9.79)	80	3.03
25	$[\text{Ni}(\text{2.EthoxyEtXant})_2(3,5.\text{Lu})_2]$	Light Green	*138	25.84	9.73 (9.52)	98	2.97
26	$[\text{Ni}(\text{2.EthoxyEtXant})_2(\text{iso.Q})_2]$	Green	*138	24.74	9.07 (8.87)	98	2.91
27	$[\text{Ni}(\text{2.EthoxyEtXant})_2(\text{en})]$	Light Brown	*248	5.94	13.05 (12.75)	85	2.94
28	$[\text{Ni}(\text{2.EthoxyEtXant})_2(\text{phen})]$	Light Green	*240	31.82	10.31 (10.06)	97	3.08
29	$[\text{Cu}(\text{2.EthoxyEtXant})_2]$	Yellow	*144	7.27	16.14 15.88	82	1.95
30	$[\text{Cu}(\text{2.EthoxyEtXant})_2(\text{py})_2]$	Green Yellow	*150	30.77	11.51 (10.30)	100	2.01
31	$[\text{Cu}(\text{2.EthoxyEtXant})_2(4.\text{pic})_2]$	Yellow	*120	9.77	10.96 (10.78)	97	2.12
32	$[\text{Cu}(\text{2.EthoxyEtXant})_2(3,5.\text{Lu})_2]$	Green	*140	32.44	10.45 (10.22)	92	2.09
33	$[\text{Cu}(\text{2.EthoxyEtXant})_2(\text{iso.Q})_2]$	Dark green	*130	20.44	9.75 (9.48)	97	1.98
34	$[\text{Cu}(\text{2.EthoxyEtXant})_2(\text{en})]$	Yellow brown	*80	5.44	13.98 (13.62)	78	2.15
35	$[\text{Cu}(\text{2.EthoxyEtXant})_2(\text{phen})]$	Light Green	*98	30.82	11.07 (10.92)	98	2.06
36	$[\text{Zn}(\text{2.EthoxyEtXant})_2]$	White	< 300	3.07	16.53 16.21	68	Dia
37	$[\text{Zn}(\text{2.EthoxyEtXant})_2(\text{py})_2]$	White	*240	6.17	10.81 (10.55)	68	Dia
38	$[\text{Zn}(\text{2.EthoxyEtXant})_2(4.\text{pic})_2]$	White	*225	7.77	11.24 (11.01)	88	Dia
39	$[\text{Zn}(\text{2.EthoxyEtXant})_2(3,5.\text{Lu})_2]$	White	*320	23.54	10.72 (10.43)	72.5	Dia
40	$[\text{Zn}(\text{2.EthoxyEtXant})_2(\text{iso.Q})_2]$	White	< 300	10.44	10.00 (8.99)	62	Dia
41	$[\text{Zn}(\text{2.EthoxyEtXant})_2(\text{en})]$	White	*240	3.44	14.33 (14.12)	68	Dia
42	$[\text{Zn}(\text{2.EthoxyEtXant})_2(\text{phen})]$	White	*288	31.82	11.36 (11.2)	74	Dia
*Decomposition							

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

No.	Compound	UV bands (cm^{-1})	IR spectra (cm^{-1})		
			$\nu(\text{C} - \text{O})$	$\nu(\text{C} - \text{S})$	$\nu(\text{M}-\text{S})$
	(2-EthoEtXant)K		1111	1001	-----
1	[Mn(2.EthoxyEtXant) ₂]		1242	915	426
2	[Mn(2.EthoxyEtXant) ₂ (py) ₂]		1220	915	420
3	[Mn(2.EthoxyEtXant) ₂ (4.pic) ₂]		1252	930	420
4	[Mn(2.EthoxyEtXant) ₂ (3,5-Lu) ₂]		1225	930	430
5	[Mn(2.EthoxyEtXant) ₂ (iso.Q) ₂]		1250	945	430
6	[Mn(2.EthoxyEthxXant) ₂ (en)]		1228	945	438
7	[Mn(2.EthoxyEtXant) ₂ (phen)]		1234	937	420
8	[Fe(2.EthoxyEtXant) ₂]	9090, 40983	1242	975	420
9	[Fe(2.EthoxyEtXant) ₂ (py) ₂]	10758, 31250	1254	945	418
10	[Fe(2.EthoxyEtXant) ₂ (4.pic) ₂]	11086, 44247	1252	940	422
11	[Fe(2.EthoxyEtXant) ₂ (3,5.Lu) ₂]	11025, 30769	1248	945	420
12	[Fe(2.EthoxyEtXant) ₂ (iso.Q) ₂]	9861, 34095	1248	930	411
13	[Fe(2.EthoxyEtXant) ₂ (en)]	10331, 30817	1215	899	418
14	[Fe(2.EthoxyEtXant) ₂ (phen)]	10081, 31221	1233	958	420
15	[Co(2.EthoxyEtXant) ₂]	16556, 32616	1223	935	428
16	[(Co(2.EthoxyEtXant) ₂ (py) ₂]	11905, 17007, 22271, 31008	1237	915	418
17	[Co(2.EthoxyEtXant) ₂ (4.pic) ₂]	11905, 16447, 20704, 32000	1238	914	420
18	[Co(2.EthoxyEtXant) ₂ (3,5.Lu) ₂]	11904, 17170, 21322, 31746	1244	935	413
19	[Co(2.EthoxyEtXant) ₂ (iso.Q) ₂]	9606, 15808, 20492, 35212	1225	930	428
20	[Co(2.EthoxyEtXant) ₂ (en)]	9843, 16666, 20833, 37037	1252	930	418
21	[Co(2.EthoxyEtXant) ₂ (phen)]	10000, 17065, 22391, 31786	1223	945	418
22	[Ni(2.EthoxyEtXant) ₂]	9434, 13994, 28653	1261	937	413
23	[Ni(2.EthoxyEtXant) ₂ (py) ₂]	9398, 15038, 24213, 33898	1232	914	420
24	[Ni(2.EthoxyEtXant) ₂ (4.pic) ₂]	9294, 15106, 24213, 38023	1259	945	420
25	[Ni(2.EthoxyEtXant) ₂ (3,5.Lu) ₂]	10352, 15106, 22492, 37594	1275	935	428
26	[Ni(2.EthoxyEtXant) ₂ (iso.Q) ₂]	10320, 15291, 22321, 34602	1200	953	424
27	[Ni(2.EthoxyEtXant) ₂ (en)]	10246, 15873, 26667, 36563	1275	960	424

28	[Ni(2.EthoxyEtXant) ₂ (phen)]	9434, 13405, 23256, 33864	1263	937	420
29	[Cu(2.EthoxyEtXant) ₂]	9690, 31769	1207	957	420
30	[Cu(2.EthoxyEtXant) ₂ (py) ₂]	14514, 36900	1209	978	420
31	[Cu(2.EthoxyEtXant) ₂ (4.pic) ₂]	9990, 31153	1209	958	420
32	[Cu(2.EthoxyEtXant) ₂ (3,5.Lu) ₂]	14620, 31646	1209	958	420
33	[Cu(2.EthoxyEtXant) ₂ (iso.Q) ₂]	13158, 33411	1209	958	422
34	[Cu(2.EthoxyEtXant) ₂ (en)]	13514, 36232	1281	991	403
35	[Cu(2.EthoxyEtXant) ₂ (phen)]	14134, 33500	1217	930	422
36	[Zn(2.EthoxyEtXant) ₂]		1275	945	420
37	[Zn(2.EthoxyEtXant) ₂ (py) ₂]		1260	945	426
38	[Zn(2.EthoxyEtXant) ₂ (4.pic) ₂]		1217	945	409
39	[Zn(2.EthoxyEtXant) ₂ (3,5Lu) ₂]		1230	939	418
40	[Zn(2.EthoxyEtXant) ₂ (iso.Q) ₂]		1270	960	426
41	[Zn(2.EthoxyEtXant) ₂ (en)]		1275	960	418
42	[Zn(2.EthoxyEtXant) ₂ (phen)]		1230	915	424

REFERENCES

- [1]. Semeniuc RF, Reamer TJ, Blitz JP, Wheeler KA, Smith MD. . Functionalized O-alkyldithiocarbonates: a new class of ligands designed for luminescent heterometallic materials. *Inorganic Chemistry*. 2010;49(6):2624–2629.
- [2]. Gupta B, Kalgotra N, Andotra S, Pandey SK. O-Tolyl/benzyl dithiocarbonates of phosphorus(III) and (V): syntheses and characterization. *Monatshefte für Chemie*. 2012;143(7):1087–1095.
- [3]. Bakbardina OV, Pukhnyarskaya IY, Gazalieva MA, Fazylov SD, Makarov EM Synthesis and fungicidal activity of S-amino derivatives of O-alkyldithiocarbonic acids. *Russian Journal of Applied Chemistry*. 2006;79(10):1726–1728.
- [4]. Abramov AA, Forsberg KSE. Chemistry and optimal conditions for copper minerals flotation: theory and practice. *Mineral Processing and Extractive Metallurgy Review*. 2005;26(2):77–143.
- [5]. Chaudhari S, Tare V. Heavy metal-soluble starch xanthate interactions in aqueous environments. *Journal of Applied Polymer Science*. 1999;71(8):1325–1332.
- [6]. Ara I, Bahiji F. E, Lachkar M, Larbi B. Synthesis and characterization of ethylxanthato complexes of zinc(II) with P-donor ligands. *Transition Metal. Chem.*, 2003, 28,908–912.
- [7]. Victoriano L. I, Cortes, H. B. Cuprous dithiocarbamates - syntheses and reactivity. *J. Coord. Chem.*, 1996, 39,231–239.
- [8]. Coucouvanis. D. Coordination chemistry of dithio ligands. *Prog. Inorg. Chem*. 1979.,26,301,274.
- [9]. Bond A. M, Martin R. L. Electro chemistry and Redox Behaviour of transition Metal Dithiolate. *Coord. Chem. Rev*. 1984,54,23.
- [10]. Cox M. J, Tiekink E. R. The diverse coordination patterns in the structures of zinc, cadmium and mercury bis(1,1-DITHIOLATES). *Rev.Inorg. Chem*. 1997,17,1.
- [11]. Magnus. K. A , Ton-That. H. and Carpenter. J.E. RECENT. Structure work on the oxygen transport protein Hemocyanin. *Chem. Rev*. 1994,94,727-735
- [12]. Geary W.J. The use of conductivity measurements in organic solvents for characterization of coordination compounds. *Coord.Chem.Rev*. 1971,7,8-122 .
- [13]. Nicholls .D. The Chemistry of Iron, Cobalt and Nickel. Pergamon press,Oxford,1st Ed. 1973 , pp.1037, 1087, 1088,1090, 1091,1093, 1151,1154.
- [14]. Coucouvanis. D. and Fackler. J.P. Square-planar sulfur complexes.VI. reactions of bases with xanthate, dithiocarbamates, and dithiolates of nickel(II) *Inorg. Chem*. 1967, 6, 2047-2053
- [15]. Siddiqi .K.S. and Nishat. N. Synthesis and characterization of succinimide and phthalimidedithiocarbamate and their complexes with some transition metal ions. *Synth. Reac. Inorg. Met-Org. Chem.*, 2000, 30(8) 1505 -1518
- [16]. Martell. A.E. 1971. “Coordination Chemistry”, Van Nostrand Reinhold, New York., p.1.
- [17]. Onwudiwe. D. C., and Ajibade. P. A . Synthesis and characterization of metal complexes of N-alkyl-N-phenyl dithiocarbamates. *Polyhedron*, 2010,29 ,1431-1436.
- [18]. Singh.N.; Singh.N.K. and Kaw. C. Synthetic and spectroscopic studies of xanthate-bridged heterobimetallic complexes containing diamagnetic and paramagnetic metal ions. *Bull. Chem. Soc. (Jpn.)*, 1989, 62, 3328-3333 .

- [19]. Cookson. J.; Emma. A.L.E. ; John .P.M ,Christopher .J.S .; Rowena. L.P.; Andrew. R.C, Michael G.B.D., and Paul D. Metal directed assembly of large dinuclearcopper(II) dithiocarbamate Macrocyclic complexes. *Inorg Chim Acta.*, 2010, 363, 1195-1203
- [20]. Lever. A.B.P. *Inorganic Electronic Spectroscopy* (Second edition),Elsevier, Amsterdam,1984 ,pp357.
- [21]. Sarwar.M.; Ahmad. S.; Ahmad. S .; Ali. S. and Ahmed. S. Awan.Copper(II) complexes of pyrrolidinedithiocarbamate. *Trans Met Chem.* 2007, 32,199–203.
- [22]. Serrano. J. L.; Garcí'a . L.; Pe´rez. J.; Pe´rez E.; Sa´nchez. G.; Garcí'a .J.;Lo´pez. G.; Garcí'a. G. and Molins. E. New dithiocarbamate and xanthate complexes of nickel(II)with iminophosphines. *Chim. Acta* .2003,355 ,33_40 .
- [23]. Rathore. H. S.; Varshney. G.; Mojumdar. S. C. and Saleh. M. T. Copper (II) complexes of pyrrolidinedithiocarbamate. *Ther. Anal. And Calorim*, . 2007, 90 (3), 681–686..