

Synthesis and Characterization of New Co(II), Ni(II) and Cu(II) Complexes and Adducts with Tetramethyl thiuram monosulfide

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Abstract

The present investigation involves the synthesis of some new Co(II), Ni(II) and Cu(II) complexes with tetramethyl thiuram monosulfide and their adducts with monodentate donor ligands (triphenyl phosphine) gave 1:2 adducts, while with bidentate donor ligand (1,10-phenanthroline) form 1:1 adducts. The complexes and adducts were characterized by their elemental analysis, IR and UV-Vis spectroscopy, conductivity and magnetic measurements. Conductivity data in DMSO showed that some of the complexes and adducts are non-conductive assigning the formula $[MLCl_2]$ or $[M(L)_2Cl_2]$ and some of them are 1:2 conductive assigning the formula $[M(L)(L')Cl_2]$. Explanations for the structural elucidation of these complexes which have tetrahedral geometry and the adducts which are a signal as octahedral environment.

	Cu(II)	Ni(II)	Co(II)
		-1:10	1:2
			.1:1
		.	
$[MLCl_2]$			
	$[M(L)(L')]Cl_2$	1:2	$[M(L)_2Cl_2]$

Introduction

In recent years, there has been intensive activity involving the synthesis and evaluation of the biological activities of nitrogen and sulfur containing substituted mercapto compounds and their *metal* complexes [1-3].

Thiuram sulfides, $R_2NC(S)SnC(S)NR_2$, ($n=2$) (R_4tds) called thiuram disulfides are known on account of their biological activity, which leads to applications as fungicides, rubber vulcanization accelerators agent of alcoholism therapy [4-5], as well as their ability to stabilize high oxidation states in transition metals [6]. The monosulfides ($n=1$) R_4tms , perhaps because they lack the wide breadth of applications known for the disulfides in agriculture and experimental medicine, have been much less extensively studied, and where such studies deal with the subject of interaction of monosulfides with *metal* species, the field remains virtually unexplored [7].

Typical reactions of thiuram mono and disulfides with metal species fall under three distinct categories (a) adduct formation (b) ligand reduction with concomitant degradation to dithiocarbamate and / or thiocarboximide ligand and (c) thiuram oxidation.

The reactions of $CoCl_2$ and $NiCl_2$ with tetramethyl thiuram monosulfide in boiling ethanol produces $[Co(dtc)_3]$ and $[Ni(dtc)_2]$ through a session of C-S-C and the *metal* ions were not oxidized the observation was studied by Ojima *etal* [8].

The crystal structure of $\{[(C_5H_{10})_2tmsCuI]_2\}$, reveals a centrosymmetric dimer in the solid state [9]. The copper atoms are approximately tetrahedral by one iodine two sulfur atom from one

tetramethyl thiuram monosulfide and by one bridging sulfur atom from another monosulfide units.

Victuriano *etal* [10-11] showed that the reaction of acetonitrile solutions of cuprous iodide and Et_4tms leads to a crystalline phase of composition $[(CuI)_5(Et_4tms)_2]$. As an extension to our comprehensive studies on platinum group *metal* complexes and some complexes of Co(II), Ni(II) and Cu(II) with sulphur containing ligands [13-15], we are presenting here the reaction of tetramethyl thiuram monosulfide with salts of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ in 1:1 and 2:1 ligand to *metal* molar ratio and their adducts with mono and bidentate donor ligands.

Experimental

All chemical used were of high purity. Analyses of the complexes were carried out using a CHN elemental analyzer model 1100 (Carlo Erba). The *metal* content was estimated spectrophotometrically using Shimadzu Atomic Absorption 670 spectrophotometer. Melting point and decomposition temperatures were determined on a Buchi 510 melling point apparatus and were uncorrected. Infrared spectra were recorded using Perkin-Elmer 580B spectrophotometer in the range $4000-200cm^{-1}$ as CsI pellets. The electronic spectra were recorded on Shimadzu UV.Vis spectrophotometer UV-160 for $10^{-3}M$ solution of the complexes in DMSO at $25^\circ C$. Conductivity measurements were carried out on $10^{-3}M$ solution of the complexes in DMSO at ambient temperature. Magnetic measurements were carried out on the solids by the Faradays method using Bruker BM6 instrument.

Preparation of compounds

Starting materials

The compound $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, 1,10-

phenanthroline, triphenylphosphine and tetramethyl thiuram monosulfide were commercial products and used without further purification.

Preparation of complexes

The *metal* salts (1mmol) was dissolved in ethanol (15cm³) and the resulting solution was filtered through celite to remove any dissolved and solid. The filtrate was added to the solution of the ligand (1 or 2mmol) in ethanol (10 cm³) and the mixture was refluxed for ca 2h. The solution was reduced in volume to ca (5 cm³) and the solid thus formed was filtered off washed several times with ethanol and with diethylether then dried under vacuum for several hours.

Preparation of the adducts [M(L)₂(L⁻)]Cl₂ and [M(L)₂(L⁻)]Cl₂ L⁻=Phen or PPh₃

A mixture of the complex [M(L)Cl₂] or [M(L)₂Cl₂] (0.001 mol) in dimethyl formamide (15cm³) and 1,10-phenanthroline monohydrate (0.20g, 1mmol) in methanol (5 cm³) were stirred at room temperature for 8h. The solution became dark colours, and the mixture was then heated on water bath. The solid was then collected, washed with methanol and ether then dried in vacuum. Similar procedure used for the preparation of PPh₃ adducts.

Results and Discussion

The physical properties of the solid complexes of cobalt (II), nickel(II) and copper (II) with tetramethyl thiuram monosulfide and their adducts with PPh₃ and Phen are presented in Table 1. The complexes are quite stable in dry air and are very slowly affected by moisture, they are fair stable to heat and have been found to melt (decompose) at 142-212°C. They are insoluble in most organic solvent except for DMF or DMSO.

The complexes were prepared by the reaction of *metal* chloride with

tetramethyl thiuram monosulfide, however, was found not to decompose to N,N-dimethyl dithiocarbamate anion as found by Ojima *etal* [18].

The most important IR assignment of the ligand as well as their bonding sites (Table 2) have been determined by a careful comparison of the spectra of the ligand with those of their complexes. The IR spectra of the ligand showed medium band at 680cm⁻¹ assigned to ν(C-S-C) vibration and this remained unchanged in the spectra of all complexes. Another band appearing at 1025cm⁻¹ in the free ligand which were assigned to tetramethyl thiuram monosulfide(C=S) vibration, was found to decrease by ca 10-27cm⁻¹ upon complexation. This indicate that this group had been involved in the coordination with *metal* ion through sulfur atoms [16]. Moreover, the IR spectra of the complexes showed new band at 370-360cm⁻¹, which is tentatively assigned to ν(M-S). Further The IR spectra of the complexes showed another new band in the region 290-340cm⁻¹ which may well be due to ν(M-Cl).

Furthermore, The IR spectra of the adducts show a medium band around 980-1015cm⁻¹ which assigned to ν(C=S) indicating that the ligand coordinated through sulfur. Further support for this was obtained from the appearance of a new band at 370-410cm⁻¹, which is assigned to ν(M-S), while the ν(M-N) absorption for phenanthroline adducts are in good agreement with the reported values of [Cl₂MR₂C=CR₂M'Cl₂], M=M'=Ni, Pd or Pt which fall in the 421-470cm⁻¹ range [17]. The ν(M-P) band is observed at 484-515cm⁻¹ indicating the coordination occur from phosphorus atom; similar results was found else where [18].

Magnetic properties

The magnetic moment data of these complexes calculated from the corrected magnetic susceptibilities determined at room temperature are given in Table 1. The μ_{eff} values reported for the complexes are slightly higher than spin-free value of respective metal ions indicating tetrahedral geometry for the complexes (1-3) and (7-12) as well as an octahedral geometry for the complexes (4-6) and (12-18) [19].

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Electronic spectra

The electronic spectra of Co(II) complexes No. (1, 7, 10) recorded in solution, show a number of bands at 11235-13322 cm^{-1} due to ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_1(\text{P})$ (ν_3) transition in tetrahedral symmetry, as those reported for $[\text{CoCl}_4]^{2-}$ and $[\text{CoI}_4]^{2-}$ [20]. While the cobalt (II) complexes No. (4, 13, 16) show three bands at 10492-12991, 13112-15337 and 26201-28831 cm^{-1} which may attributed to transitions ${}^4\text{T}_1(\text{F}) \longrightarrow {}^4\text{T}_1(\text{F})$ (ν_1), ${}^4\text{T}_1(\text{F}) \longrightarrow {}^4\text{A}_2(\text{F})$ (ν_2) and ${}^4\text{T}_1(\text{F}) \longrightarrow {}^4\text{T}_1(\text{P})$ (ν_3) respectively. These values suggest octahedral geometry for these complexes [21].

The electronic spectra of Ni(II) complexes No. (2, 8, 11) the observed bands at 11454-15211 cm^{-1} are due to the transition ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$ (ν_3) in tetrahedral geometry [22]. Where as the Ni(II) complexes No. (5, 14 and 17) show the presence of three d-d transition bands at 10550-12520,

13157-15202, 27027-27472 cm^{-1} regions assignable to the transitions ${}^3\text{A}_2(\text{F}) \longrightarrow {}^3\text{T}_2(\text{F})$ (ν_1), ${}^3\text{A}_2(\text{F}) \longrightarrow {}^3\text{T}_2(\text{F})$ (ν_2) and ${}^3\text{A}_2(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$ (ν_3) respectively. This is consistent with the octahedral geometry of the complexes [21].

In the electronic spectra of the Cu(II) complexes No. (3, 9, 12) the observed band at 12091-12990 and 15211-15748 cm^{-1} which are correspond to the transition ${}^2\text{B}_1\text{g} \longrightarrow {}^2\text{A}_2\text{g}$ and other transitions at 28900-31200 which correspond to charge transfer, which consistent with tetrahedral geometry [23]. Three shoulder bands appear in the Cu(II) complexes No. (6, 15 and 18) at 10550-13220, 15072-15337 and 27027-28610 cm^{-1} which may be assigned to ${}^2\text{B}_1\text{g} \longrightarrow {}^2\text{A}_1\text{g}$, ${}^2\text{B}_1\text{g} \longrightarrow {}^2\text{B}_2\text{g}$ and ${}^2\text{B}_1\text{g} \longrightarrow {}^2\text{E}_\text{g}$ transition respectively. The E_g ground state is highly susceptible to Jahn-teller configuration stability, due to which Cu(II) ion in the complexes shows distorted octahedral geometry [21].

The molar conductivities of 10^{-3}M solution of the complexes (Table 1) indicate that the complexes No. (1-6) are non electrolyte in DMSO while the complexes (7-18) are 1:2 electrolytes [24].

According to the above measurements, we suggest the following structures of the complexes and adducts as in Fig. 1.

Table 1: Physical properties and elemental analysis of the metal complexes and adducts

Seq.	Compounds	Colour	m.p. (°C)	Analysis (Calc)/Found			Cond. Λ $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	μ_{eff}
				C	H	N		
1	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{CoCl}_2]$	Pale brown	145	(21.30) 21.00	(3.57) 3.35	(8.28) 8.01	15.2	3.59
2	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{NiCl}_2]$	Greenish yellow	146	(21.32) 21.11	(3.52) 3.22	(8.16) 8.01	12.5	3.96
3	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{CuCl}_2]$	Brown	171	(21.02) 21.0	(3.57) 3.30	(8.29) 8.13	16.6	2.16
4	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{CoCl}_2]$	Pale green	116	(26.36) 26.08	(4.42) 4.10	(10.25) 10.03	19.3	4.80
5	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{NiCl}_2]$	Green	177	(26.38) 26.018	(4.38) 4.00	(10.18) 10.08	9.5	3.09
6	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{CuCl}_2]$	Pale brown	123	(26.14) 26.01	(4.42) 4.30	(10.25) 10.16	9.9	1.48
7	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Co}(1,10\text{-Phen})\text{Cl}_2]$	Brown	142	(41.7) 41.5	(3.88) 3.61	(10.8) 10.71	72.5	3.98
8	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Ni}(1,10\text{-Phen})\text{Cl}_2]$	Pale brown	175	(41.71) 41.40	(3.85) 3.75	(10.71) 10.52	75.0	4.17
9	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Cu}(1,10\text{-Phen})\text{Cl}_2]$	Pale green	192*	(41.33) (41.10)	(3.89) 3.60	(10.81) 10.66	69.8	2.15
10	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Co}(\text{PPh}_3)_2\text{Cl}_2]$	Green	133	(58.46) 58.22	(4.90) 4.79	(3.24) 3.06	77.2	4.21
11	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$	Brown	210	(58.48) 58.26	(4.88) 4.66	(3.23) 3.10	82.3	3.92
12	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)\text{Cu}(\text{PPh}_3)_2\text{Cl}_2]$	Dark green	150	(58.15) 58.01	(4.90) 4.81	(3.24) 3.08	71.6	1.94
13	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Co}(1,10\text{-Phen})\text{Cl}_2]$	Pale brown	212*	(39.65) 39.33	(4.43) 4.26	(11.56) 11.40	72.3	4.83
14	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Ni}(1,10\text{-Phen})\text{Cl}_2]$	Pale green	162	(39.67) 39.51	(4.41) 4.31	(11.40) 11.22	76.4	3.01
15	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Cu}(1,10\text{-Phen})\text{Cl}_2]$	Green	177	(39.40) 39.11	(4.43) 4.20	(11.57) 11.31	80.2	1.47
16	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Co}(\text{PPh}_3)_2\text{Cl}_2]$	Dark brown	172	(53.82) 53.66	(5.08) 4.93	(5.23) 5.00	76.9	4.65
17	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$	Yellow	181	(53.87) 53.70	(5.06) 4.98	(5.21) 5.11	68.6	3.16
18	$[(\text{C}_6\text{H}_{12}\text{N}_2\text{S}_3)_2\text{Cu}(\text{PPh}_3)_2\text{Cl}_2]$	Yellow	169	(53.62) 53.43	(5.08) 4.88	(5.23) 5.08	77.2	1.80

* Decomposition temperature

Table 2: IR spectra (cm⁻¹) and electronic spectra of the ligand and their metal compounds and adducts

Comp.	$\nu(\text{C}=\text{S})$	$\nu(\text{C}^{\equiv}\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{P})$	$\nu(\text{M}-\text{Cl})$	μ_{max} (UV)
(C ₆ H ₁₂ N ₂ S ₃)	1025(s)	1461(m)	-	-	-	-	
1	1010(S)	1472(w)	360(w)	-	-	262(w)	11235, 13322
2	1021(W)	1483(s)	382(w)	-	-	316(w)	12250
3	1015(w)	1466(m)	351(w)	-	-	295(w)	12993, 15211, 28910, 30395
4	1009(w)	1488(m)	422(w)	-	-	332(m)	10492, 11612, 13112
5	1011(m)	1493(w)	410(m)	-	-	329(m)	12120, 15202, 27470
6	1007(m)	1480(w)	372(w)	-	-	339(m)	11620, 12109, 15072, 28610
7	1010(w)	1476(m)	370(w)	422(w)	-	-	11905, 12235
8	1006(m)	1468(s)	410(w)	470(w)	-	-	11545
9	1007(m)	1488(w)	380(w)	445(m)	-	-	13774, 15748, 31250
10	1020(m)	1495(w)	402(w)	-	475(w)	-	11481, 12091
11	1012(s)	1490(w)	391(m)	-	482(w)	-	12091, 15121
12	1009(m)	1473(w)	366(w)	-	492(m)	-	12091, 15625, 28409 30211
13	1009(w)	1479(w)	372(m)	421(m)	-	-	10615, 11037, 12091, 15337, 28831
14	998(w)	1498(m)	400(w)	429(m)	-	-	12520, 14947, 15479, 27027
15	1013(w)	1498(w)	410(m)	436(s)	-	-	13220, 15112, 27027
16	1001(w)	1501(s)	390(s)	-	489(w)	-	10515, 12091, 14662, 26178, 27027
17	1015(w)	1463(m)	382(m)	-	478(w)	-	10550, 12091, 13157, 27472
18	1014(w)	1485(m)	399(m)	-	485(w)	-	12091, 15337, 28490

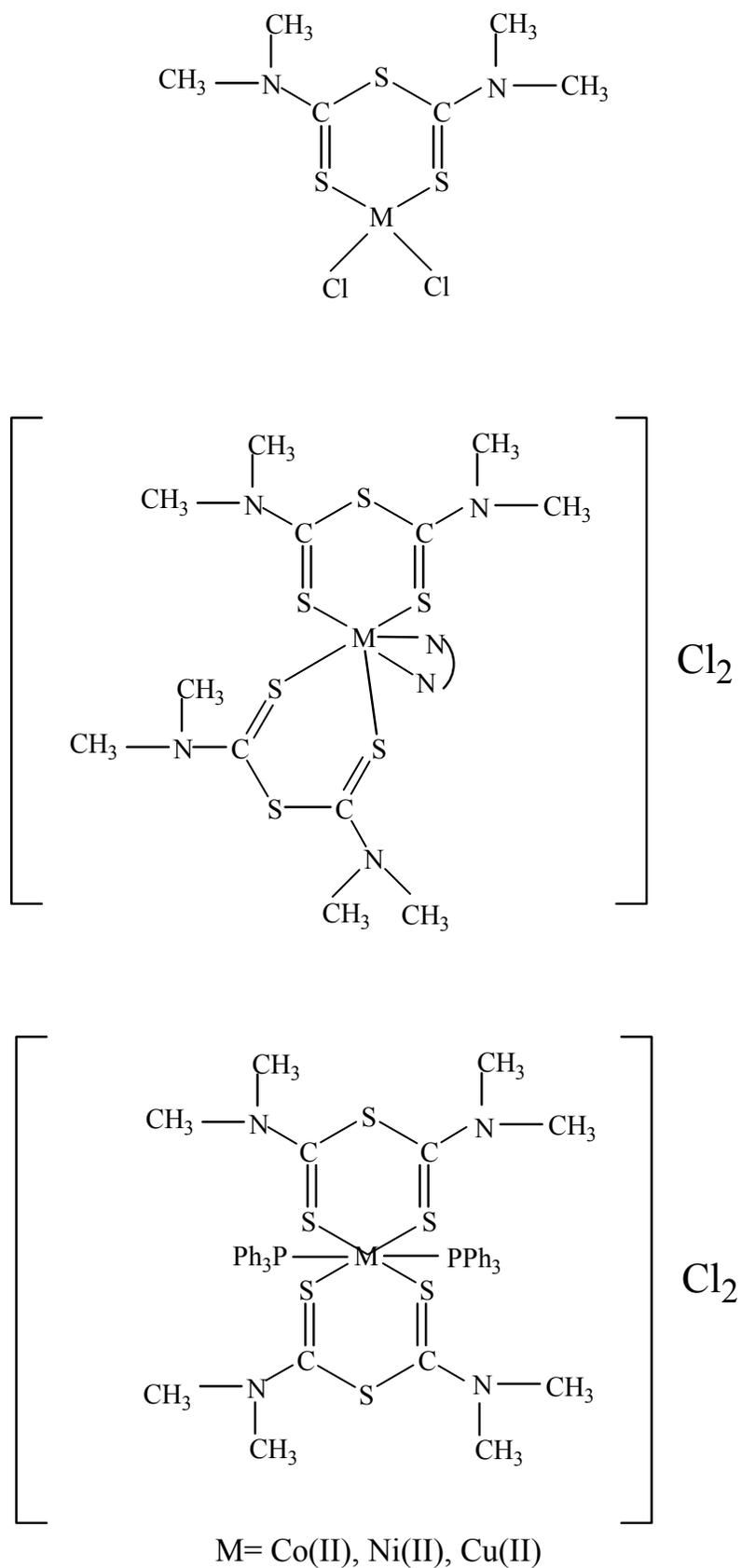


Fig. 1: Suggested structures for complexes and adducts

References

1. R.N. Sharma, A. Kumar, A. Kumari, H.R. Singh and R. Kumar, *Asian J. Chem.*, 2003, **15**, 57.
2. B. Kersting, *Z. Naturforsch.*, 55b, 961 (2000).
3. D. Won and C. Lee, *Tetrahedron Letters*, 2001, **42**, 1969.
4. G.D. Thorn and R. Ludwig "The dithiocarbamates and related compounds" Elsevier, Amsterdam, (1981).
5. T. Kiston, "Education in Chemistry", 43 (1985).
6. J.J. Steggerda, J.A. Cras and J. Willemsse; *Rec. Trav. Chim.* 1981, **100**, 41.
7. L.I. Victoriano, *Coord. Chem. Rev.*, 2000, **196**, 383.
8. I. Ojima, T. Onishi, T. Lwamoto, N. Inamoto and K. Tamarn, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 65.
9. P.J.H.A.M. Vandeleemup, J. Willemsse, J.A. Cras and L. Gran Rec. Trav. *Chim. Pays Bas*, 1979, **98**, 413.
10. L. Victoriano, M.T. Garland and A. Vega, *Inorg. Chem.*, 1997, **36**, 688.
11. L. Victoriano, M.T. Garland and A. Vega, *Inorg. Chem.*, 1998, **37**, 2000.
12. L. Victoriano, M.T. Gialand and A. Vega, *J. Chem. Soc. Dalton trans*, 1127 (1998).
13. T.A. Al-Allaf, N.A. Buttrus and A.R. Yousif, *Asian. J. Chem.*, 2000, **12(2)**, 527 .
14. N.H. Buttrus, A.K. Hussain and T.A.K. Al-Allaf, *Asian J. Chem.*, 2003, **15(2)**, 1612.
15. N.H. Buttrus and E.H. Mohamed, *J. Educ. Sci*, 2002, **14(2)**, 9.
16. A. Delzotto, A. Mezzetti, P. Rigo, M. Bressan, P. Morandic and A. Morvillo, *Inorg. Chim. Acta*, 1989, **158**, 151.
17. L.J. Al-Hayaly, N.H. Buttrus and T.A.K. Al-Allaf, *Asian J. Chem.*, 2002, **14 (3-4)**, 1421.
18. G.K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.
19. V.S. Shrivastara, C.P. Bhasin and G.C. Saxena, *J. Indian Chem. Soc.*, 1986, **LXIII**, 865.
20. H.H. Bayonmi, E.M. Shoukry and M.M. Mostafa, *Synth. React. Inorg. Met-Org. Chem.*, 2001, **31 (4)**, 579.
21. L. Sacconi, "Electronic Structures of transition metal chemistry, 1968.
22. P.P. Bharava, R.Bembi and M. Tyagi, *J. Indian. Chem. Soc.*, 1983, **LX**, 214.
23. M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A.C. Villa and C.Guasitii, *J.Chem.Soc. Dalton Trans.*, 1357 (1990).
24. W. Geary, *J. Coord. Chem. Rev.*, 1971, **81**, 7 .