

INTRODUCTION

Coordinated thiolato sulfur atoms tend to make bridge with variety of metal ions and considerable attention has been focused on sulfur bridged polynuclear structures derived from $[M(\text{thiolato-S})_2(\text{amin-N})_2]$, $\{M=\text{Ni(II) or Pd(II)}\}$ mononuclear complexes (Deeming et al., 1988; Adhikary et al., 1997; Kersting et al., 1999; Zhang et al., 2003). It has been recognized that $[M(\text{NH}_2\text{CH}_2\text{S})_2]$ compounds react readily with divalent metal ions such as Ni(II), Cd(II) and Pd(II) to give S-bridged polynuclear complexes which was studied by (Kono et al., 1994).

The structural chemistry of metal complex and organometallic dithiophosphates, dithiophosphinates and dithiophosphonates, Oxidation of cobalt (II) di(2ethylhexyl) dithiophosphate by the corresponding disulfane, using the isomolar series method was studied by has been reviewed by (Haiduc and Goh, 2002).

Crystalline nickel(II) dithiophosphate complexes $[\text{Ni}\{\text{S}_2\text{P}(\text{OR})_2\}_2]$ are formed in the reaction of $[\text{Ni}\{\text{P}(\text{OPh})_3\}_4]$ with $(\text{RO})_2\text{P}(\text{S})\text{-SSP}(\text{S})(\text{OR})_2$ ($\text{R}=\text{Pr, Ph}$) in refluxing chloroform (Haiduc and Goh, 2002). Bis (dialkyldithio-phosphato) platinum (II) complexes $[\text{Pt}\{\text{S}_2\text{P}(\text{OR})_2\}_2]$ with $\text{C}_1\text{-C}_{18}$ alkyl chain ($\text{R}=\text{Me, Et, Pr, Bu, dodecyl and octadecyl}$) were prepared by oxidative addition of bis (dialkylthiophosphoryl) disulfanes to tris (Styrene) platinum(0) was reported by (Gianini et al., 2000).

The crystal structures of $[\text{Ni}(12)\text{ane N}_3\text{-mc}_1]\{\text{S}_2\text{P}(\text{OEt})_2\}[\text{PF}_6]$ and $[\text{Ni}(12)\text{ane N}_3\text{-mc}_1]\{\text{S}_2\text{P}(\text{p-CH}_3\text{OPh})(\text{O}^i\text{pr})\}[\text{PF}_6]$, where $((12)\text{aneN}_3\text{-mc}_1) = 2,4,4\text{-trimethyl-1,5,9 triazacyclododec-1-ene}$ were determined using X-ray single crystal by (Santana et al., 2002), they showed that the dithiophosphate or dithiophosphonate are bonded to nickel atom as chelating S,S ligand and the nickel atoms are in distorted square pyramidal geometry.

The copper *o,o'*-dialkyldithiophosphate complexes $[\text{Cu}_4\{\text{S}_2\text{P}(\text{OR})_2\}_4]$ ($\text{R}=\text{Bu}$) were claimed by a patent as a product formed by treating $(\text{RO})_2\text{P}(\text{S})\text{SSP}(\text{S})(\text{OR})_2$ with an excess of activated copper by (Bridger, 1986). The complex salt $[\text{Cu}(\text{en})_2][(\text{EtO})_2\text{P}(\text{S})\text{S}]_2$, $\text{en}=\text{ethylene diamine}$ were prepared and characterized by X-ray diffraction method by single crystal by (Fun et al., 2002), the Cu atom lies on a center of inversion and is coordinated in a slightly square planer geometry by four N atoms from two ethylenediamine, the $(\text{EtO})_2\text{P}(\text{S})\text{S}$ act as counter ions.

In view of these interesting results and as continuation of our comprehensive studies of transition and non transition metal complexes with sulfur containing ligands (Buttrus and Mohand, 2002; Buttrus et al., 2005; Buttrus and Alomeri, 2005) we have prepared tri and pentanuclear complexes starting with the tin compound $[\text{Sn}\{\text{S}_2\text{P}(\text{EtO})_2\}]$ which was prepared by oxidative addition of bis (thiophosphoryl) disulfide.

EXPERIMENTAL

General:

IR spectra were recorded on Perkin-Elmer 580B IR spectrophotometer in the $(4000\text{-}200\text{ cm}^{-1})$ range using Nujol mulls or CsI discs. The metal content was estimated spectrophotometrically using Shimadzu AA670. Conductivity measurements were made on 10^{-3} M solution of the complexes in dimethylsulfoxide (DMSO) solvent at ambient temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV/Vis spectrophotometer UV-160 for 10^{-3} M solutions of the

complexes in DMSO using 1 cm quartz cell. The magnetic measurements were carried out at 25°C on the solid by Faradays method using Bruker BM6 instrument.

Materials:

The most common method used for the preparation of bis-(thiophosphoryl) disulfanes is based upon the oxidation of alkali metal salts of dithiophosphoric acids with iodine in alcoholic medium according to a literature method (Haiduc and Goh, 2002).



1-Preparation of [Sn{S₂P(OEt)₂}₄]:

A mixture of finely cut tin metal (1.19g, 0.001mol) and bis (thiophosphoryl) disulfide (7.39g, 0.02 mol) in toluene (40 cm³) was refluxed for 12h. The unreacted tin (0.01g) was removed by filtration, and the resultant solution was reduced to ca 1/3 of its volume. The resulting solid was then collected by filtration, washed with petroleum ether (b.p 60-80%) and dried in vacuum.

2-Preparation of [Sn₃{S₂P(OEt)₂}₄Cl₄]:

The compound [Sn{S₂P(OEt)₂}₄] (0.86g, 0.001mol) was dissolved in ethanol (15 cm³) and a solution of SnCl₂.2H₂O (0.45g, 0.002mol) in distil water (10 cm³) was added.

The reaction mixture was stirred with reflux for 2h. The solution was then evaporated to (10 cm³) giving a colored precipitate, which was filtered, washed with ethanol then diethyl ether and dried in vacuum.

3-Preparation of [Sn{S₂P(OEt)₂}₄(MCl₂)_n] complexes M = (Co, Ni or Cu), n=2 or 4:

A clear solution [Sn{S₂P(OEt)₂}₄] (1mmol) methanol (10 cm³) was added to a solution of MCl₂.6H₂O (M=Co or Ni) or CuCl₂.4H₂O (2mmol or 4 mmol) in distil water (10 cm³). The mixture was stirred under reflux for ca.2h. The solid thus obtained was filtered off, washed with warm water, methanol then diethyl ether and dried under vacuum for several hours.

4- Preparation of [Sn₃{S₂P(OEt)₂}₄Cl₄(MCl₂)₂] complexes (M=Co, Ni or Cu):

The complexes were prepared by using similar procedure except using [Sn₃{S₂P(OEt)₂}₄Cl₄] (1mmol) in acetone (10 cm³).

RESULTS AND DISCUSSION

The reaction of bis(thiophosphoryl) disulfide with tin metal in refluxing toluene in 1:2 metal to ligand molar ratio afford the compound tetrakis-(o,o'-diethyldithio phosphate) tin(IV), [Sn{S₂P(EtO)₂}₄], through oxidative addition reaction:



The reduction of bis(thiophosphoryl) disulfide through the scission of -S-S- bond results in incorporation of the dithiophosphate fragments into tin compound sphere, while the tin metal oxidized from Sn⁰ → Sn⁺⁴, which is clearly similar to known reactions involving the conversion In⁰ → In⁺³ or Sn⁺² → Sn⁺⁴ (Buttrus, 1998).

The multinuclear complexes were prepared by adding aqueous solution of metal (II) chloride to alcoholic solution of [Sn{S₂P(OEt)₂}₄] in (1:2) or (1:4) molar ratio gave tri and pentanuclear complexes of the general formula [Sn₃{S₂P(OEt)₂}₄Cl₄], [Sn{S₂P

(OEt)₂}₄(MCl₂)_n] and [Sn₃{S₂P(OEt)₂}₄Cl₄(MCl₂)₂] where n=2 or 4 as in the following equations:



The nucleophilicity of the thiolate sulfur atom in the tin compound is responsible for the formation of these new complexes.

The physical properties of the complexes are listed in (Table 1). The complexes are quite stable in dry air, they are insoluble in most organic solvent, but soluble in dimethyl-sulfoxide (DMSO).

The most important IR assignments of tin compound are listed in Table(2). The characteristic IR bands that are sensitive to molecular structure are the stretching modes of P=S, P-S, P-O-C and Sn-S bands. In particular the $\nu(\text{P}=\text{S})$ band in the region 725 cm⁻¹ and the $\nu(\text{P}-\text{S})$ band in the region 545 cm⁻¹ for symm. and 635 cm⁻¹ for asymmetric vibration, while the $\nu(\text{P}-\text{O}-\text{C})$ band in the region 1150 cm⁻¹, these bands are known to depend on the nature of coordination of dithiophosphate to metal ion (Buttrus et al., 2002). The dithiophosphate ligand in [Sn{S₂P(OEt)₂}₄] compound act as monodentate through sulfur atoms of $\nu(\text{P}-\text{S})$ only (Table 2). Further support for this coordination was provided by the appearance of the band about 355 cm⁻¹ which is assigned to $\nu(\text{Sn}-\text{S})$ (Molloy et al., 1995).

The multinuclear complexes display bands characteristic of coordinated dithiophosphate ligand, absorption in the range 681-710 cm⁻¹ region due to $\nu(\text{P}=\text{S})$ mode indicate bidentate bridging nature of dithiophosphate (Gray et al., 2003). The shift to lower frequency in the $\nu(\text{P}=\text{S})$ band of dithiophosphate ligand in trinuclear complexes indicating the involvement of sulfur atom of the ligand in the coordination with metal ions, while in pentanuclear complexes the bands $\nu(\text{P}-\text{S})$ was found to be responsible for the formation of these complexes (Table 2).

Further support for the formation of new complexes is provided by the appearance of new band with in the 363-390 or 400 cm⁻¹ range characteristic of the bidentate

tetrathio tin complexes  and are tentatively attributed to $\nu(\text{M}-\text{S})$ M=Co, Ni or Cu

(AL-Hayaly et al., 2005). Further more the IR spectra of the multinuclear complexes showed another band with in the 239-315 cm⁻¹ range which may be assigned to $\nu(\text{M}-\text{Cl})$ (Buttrus and Mohammad, 2002).

The electronic spectrum of tin compounds and the multinuclear complexes were recorded as 10⁻³ M solution in DMSO and the results are listed in Table (2). The bands observed in the range 30120-40160 cm⁻¹ are due to $\pi-\pi^*$ or $n-\pi^*$ within the dithiophosphate group, while the new additional band was observed in the range 26737-28011 cm⁻¹, this can be attributed to charge transfer from filled ligand orbital to the vacant tin anti bonding orbitals.

The electronic spectra of Co(II) complexes (3 and 9), show a bands in the visible region 13717-16366 cm⁻¹ are generally considered to correspond to the transition from singlet level of F atate (⁴A₂) to the P state (⁴T₁) which is consistent with tetrahedral geometry (Bayoumi et al., 2001), as well as a charge transfer bands at 22727-28910 cm⁻¹. The Co(II) complex (6) show bands at 13679 and 16129 cm⁻¹ which may be assigned to ²A_{1g} → ²E_g' transition in square planar geometry.

The electronic spectra of Ni (II) complex (4) show the presence of three bands in the region 10917-26109 cm⁻¹ which are assigned to ${}^3A_{2g} \longrightarrow {}^3T_{2g} (F)(\nu_1)$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g} (p)(\nu_3)$ transitions respectively. This shows that the structure is in an octahedral geometry. While the Ni(II) complexes (7 and 10), the observed bands at 12319-17182 cm⁻¹ are due to the transition from ${}^3T_1(F) \longrightarrow {}^3T_1(p)$ in tetrahedral geometry (Mustafa et al., 2004).

The electronic spectra of Cu (II) complexes (5 and 11) showed bands at 12196 and 17152 cm⁻¹ which correspond to the transition ${}^2T_{2g} \longrightarrow {}^2E_g$ and other transition at 27548 and 28102 cm⁻¹ correspond to the charge transfer, this shows that the Cu(II) complexes have tetrahedral geometry, while Cu(II) complexes (8) show a band at 11230 cm⁻¹ which may be assigned to ${}^2B_{1g} \longrightarrow {}^2A_{1g}$ transition and charge transfer transition at 26131 and 29301 cm⁻¹, which indicate that Cu(II) has distorted octahedral geometry. (Chandra and Gupta, 2001).

The results of magnetic measurements are listed in Table (1). The Co(II) complexes (3, 9 and 6), their magnetic moments were found to be (4, 25, 4.26 and 2.12 B.M) respectively, these values correspond to a tetrahedral and low spin square planar geometry for the complex (6) (Amin et al., 2004). The magnetic moment of Ni(II) complexes (4, 7 and 10), are 3.16, 4.01 and 3.88 B.M suggest octahedral for complex (4) and tetrahedral geometry for the other two complexes. The Cu(II) complexes (5, 11 and 8) have magnetic moments of 2.12, 1.74 and 1.77 B.M correspond to tetrahedral and octahedral geometry.

From the above discussion, the following structures (Fig 1), can be suggested for the compounds and the complexes.

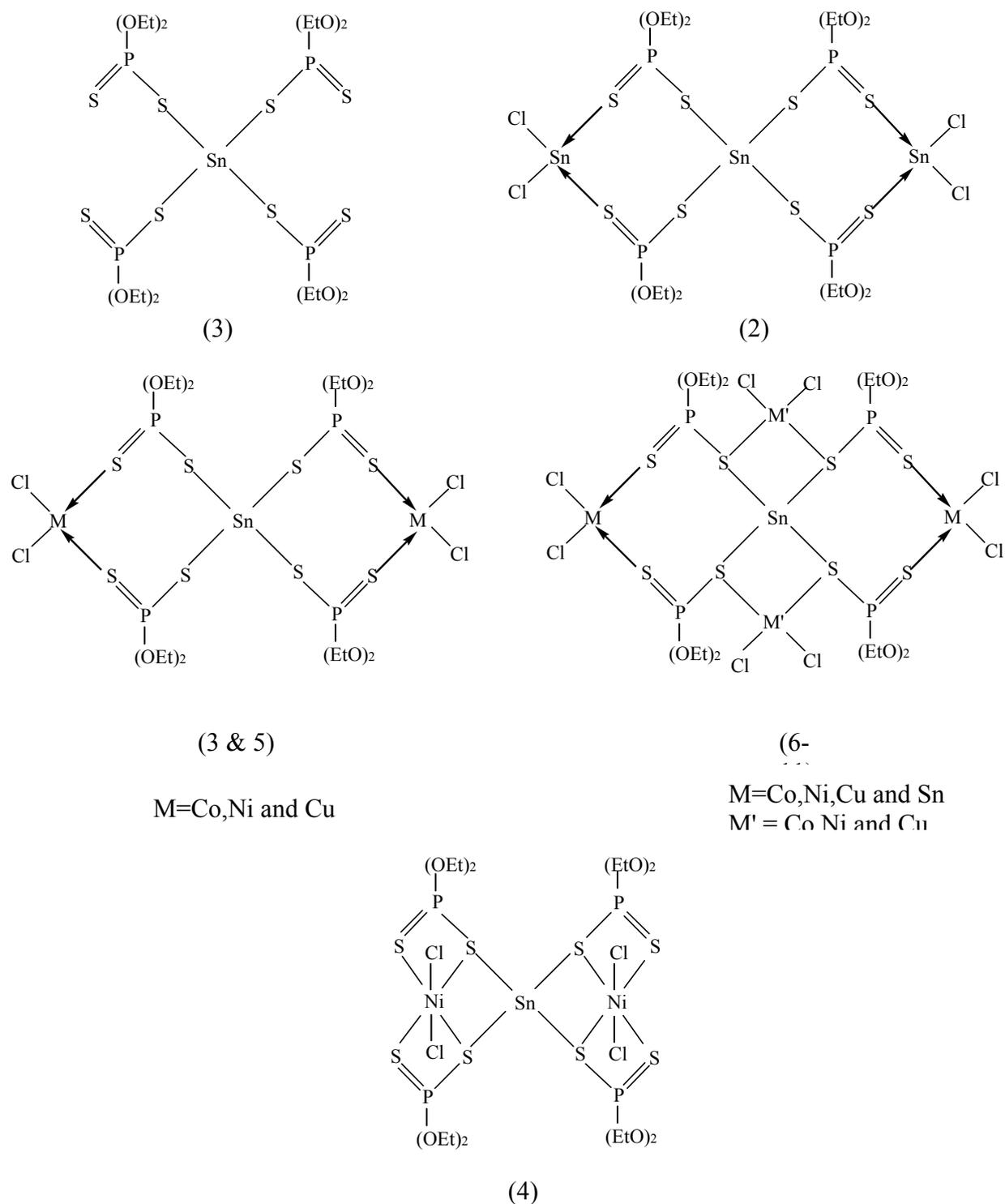


Fig. 1 : Suggested structure for tin compound and complexes.

Table 1: Physical properties of the tin compounds and their complexes.

No.	complex	Colour	Yield %	Decomposition temperature (C) ^o	Analysis (found) Calc.%		Λ Ohm ⁻¹ . cm ² .mol ⁻¹
					Sn	M	
1	[Sn{S ₂ P(OEt) ₂ } ₄]	Greenish yellow	72	220-222	(13.42) 13.80	---	24
2	[Sn ₃ {S ₂ P(OEt) ₂ } ₄ Cl ₄]	Yellow	75	256-258	(28.98) 28.8	---	3
3	[Co ₂ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₄]	Dark brown	75	232-234	(10.63) 10.62	(10.24) 10.54	19.9
4	[Ni ₂ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₄]	Pale green	83	198-200	(10.23) 10.62	(10.69) 10.39	23
5	[Cu ₂ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₄]	Pale blue	72	242-244	(10.80) 10.50	(10.8) 11.25	17
6	[Co ₄ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₈]	Pink	67	373-376	(8.95) 8.62	(17.63) 18.03	8
7	[Ni ₄ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₈]	Black	80	204-207	(8.35) 8.60	(17.17) 17.02	20
8	[Cu ₄ Sn{S ₂ P(OEt) ₂ } ₄ Cl ₈]	Dark orange	78	199-203	(8.71) 8.50	(17.87) 18.15	7
9	[Co ₂ Sn ₃ {S ₂ P(OEt) ₂ } ₄ Cl ₈]	Dark gray	66	250-252	(23.34) 23.74		13
10	[Ni ₂ Sn ₃ {S ₂ P(OEt) ₂ } ₄ Cl ₈]	Dark green	67	138-140	(23.80) 23.80		21
11	[Cu ₂ Sn ₃ {S ₂ P(OEt) ₂ } ₄ Cl ₈]	Dark green	53	158-160	(23.83) 23.58		9

Table 2: Electronic and IR spectral data of the complexes.

No.	U.V.-Vis bands λ_{\max} (cm ⁻¹)	Selected IR bands (cm ⁻¹)					
		$\nu(\text{P}=\text{S})$	$\nu(\text{P}-\text{S})$		$\nu(\text{Sn}-\text{S})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
			Sym.	Asym.			
1	26737,29940,37878	725 _w	545 _m	635 _s	355 _s	---	---
2	28011,30120,401160	690 _m	519 _{vw}	625 _{vw}	360 _m	---	293 _m
3	13717,16366,28910	700 _s	530 _m	627 _w	342 _m	363 _w	315 _m
4	10917,16474,26109	693 _s	537 _w	644 _m	346 _m	357 _m	255 _w
5	17152,27548	702 _m	543 _m	625 _s	338 _m	370 _m	245 _s
6	13679,15455,16129	689 _s	529 _m	631 _{vw}	322 _w	410 _w	249 _s
7	15527,17182,27855	681 _w	538 _m	620 _w	339 _s	400 _m	303 _m
8	11230,26131,29301	698 _w	536 _{vw}	625 _s	341 _m	400 _m	239 _w
9	14224,16260,28312	702 _s	540 _m	650 _s	334 _w	383 _w	244 _w
10	12319,15873	684 _w	531 _m	645 _m	351 _s	372 _m	295 _s
11	12196,28102	700 _m	538 _m	649 _{vw}	352 _m	380 _m	253 _m

REFERENCES

- Adhikary, B., Liu, S. and Lucas, R.C., 1997. Complexes of cobalt, nickel, palladium and silver with N₂S_X (X=3 or 4) ligands involving aromatic nitrogen and thioether donors, *Inorg. Chim. Acta*, 261, pp.15-21.
- AL-Hayaly, L.J., Buttrus, N.H., Tarq, F. and Al-Allaf, T.A.K., 2005. Trinuclear platinum group metals complexes with *o*-aminophenyl thiolatotin (IV), *Jord.J. Appl. Sci.*, 7(1), pp.67-70.
- Amin, O.H., AL-Hayaly, L.J., AL-Jibori, S.A. and AL-Allaf, T.A.K., 2004. Hetero-bimetallic complexes of Palladium (II) and Platinum (II) bridged by ligand 5-phyney-1,3,4-oxadiazole-2-thione, *Polyhedron*, 23, pp.2013-2020.
- Bayoumi, H.A., Shoukry, E.M. and Mostafa, M.M., 2001. N-2-[4,6-dimethylpyridyle]-N'-phenylthiourea (HDMPyPt) transition metal complexes, *Synth.React. Inorg. Met. Org. Chem.*, 31(4), pp.579-598.
- Bridger, R.F., US Patent, US 4,582,920, 1986. *Chem. Abstr.*, 105, 1986, 115214.
- Buttrus, N.H., 1998. Coordination compounds of bismuth(III) derivatives of di(*o*-aminophenyl) disulfide and di(*p*-tolyl)disulfide, *Synth. React. Inorg. Met-Org. Chem.*, 28(10), pp.1643-1652.
- Buttrus, N.H. and AL-Omari, A.F., 2005. Synthesis and characterization of trinuclear complexes and adducts through oxidative addition reaction of thiuramdisulfide, *Ref.J. Sci.*, 16(3), pp.138-145.
- Buttrus, N.H. and Mohamed, E.H., 2002. Synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with aryl thioether derivatives. *J. Educ. Science* 14(2), pp9-15.
- Buttrus, N.H., Dawood, S.K. and Mubarak, L.A., 2005. Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with mixed ligands thioether and ethylenediamine ligand, *Raf. Jor. Sci.* Accepted.
- Buttrus, N.H., Monsour, S.S. and Abudall, S., 2002. Synthesis and characterization of dinuclear Zn(II), Cd(II) and Hg(II) complexes with 1,1,2,2-tetrakis-(*o,o'*-dialkyldithiophosphate) ethylene, *J. Edu. Sci.*, 14(4), pp.12-18.
- Chandra, S. and Gupta, K., 2001. Template Synthesis and characterization of Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes with polydentate 18-membered macrocyclic ligand, *Synth.React. Inorg. Met-Org. Chem.*, 31(4), pp.661-672.
- Deiming, A.J. and Meah, M.N., 1988. Di-and-tri-nuclear complexes of palladium (II) containing doubly- and triply-bridged pyridine-2-thionato ligands: Crystal structure of [Pd₃(C₆H₄-CH₂NMe₂)₃(pys)₂][BF₄], *J. Chem. Soc. Dalton Trans.*, pp.2193-2199.
- Fun, H.K., Hao, Q.L., Wu, J., Yang, X.J., Lu, L.D., Wang, X., Chantrapomma, S., Razak, I.A. and Usman, A., 2002. Bis(ethylenediamine)copper (II) bis(*o,o'*-diethyl-dithiophosphate), *Acta Cryst. C* 58, m87-m88.
- Gianini, M., Caseri, W.R., Gramlich, V. and Sater, U.W., 2000. Synthesis and Characterization of liquid platinum compounds. *Inorg. Chim. Acta*, 299, 199 p.
- Gray, I.P., Milton, H.L., Slawin, A.M.Z. and Woollins, J.D., 2003. Synthesis and structure of [Fe(RO)PS₂]⁻ complexes, *Dalton Trans*, 17, pp.3450-3457.
- Haiduc, I. and Goh, L.Y., 2002. Reaction of bis(thiophosphoryl)disulfanes and bis(thiophenyl)disulfanes with metal species: An alternative convenient route to metal complex and organometallic dithiophosphates and dithiophosphonates, *Coord. Chem. Rev.*, 224, pp.151-170.

- Kersting, B., Steinfeld, G., Fritz, T. and Hausmann, J., 1999. Novel synthesis of macrocyclic amin-thiophenolate ligands x-ray crystal structure of a Ni₄ complex of a N₈S₄ ligand Eur.J.Inorg.Chem., pp.2167-2172.
- Kono, T., Yonenobu, K., Hidaka, J. and Okamoto, K., 1994. A new class of S-bridged hexanuclear complexes with amino thiolate ligand. Formation and structural characterization of [Pd₂{Ni(aer)₂}_x{Pd(aet)₂}_{4-x}] Br,X=0-4,aet=2 aminoethanethiolate, Inorg.Chem., 33, pp.861-864.
- Molloy, K.C., Mahan, M.F., Haiduc, I. and Silvestru, C., 1995. Solid state supramolecular structure of (tetraphenyldithioimido diphosphinato) trimethyltin (IV). Benzen. [Me₂Sn(SPPPh₂)₂N.C₆H₆]. Polyhedron, 14 (9), pp.1169-1174.
- Mustafa, I.A. and AL-Assady, H., 2004. Di and tetranuclear shiff-base complexes derived from 3,3-diamio-benzidine and acetylacetone, National J.Chem.,13, pp.65-72.
- Santana, M.D., Garcia, G.N., Ararro, C.M., Lozano, A.A., Perez, J., Garcia, L. and Lopez, G., 2002. Dithiophosphate and dithiophosphonate complexes of pentanickel (II) containing the macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, polyhedron, 19, pp.1935-1942.
- Zhang, S., Wang, S., Wen, Y. and Jiao, K., 2003. Synthesis and crystal structure of hexakis(imidazole) nickel (II) *o,o'*-diphenyldithio-phosphate [Ni(Im)₆][Ph₂O₂PS₂]₂ Molecules,8, pp.866-872.