------ Raf. J. Sci., Vol. 26, No.1, pp. 49-55, 2017------

Preparation and Characterization of some Transition Metal Complexes with Crotyl xanthate Ligand and their Adducts with Nitrogen Bases

Saad E. Al- Mukhtar Hiba F. Al-Katib Lana A. Al-Nuaimy
Department of Chemistry/ College of Science/ University of Mosul

(Received 9 / 6 / 2013 ; Accepted 7 / 10 / 2013)

ABSTRACT

A new series of xanthate complexes of the general formula $[M(Crotxant)_2]$, $[M(Crotxant)_2.nL]$ where M = Fe(II), Co(II), Ni(II), Cu(II), Crotxant = Crotyl xanthate, n = 2,L = pyridine, quinoline, 4-picoline, n = 1, L = ethylenediamin , 1,10- phenanthroline. All the isolated complexes have been prepared and characterized by atomic absorption, molar conductivity, Infrared, electronic absorption spectra and magnetic measurement.

The conductivity measurements proved the non-electrolytic behaviour of all compounds, magnetic susceptibility measurements and electronic spectra show a tetrahedral geometry for complexes of the type $[M(Crotxant)_2]$ and octahedral geometry for complexes of the type $[M(Crotxant)_2.nL]$.

Keywords: xanthate, Nickel(II), Cobalt(II), Copper(II), Iron(II).

تحضير وتشخيص بعض معقدات عناصر السلسلة الانتقالية الأولى مع ليكاند كروتايل زانثيت وعدد من القواعد النيتروجينية

الملخص

حضرت معقدات جديدة للزانثيت ذات الصيغة $[MCrotxant)_2]$ ، $[M(Crotxant)_2.nL]$ حيث أن:
M=Fe(II) , Co(II), Ni(II) and Cu(II) Crotxant = كروتايل زانثيت , n = 2 , L = بيريدين , كوينولين,
10,1 - فينانثرولين , اثيلين ثنائي الأمين = n = 1 , L , 4- بيكولين. شخصت المعقدات المحضرة بواسطة قياسات الامتصاص الذري والتوصيلية المولارية وأطياف الأشعة تحت الحمراء والأطياف الالكترونية والقياسات المغناطيسية، دلت قياسات التوصيلية المولارية على السلوك غير الالكتروليتي لجميع المعقدات ودلت القياسات المغناطيسية والأطياف الالكترونية على اتخاذ المعقدات شكل رباعي السطوح للصيغة $[M(Crotxant)_2]$ وثماني السطوح للصيغة $[M(Crotxant)_2.nL]$.

INTRODUCTION

Xanthates and related ligands as well as transition-metal complexes in which a 1,1-dithiolate ligand forms a four-membered ring with the metal ion have been extensively investigated (Coucouvanis, 1970). 1,1- dithiolate ligands found many applications ranging from flotation agents to radical polymerization (Haiduc, 2007; Coote and Radom, 2004; Wan *et al.*, 2005; Tiekink and Haiduc, 2005). Xanthate ligands $[ROCS_2]$ are known to coordinate metal centers in a variety of coordination modes, e.g. monodentate, bidentate chelating or bridging (Haiduc, 2003). The ligands can be easily prepared and their properties can be suitably modified by the appropriate choice of the O bound substituents. Further, the metal xanthate complexes show that the interesting thermal behaviour and thermal decomposition of such complexes can be a useful route to metal sulfides (Hill *et al.*, 1994). Recently, metal alkylxanthate compounds have been used as synthetic precursors for the generation of metal sulfide nanostructures (Bessergenev *et al.*, 1995; Bessergenev *et al.*, 1998; Pradhan *et al.*, 2003). In view of this, we decided to explore the suitability of crotyl xanthates complexes with Fe(II), Co(II), Ni(II) and Cu(II) as single-source precursors for the preparation of nanocrystalline transition metal sulfide.

EXPERIMENTAL

Materials and instrumentation

The reagents and solvents were of analytical grade. (1,10)- Phenanthroline, crotyl alcohol, carbon disulfide were purchased from Merck Company,pyridine,4-picoline,quinoline were purchased from BDH company. All melting points were determined on a Gallen Kamp and Electro thermal 9300 Digital-Series apparatus were uncorrected. The IR. – Spectra using (KBr disc) were recorded on Perkin – Elmer 590B Spectrophotometer. UV –Visible spectra were recorded using a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of complexes in DMF as solvent, the magnetic susceptibilities were measured at 25°C on the solid by the Faraday method using Brucker BM6 instrument. Diamagnetic corrections were calculated using Pascal's constants. Conductivities were measured with a Conductivity Hard-Held Meter LF 330 (WTW GmbH) at 25 °C. Metal% was determined using atomic absorption elemental Analyzer Model 1106.

Synthesis of potassium crotylxanthate (K Crotxant) (Vogel, 2008)

To a solution of (5.61 g, 0.1 mol) potassium hydroxide in water, (7.20g, 0.1 mol) of crotyl alcohol was added with stirring. The mixture was cooled in an ice-bath, to this mixture carbon disulfide (7.60 g, 0.1 mol) was added dropwise with a continuous stirring for 30 min. in the ice-bath, then allowed to reach room temperature and diethyl ether (50 cm^3) was added. The yellow precipitated formed was filtered off washed with ether and dried under vacuum.

Synthesis of Complexes

A. Synthesis of [M $(Crotxant)_2$]

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

A solution of (K Crotxant) (0.002 mol) in 50% ethanol was added to ethanolic solution of $FeCl_2.4H_2O$(0.198,0.001 mol), $CoCl_2.6H_2O$(0.237g, 0.001 mol), $NiCl_2$. $6H_2O$ (0.237g, 0.001 mol) or $CuCl_2.2H_2O$ (0.170 g, 0.001 mol) dropwise with constant stirring at room temperature. The green precipitate formed was filtered off and washed with ethanol then with diethyl ether and dried under vacuum.

B. Synthesis of [M $(Crotxant)_2.L_2$]

L= Pyridine, isoquinoline, 4-picoline

These Complexes were prepared similarly as in (A) The precipitate formed was treated with (0.002 mol) of (Pyridine, isoquinoline, 4-picoline) dropwise with continuous stirring for 30min, the precipitate formed, was filtered and washed with ethanol then dried under vacuum.

C. Synthesis of complex [M $(Crotxant)_2$(L)]

L=1,10-phenanthroline, ethylene diamine

Prepared similarly as in (A). The precipitate formed was treated with (0.001mol) of (1,10-phenanthroline,ethylenediamine) dropwise with continuous stirring for 30min, the precipitate formed was filtered, washed with ethanol, then dried under vacuum.

RESULTS AND DISCUSSION

The new ligand was prepared by the reaction of Crotyl alcohol with potassium hydroxide and carbon disulphide. The complexes were prepared through the direct reaction of the metal chlorides, $FeCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, or $CuCl_2$. $2H_2O$ with the above ligand in (1:2) molar ratio. The values of molar conductivity in dimethyl formamide solution of the complexes range from (2.1-39) $\Omega^{-1}.cm^2.mol^{-1}$, which are within the values for the non electrolyte type (Geary , 1971).

Infrared spectral studies

The important IR bands of the ligand and its complexes are listed in Table (2). The υ(C - O) and υ(C- S) were observed in the ranges of (1147-1211)cm^{-1} and (940-1050)cm^{-1} respectively. 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 (408-445)cm^{-1} which can be considered as an evidence for the coordination of metal to sulfur υ(M-S). (Raya *et al.*, 2006)

Electronic spectral studies

The UV-Visible spectra of the complexes in 10^{-3} M solution DMF are recorded; the results are listed in Table (2). The Fe(II) complex (1) give an absorption band at (9523cm^{-1}), which corresponds to ($^5E \rightarrow {}^5T_2$) transition in a tetrahedral geometry (Nicholls, 1973). Complexes (2-6) show absorption bands at the range (9803-10964) cm^{-1}, which were assigned to ($^5T_2g \rightarrow {}^5Eg$) transition in an octahedral geometry (Coucouvanis and Fackler, 1967).

The Co(II) complex (7) exhibited two absorption bands at (10093 cm^{-1}) and (13921cm^{-1}) which were assigned to ($^4A_2(F) \rightarrow {}^4T_1(F)$,($^4A_2(F) \rightarrow {}^4T_1(P)$)) transitions respectively (Siddiqi and Nishat, 2000), in tetrahedral configuration of this complex. The ($^4A_2(F) \rightarrow {}^4T_2(F)$) transition is out of the range of the instrument used. Complexes (8-12) show three absorption bands at the range (10183-10692cm^{-1}), (13009-15069cm^{-1}) and (19064-21432 cm^{-1}), which were assigned to ($^4T_1g(F) \rightarrow {}^4T_2g(F)$), ($^4T_1g(F) \rightarrow {}^4A_2g(F)$) and ($^4T_1g(F) \rightarrow {}^4T_1g(P)$) transitions in an octahedral geometry (Martel, 1971).

The Ni(II) complex (13) show two absorption bands at (10224 cm^{-1}),(13572 cm^{-1}) which were assigned to ($^3T_1(F) \rightarrow {}^3A_2(F)$) and ($^3T_1(F) \rightarrow {}^3T_1(P)$) transitions in a tetrahedral geometry (Nicholls, 1973), respectively, the complexes (14-18) show three absorption bands in the range (10157-11806 cm^{-1}), (15726-17921 cm^{-1}) and (19305-20765cm^{-1}), which were assigned to ($^3A_2g(F) \rightarrow {}^3T_2g(F)$), ($^3A_2g(F) \rightarrow {}^3T_1g(F)$) and ($^3A_2g(F) \rightarrow {}^3T_1g(P)$) transition in an octahedral geometry (Singh *et al.*, 1989).

The Cu(II) complex (19) give an absorption band at (96682 cm^{-1}), which corresponds to ($^2T_2 \rightarrow {}^2E$) transition in tetrahedral geometry (Cookson *et al.*, 2010), the complexes (20-24) show a broad band in the region (12121-12500 cm^{-1}), which was assigned to ($^2Eg \rightarrow {}^2T_2g$) transition which may be formed from the combination of three transitions ($^2B_1g \rightarrow {}^2A_1g$), ($^2B_1g \rightarrow {}^2B_2g$) and ($^2B_1g \rightarrow {}^2Eg$) in an octahedral configuration (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), Ni(II) and Cu(II) complexes (1,7,13 and 19) are in the range (2.25-5.2B.M) suggest a tetrahedral geometry . The high value for complex (7) is due to second order orbital contribution. Finally the magnetic moment values of the other complexes (2-6,8-12,14-18,20-24) were in the range (1.70-5.70 B.M.) suggesting an octahedral geometry (Nicholls, 1973).

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

No.	compound	Decomposition Temp. ($^\circ$C)	Color	Λ_M cm^2. ohm^{-1}.mol^{-1}	μ_{eff} B.M (25^{o}C)	% Calculated (Metal found)
L	K(Crotxant)	> 290	yellow	-		
1.	[Fe (Crotxant)$_2$]	260	Yellowish red	2.1	4.99	16.19(15.8)
2.	[Fe(Crotxant)$_2$(py)$_2$]	210	Dark yellow	9.8	4.89	9.33(10.2)
3.	[Fe (Crotxant)$_2$(qui)$_2$]	185	Yellowish red	13.28	4.94	10.58(11.34)
4.	[Fe (Crotxant)$_2$(4-pic)$_2$]	185	Yellowish red	16.0	4.50	11.16(11.78)
5.	[Fe (Crotxant)$_2$en]	>300	Dark yellow	18.8	4.98	13.89(14.56)
6.	[Fe (Crotxant)$_2$1,10phen]	210	Brown	9.64	5.1	10.69 (9.94)
7.	[Co (Crotxant)$_2$]	258	Violet	17.5	5.2	16.69 (16.5)
8.	[Co (Crotxant)$_2$)$_2$(py)$_2$]	>250	Brown	18.0	5.7	11.52(11.14)
9.	[Co (Crotxant)$_2$(qui)$_2$]	148	Dark brown	18.4	5.6	9.64 (9.5)
10.	[Co (Crotxant)$_2$(4-pic)$_2$]	246	Light violet	21.5	5.3	10.92 (9.74)
11.	[Co (Crotxant)$_2$en]	110	Brown	20	5.10	5.8 (6.25)
12.	[Co (Crotxant)$_2$1,10phen]	140	Dark brown	4.8	4.03	11.04(10.88)
13.	[Ni (Crotxant)$_2$]	270	Green	39	2.71	16.61 (15.0)
14.	[Ni (Crotxant)$_2$(py)$_2$]	145	Green	12.8	2.93	11.47 (10.6)
15.	[Ni (Crotxant)$_2$(qui)$_2$]	150	Gray	14.2	3.81	9.59 (10.25)
16.	[Ni (Crotxant)$_2$(4-pic)$_2$]	100^*	Black	20	3.3	10.88 (9.98)
17.	[Ni (Crotxant)$_2$en]	110	Pink	20.1	3.36	14.27(15.42)
18.	[Ni (Crotxant)$_2$1,10phen]	150	Dark brown	14.7	2.78	10.99(10.91)
19.	[Cu (Crotxant)$_2$]	138	Green	20	2.25	17.76(16.67)
20.	[Cu(Crotxant)$_2$(py)$_2$]	148	Green	5.5	2.30	12.31(12.66)
21.	[Cu (Crotxant)$_2$(qui)$_2$]	145	Green	10.0	2.05	10.31 (10.5)
22.	[Cu (Crotxant)$_2$(4-pic)$_2$]	150	Black	21.6	2.18	11.68(11.53)
23.	[Cu (Crotxant)$_2$en]	110	Green	17.5	1.70	15.28(15.33)
24.	[Cu (Crotxant)$_2$1,10phen]	150	Dark Green	8.0	2.09	11.81(12.1)

Table 2: Selected IR bands (cm^{-1}) and electronic spectral data of the ligand and it is metal complexes

No.	compound	ν(C-S)	ν(C-O)	ν(M-S)	d-d absorption cm^{-1}
L	K(Crotxant)	1050	1147	-	-
1.	[Fe (Crotxant)$_2$]	1022	1180	445	9523
2.	[Fe(Crotxant)$_2$(py)$_2$]	1020	1184	420	9803
3.	[Fe (Crotxant)$_2$(qui)$_2$]	1028	1184	420	10207
4.	[Fe (Crotxant)$_2$(4-pic)$_2$]	1020	1186	418	9833
5.	[Fe (Crotxant)$_2$en]	1022	1188	426	10964
6.	[Fe (Crotxant)$_2$1,10phen]	1024	1170	420	10917
7.	[Co (Crotxant)$_2$]	964	1207	415	10093,13921
8.	[Co (Crotxant)$_2$ (py)$_2$]	1041	1178	410	10325,13009,19064
9.	[Co (Crotxant)$_2$(qui)$_2$]	1022	1165	408	10224,13578,21432
10.	[Co (Crotxant)$_2$(4-pic)$_2$]	1028	1161	410	10692,15069,19982
11.	[Co (Crotxant)$_2$en]	1024	1178	409	10459,14783,20759
12.	[Co (Crotxant)$_2$1,10phen]	1041	1170	410	10183,13783,20865
13.	[Ni (Crotxant)$_2$]	940	1200	440	10224, 13572
14.	[Ni (Crotxant)$_2$(py)$_2$]	964	1194	415	10163,17921,19305
15.	[Ni (Crotxant)$_2$(qui)$_2$]	960	1160	438	10157,16348,20364
16.	[Ni (Crotxant)$_2$(4-pic)$_2$]	1024	1184	435	11806,15726,20765
17.	[Ni (Crotxant)$_2$en]	1027	1153	430	10876,17301,20000
18.	[Ni (Crotxant)$_2$1,10phen]	1022	1180	428	11625,17587,20509
19.	[Cu (Crotxant)$_2$]	966	1188	420	96682
20.	[Cu(Crotxant)$_2$(py)$_2$]	1022	1209	415	12121
21.	[Cu (Crotxant)$_2$(qui)$_2$]	1026	1200	415	12290
22.	[Cu (Crotxant)$_2$(4-pic)$_2$]	980	1211	418	12376
23.	[Cu (Crotxant)$_2$en]	1022	1155	410	12500
24.	[Cu (Crotxant)$_2$1,10phen]	1028	1161	412	12476

melting point **=***

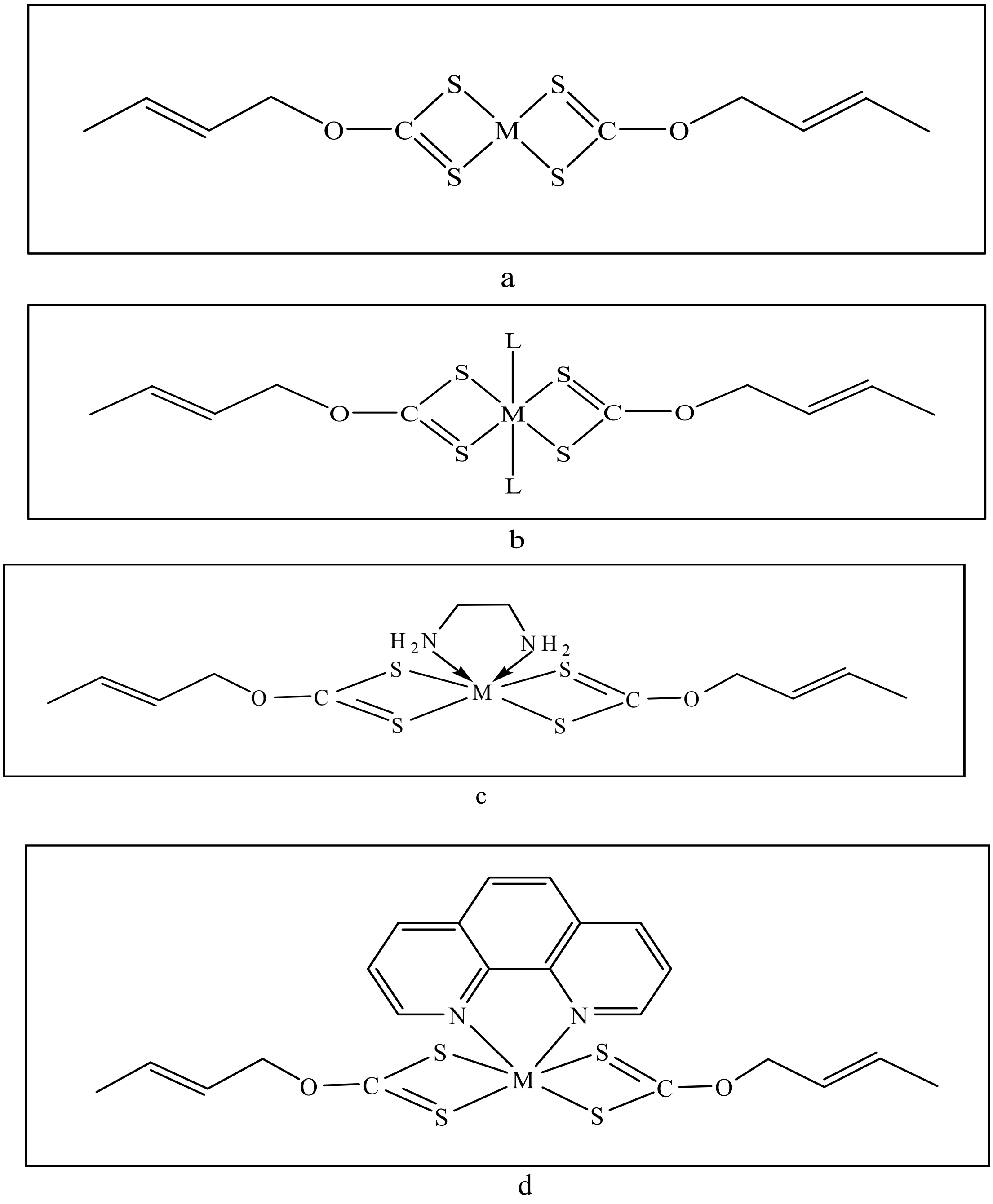

Fig. : Suggested structures (a) complexes [1, 7, 13, 19],
(b) complexes [2-4,8-10,14-16,20-22]L=py, qui., 4-pic.
(c) complexes [5, 11, 17, 23],
(d) complexes [6, 12, 18, 24]

REFERENCES

Bessergenev, V.G.; Ivanova, E.N.; Kovalevskaya, Yu.A.; Gromilov, S.A.; Kirichenko, V.N.; Zemskova, S.M.; Vasilieva, I.G.; Ayupov, B.M.; Shwarz, N.L. (1995). Optical and structural proper tees of ZnS and ZnS: Mn films prepared by CVD method citations. *Mater. Res. Bull.*, **30**(11), 1393-1400.

Bessergenev, V.G.; Bessergenev, A.V.; Ivanova, E.N.; Kovalevskaya, Yu. A. (1998). Study of In_2S_3 thin films by diffraction of synchrotron Radiation. *J. Solid State Chem.* **137**, 6-11.

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 Chim Acta.*, **363**, 1195-1203.

Coote, M.L.; Radom, L. (2004). Substituent effects in xanthate-mediated polymerization of vinyl acetate: ab initio evidence for an alternative fragmentation pathway. *Macromolecules*, **37**, 590-596.

Coucouvanis, D. (1970). The chemistry of the dithioacid and 1,1– dithiolate complexes. *Prog. Inorg. Chem.*, **11**, 233.

Coucouvanis, D.; Fackler, J.P. (1967). Square-planar sulfur complexes. VI. reactions of bases with xanthate, dithiocarbamates, and dithiolates of nickel(II). *Inorg. Chem.*, **6**, 2047.

Geary, W.J. (1971). The use of conductivity measurements in organic solvents for characterization of coordination compounds. *Coord. Chem. Rev.***7**,8.

Haiduc, I. (2007). "Handbook of Chalcogen Chemistry. In: Devillanova F (ed) New Perspectives in Sulfur, Selenium, and Tellurium". RSC Publishing, London, 593 p.

Haiduc, I. (2003). "1,1-Dithiolato Ligands Comprehensive Coordination Chemistry II. from Biology to Nanotechnology". Elsevier , Vol. 1, pp. 349-376.

Hill, J.O.; Murray, J.P.; Patil, K.C. (1994). The thermochemistry of the metal dithiocarbamate and xanthate complexes . *Rev. Inorg. Chem.*, **14**, 363 - 387.

Lever, A.B.P. (1984). "Inorganic Electronic Spectroscopy". 2nd ed., Elsevier, Amsterdam, 357p.

Martel, A.E. (1971). "Coordination Chemistry". Vannostrans Reinhold, New York., 1p.

Nicholls, D. (1973). "The Chemistry of Iron, Cobalt and Nickel". Pergamon press, Oxford,1st ed.,1037, 1087, 1088,1090, 1091,1093, 1151,1154.

Pradhan, N.; Katz, B.; Efrima, S. (2003). Synthesis of high - quality metal sulfide nanoparticles from alkyl xanthate single precursors in alkylamine solvents. *J. Phys. Chem. B.*, **107**(50), 13843–13854

Raya, I., Baba, I.; Yamin, B.M. (2006). New mixed ligand complexes of samarium(III) with dithiocarbamates and 1,10-phenanthroline. *Malaysian. J. Analy. Sci.*, **10**(1), 93-98.

Serrano, J.L.; Garcı´a, L.; Pe´rez, J.; Pe´rez, E.; Sa´nchez, G.; Garcı´a, J.; Lo´pez, G.; Garcı´a, G.; Molins, E. (2003). New dithiocarbamate and xanthate complexes of nickel(II) with iminophosphines. *Inorg. Chim. Acta.*, **355**, 33-40.

Siddiqi, K.S.; Nishat, N. (2000). Synthesis and characterization of succinimide and phthalimide dithiocarbamate and their complexes with some transition metal ions. *Synth. Reac. 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.

Tiekink, E.R.T.; Haiduc, I. (2005). Stereochemical aspects of metal xanthate complexes: molecular structures and supramolecular self-assembly. *Prog. Inorg. Chem.*, **54**, 127-319.

Vogle, A.I. (2008). "Text Book of Practical Organic Chemistry". 5th edn., Pearson Education, 793p.

Wan, D.C.; Sato, K.; Kamigaito, M.; Okamoto, Y. (2005). Xanthate-mediated radical polymerization of N-vinylpyrrolidone in fluoroalcohols for simultaneous control of molecular weight and tacticity. *Macromolecule.*, **38**, 10397-10405.