

Synthesis and Characterization of 1-(4-Chloro Phenyl)-3-(Pyrimidin -2-yl) Thiourea and its Complexes with Cobalt(II), Nickel(II), and Copper(II)

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Abstract

The new 1-(4-chloro phenyl)-3-(pyrimidin -2-yl) thiourea was synthesized from the condensation reaction of 2-amino pyrimidin with p-chlorophenyl isothiocyanate. The complexes were prepared from the reaction of the metal chloride with the ligand. The ligand and its metal complexes were characterized by spectroscopic methods (FTIR, UV-Vis, ¹H-NMR, A.A), magnetic measurements, conductance and melting point. These studies revealed square planar geometries for the Co(II), Ni(II) and Cu(II) complexes.

Keywords: 2- amino pyrimidin; p-chlorophenyl isothiocyanate and thiourea complexes.

Introduction

Thiourea are important sulfur and nitrogen containing compounds that have proved to be useful substances in drug research in recent years [1-6]. Thioureas can be used in the control of plant pathogens like penicillium expansum and fusarium oxysporum[7]. diaryl thioureas exhibited significant antifungal activity against pyricularia a okyzae and drechslera oxyzae.. The biological activity of new thiourea derivatives is scanty. Considering the biological activities of these compound [8]. The copper and cobalt complexes derived from 3-(N- phenyl) thiourea-pentanone-2 as the ligand have been synthesized. their complexation with copper and cobalt metals are crystalline in nature[9]. Thiourea (Tu) derivatives have a long history as a ligand in coordination chemistry and coordinate to a metal via both sulfur and oxygen[10]. These hard and soft donor atoms provide a multitude of bonding possibilities [11]. Hydrogen bonding behaviours of some thioureas have been investigated and it is found that the intermolecular hydrogen bond between the sulphur and a hydrogen atom on N is common[12]. Thiourea derivatives and their transition metal complexes have been known for over a century and are easily synthesized in good yields. Recently metal complexes of thiourea and thiourea analogs have been investigated[13]. Metal complex of thiourea, commonly called semi organics, include the advantages of both organic and inorganic part of the complex. A number of thiourea derivatives has been reported to form complexes with copper and cobalt. These 3-(N- phenyl) thiourea- pentanone-2 have been noticed to possess a remarkable capacity to coordinate with the transition metals giving rise to highly colored chelated structure [14-16].

Experimental

Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Physical measurements

Melting point was obtained on aBuchi SMP-20 capillary melting point apparatus and is uncorrected. Infrared spectra were recorded as (KBr) disc using (8400) (FTIR) shimadzu spectrophotometer in the range (4000-400) cm⁻¹. Uv-vis spectra for the compounds were measured in the region (200-900)nm for (10⁻³ M) solutions in EtOH at (RT) by using (Uv-vis) spectrophotometer type Shimadzu ,100. ¹H-NMR spectrum was recorded in DMSO-d₆ using aBruker 300 MHz with tetra methyl silane(TMS) as an internal standard. Metals were determined using ashimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with EtOH solutions using a pw 9526 digital conductivity meter, and room temperature magnetic moment were measured with a magnetic susceptibility balance (Jonson Matthey Catalytic System Division).

Synthetic procedures

Preparation of 1-(4-chloro phenyl)-3-(pyrimidin -2-yl) thiourea.

A solution of 2-aminopyrimidin (9.5g, 0.1mole) in ethanol (25mL) was added to a stirred solution of p-chlorophenyl isothiocyanate (16.6g, 0.1mole) in ethanol (30mL). The mixture was heated under reflux for 12h. The white precipitate was removed by filtration, washed with hot ethanol and dried at room temperature. Yield= 71%, m.p.=180-183. ¹H-NMR spectrum of the ligand: (s,1H,NH)δ 4.6 ppm, (m,7H,Ar-H) δ (6.4-8.5)ppm, (s, 1H, SH) (13.1)ppm.

Synthesis of the complexes

General method

To a hot solution of the ligand (2mmole) in ethanol(25ml) was added (1mmole) of the metal salt (metal(II) salt are hydrated chloride; $MCl_2 \cdot XH_2O$; where $M = Co(II), Ni(II)$ and $Cu(II)$: $X = 6, 6$ and 2 , respectively). The solution was stirred under reflux around 2h. A colored precipitate formed which was collected by filtration, washed with cold methanol (5ml), and dried at room temperature. Physical data for the complexes are given in Table (1).

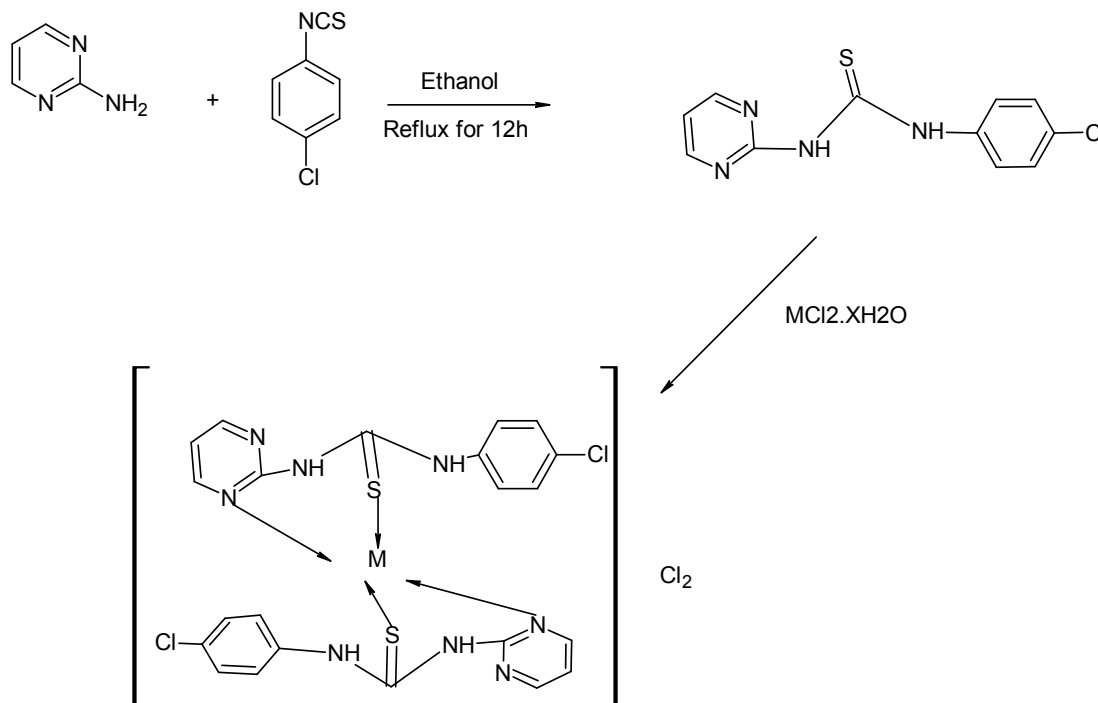
Table (1) Color, yield, elemental analysis and molar conductance values

Compound	color	Yield%	M.P	Found (Calcu.)%				Λ $cm^2 \Omega^{-1} mole^{-1}$
				M	C	H	N	
L	white	70	180-183	-	50.4 (50)	3.64 (3.41)	21.50 (21.21)	-
$[Co(L)_2]Cl_2$	Dark brown	52	270-272	8.31 (8.97)	40.72 (40.18)	2.95 (2.74)	17.98 (17.5)	67.7
$[Ni(L)_2]Cl_2$	Green	72	250-252	9.2 (8.97)	40.45 (40.20)	2.88 (2.74)	17.20 (17.06)	76.5
$[Cu(L)_2]Cl_2$	Dark green	58	282-284	9.23 (9.61)	40.1 (39.91)	2.76 (2.72)	17.02 (16.93)	65.8

Results and discussion

Chemistry:

The condensation reaction of 2-amino pyrimidin and p-chlorophenyl isothiocyanate in mole ratios of 1:1 resulted in the formation of the ligand L in good yield (Scheme(1)). The ligand was characterized by elemental analysis (Table(1)), IR(Table(2)), UV-Vis(Table(3)) spectroscopy and 1H NMR spectrum. The di-electrolyte metal complexes were synthesized by mixing at reflux 2 mmole of the ligand with 1 mmole of appropriate metal chloride. Monomeric complexes of general formula $[M(L)_2]^{+2}$ (where $M = Co^{II}, Ni^{II}, Cu^{II}$) was obtained (Scheme(1)). The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table(1)) agree well with the suggested formulas. Conductivity measurements of the complexes in EtOH solution. Lie in $65-76 cm^2 \Omega^{-1} mole^{-1}$ range, indicating their 2:1 electrolytic behavior (Table (1))[17].



Scheme(1) synthesis diagram of the ligand and complexes

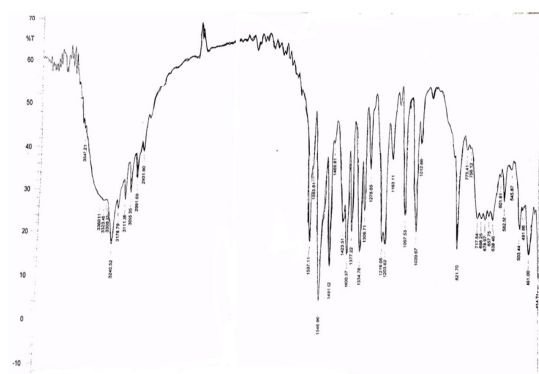
IR spectra

The important infrared bands for the ligand and its metal complexes together with their assignments are listed in (Table(2)). The IR spectra of the ligand shows bands in the region ($3524-3396 cm^{-1}$), which is assigned to the $\nu(N-H)$ vibration. The bands due to $\nu(C=N)$ and $\nu(C=S)$ vibrations are located in the regions 1552 and 1330

cm^{-1} , respectively. In the spectra of complexes, the $\nu(\text{C}=\text{N})$ group shift to higher wave numbers, this indicate the azomethine nitrogen coordinated to metal atom, the $\text{C}=\text{N}$ group frequency in FTIR will increase [18-19]. The stretching vibration of $(\text{C}=\text{S})$ group is found to shift to lower wave numbers in the spectra of all complexes in comparison with free ligand, suggesting the coordination of the sulfur atom of the $(\text{C}=\text{S})$ group to the central metal ions. All the complexes exhibited bands around $(422-453)$ and $(402-415)$, which could be assigned to vibrations of $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$, respectively[20-22].

Table (2) IR frequencies (cm^{-1}) of the compounds

Compound	$\nu(\text{N-H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
$\text{C}_{11}\text{H}_9\text{N}_4\text{SCl}$	3524,3396	1558	1292	-	-
$[\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	3238	1649	1209	499	455
$[\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	3240	1597	1203	503	461
$[\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	3215	1651	1217	488	461



Figure(2) FTIR spectra of $[\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCL})_2]\text{Cl}_2$

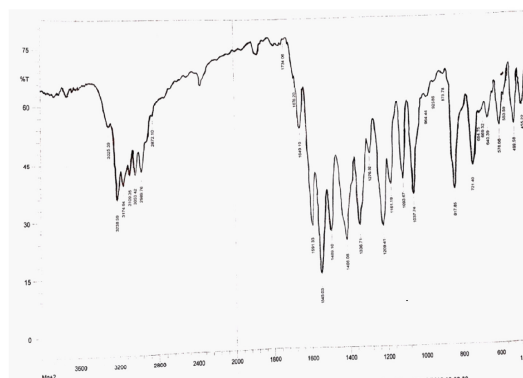


Figure. (1) FTIR spectra of the Ligand

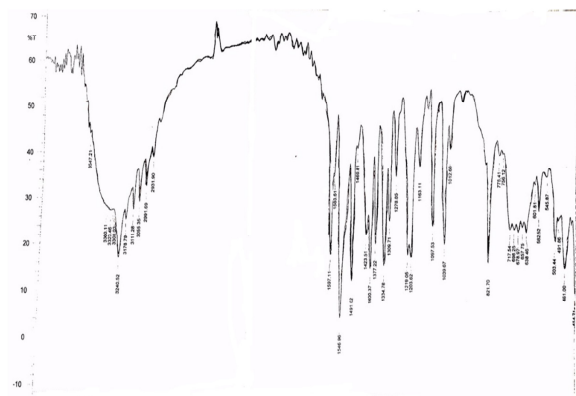
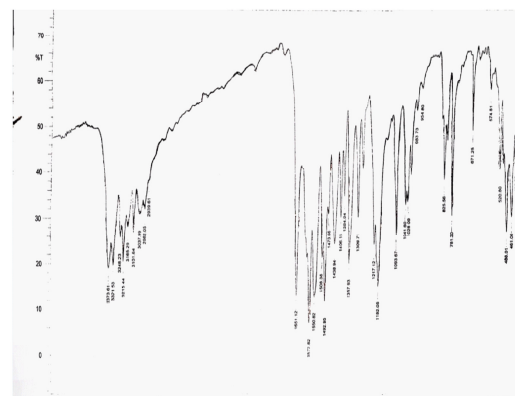


Figure (3) FTIR spectra of $[\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCL})_2]\text{Cl}_2$



Figure(4) FTIR spectra of $[\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCL})_2]\text{Cl}_2$

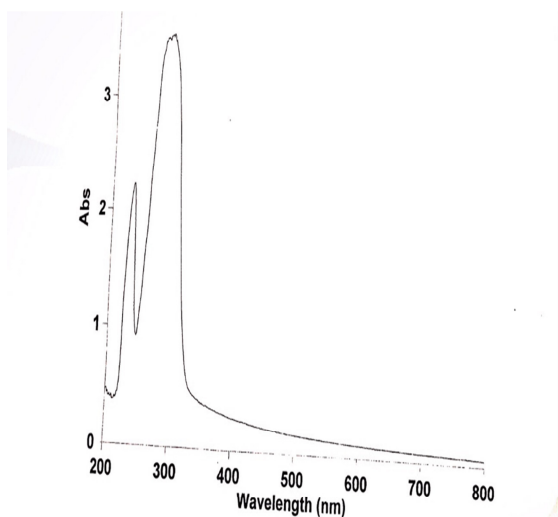
Electronic spectra and magnetic moment measurements:-

The electronic spectra and magnetic moment data of the ligand and its complexes are summarized in (Table(3)). The UV.Vis spectrum of the ligand exhibited a high intense absorption peaks at 236 and 282nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, transition respectively. The $\text{Co}(\text{II})$ complex exhibited magnetic moment value (2.50 BM) this value correspond with the square planer geometry around cobalt[23-24]. The spectrum of the $\text{Co}(\text{II})$ complex exhibited band at (17793 cm^{-1}) the band may be assigned to the ${}^2\text{A}_{1g}(\text{D}) \rightarrow {}^2\text{E}_g^1$, and the two bands values ν_1 and ν_2 does not appear in the spectrum because they lying in the range out of the instrument measurements that may by assigned to the ${}^2\text{E}_g \rightarrow {}^3\text{A}_{1g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ electronic transition respectively[25]. The $\text{Ni}(\text{II})$ complex is diamagnetic suggesting the square planar around nickel. The electronic spectrum of the $\text{Ni}(\text{II})$ complex recorded in ethanol solution displayed absorption bands at (30211 cm^{-1}) and (24831 cm^{-1}) . These bands may be assigned to the ${}^1\text{A}_{1g}(\text{D}) \rightarrow {}^1\text{E}_g(\text{G})$ and ${}^1\text{A}_{1g}(\text{D}) \rightarrow {}^1\text{B}_{2g}(\text{G})$ transition[26]. The electronic spectrum of the $\text{Cu}(\text{II})$ complex shows bands at (28571 cm^{-1}) and (20408 cm^{-1}) these band corresponded to the transitions CT and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, respectively. The position of these bands together with magnetic moment value (1.86BM)

confirms the square planer geometry around copper[27].

Table(3) magnetic moment and Uv-Vis spectral in EtOH solution

Compound	μ_{eff} (B.M)	Band position (λ) cm^{-1}	Assignment
$\text{C}_{11}\text{H}_9\text{N}_4\text{SCl}$		35460 42372	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
$[\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	2.50	17793	${}^2\text{A}_{1g}^{(D)} \rightarrow {}^2\text{E}_g^1$
$[\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	0.0	24813 30211	${}^1\text{A}_{1g}^{(D)} \rightarrow {}^1\text{B}_{2g}^{(G)}$ ${}^1\text{A}_{1g}^{(D)} \rightarrow {}^1\text{E}_g^{(G)}$
$[\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$	1.86	20408 28571	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ CT



Figure(5) UV-Vis spectra of the Ligand

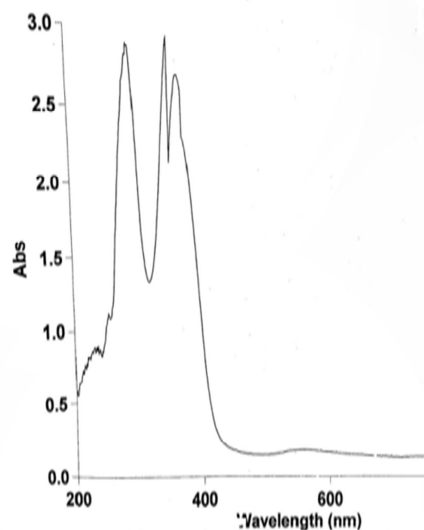


Figure (6) UV-Vis spectra of the $[\text{Co}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$

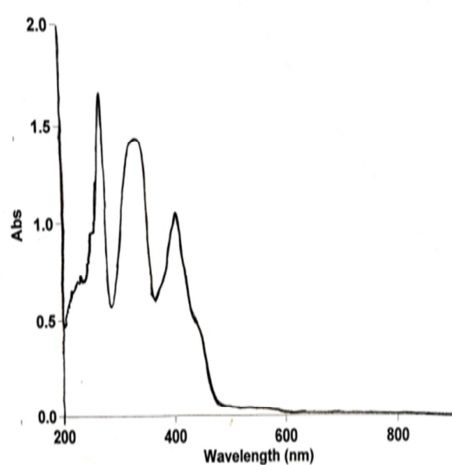


Figure (7) UV-Vis spectra of the $[\text{Ni}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$

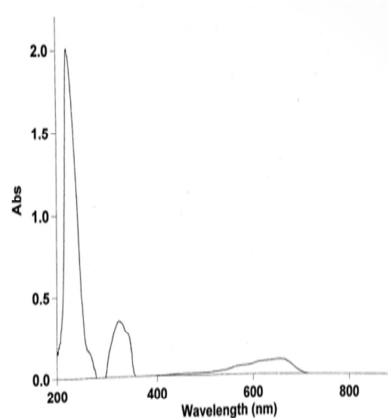


Figure (8) UV-Vis spectra of the $[\text{Cu}(\text{C}_{11}\text{H}_9\text{N}_4\text{SCl})_2]\text{Cl}_2$

References

- [1]. Vega-Perez, J.M.; Perinan, I.; Argandona, M.; Vega-Holm, M.; Palo-Nieto, C.; Burgos-MORON, E.; Lopez-Lazaro, M.; Vargas, C.; Nieto, J.J.; Iglesias-Guerra, F. Isoprenyl- thiourea and urea derivative as new farnesyl diphosphate analogues : Synthesis and in vitro antimicrobial and cytotoxic activities. *Eur. J. Med. Chem.* 2012, 58, 591-612. *Molecules* 18, 2013.
- [2]. Yao, J.; Chen, J.; He, Z.; Sun, W.; Xu, W. Design, synthesis and biological activities of thiourea containing sorafenib analogs as antitumor agent. *Bioorg. Med. Chem.* 20, 2923-2929, 2012.
- [3]. Shantharam, C.S.; Suyoga, V.D.M.; Suhas, R. Sridhara, M. B.; Channe, G.D. Inhibition of protein glycation by urea and thiourea derivatives of glycine/proline conjugated benzisoxazole analogues- Synthesis and structure-activity studies. *Eur. J. Med. Chem.* 60, 325-332, 2013.
- [4]. Yang, W., Hu, Y.; Yang, Y.S., Zhang, F., Zhang, Y.B.; Wang, X.L.; Tang, J.F.; Zhong, W.Q.; Zho, H.L. Design, modification and 3D QSAR studies of novel naphthalin-containing pyrazoline derivatives with/without thiourea skeleton as anticancer agents. *Bioorg. Med. Chem.* 21, 1050-1063, 2013.
- [5]. Keche, A.P. ; Hantnapure, G.D.; Tale, R.H.; Rodge, A.H.; Kamble, V.M. Synthesis, anti-inflammatory and antimicrobial evaluation of novel 1-acetyl-3,5-diaryl-4,5-dihydro(1H) Pyrazole derivatives bearing urea, thiourea and sulfonamide moieties. *Bioorg. Med. Chem.* 22, 6615, 2012.
- [6]. Burgeson, J.R., Moore, A.L.; Boutilier, J.K., Cerruti, N.R.; Gharaibeh, D.N.; Lovejoy, C.E.; Ambeg, S.M.; Hruby, D.E.; Tyvanagimatt, S.R.; Allen, R.D.; Daisar, D. Analysis of a series of acylthiourea derivatives possessing broad- spectrum antiviral. *Bioorg. Med. Chem Lett.* 2012, 22, 4263-4272.
- [7]. Upadhayaya, R.S.; Kulkarni, G.M.; Vasireddy, N.R.; Vandavasi, J.K.; Dixit S.S.; Sharma, V.; Chattapadhyaya, Design, synthesis and biological evaluation of novel triazole, urea and thiourea derivatives of quinolone against Mycobacterium tuberculosis. *Bioorg. Med. Chem.* 2009, 17, 4681-4692.
- [8]. Khan, S.A.; Singh, N.; Saleem, K. Synthesis, characterization and in vitro antibacterial activity of thiourea and urea derivatives of steroids. *Eur. J. Med Chem.* 2008, 43, 2272-2277.
- [9]. Mishra, S. Ninama, P. Sharma, N. Soni and R. Awate: A newly Synthesis and characterization of metal complexes of 3-(N- phenyl) thiourea-pentanone-2 as ligand *Journal of Physics: Conference Series* 365 2012.
- [10]. Burrows D A, Mare D C, *Polyhedron* 18 2665, Mahon F M 1999.
- [11]. Hederson W, Nicholson B K, Dinger M B, *Inorg. Chim. Acta* 338 210, Bennett R L 2002.
- [12]. Arslan H, Florke U, Kulcu N, Emen M F 2006 *Journal of coordination chem.* 59 223, Liu M G 1994.
- [13]. Hou W B, Xu D. Yuan D R, *Cryst. Res. Technol.* 29 939, Liu M G 1994.
- [14]. Dominguez M, Antico E, Beyer L, Aguirre A, Garcia-Granda S, *Polyhedron*, 21 1429, Salvado V 2002.
- [15]. Madan V K, *J. Indian Chem. Soc.* 68 471, Taneja A D 1991.
- [16]. Cullity B D *Elements of X-Ray Diffraction*, Second Edition, Addison-Wesley
- [17]. Geary, W.J., *Coord. Chem. Rev.* 7, 81, 1971.
- [18]. Rejane L, Leticia, Tania M, *J Braz Chem Soc* 10(3):18417, Heloisa B (1999)
- [19]. Beraldo H, Boyd L, *Trans Metal CHEM* 23:67, West D (1988).
- [20]. Nakamoto *Infrared spectra of inorganic and coordination compound.* John Wiley and New York, K (1996).
- [21]. EI-Shazly, EI-Hazmi G, Ghazy S, EI-Shahawi M, EI-Asmy A *Spectro Chim Acta* 61:243, (2005).
- [22]. EI-said F, EI-Asmy A, Kaminsky W, West D *Trans Met Chem* 28:954, (2003).
- [23]. H. Nishikawa and S. Yamada, *Bull, chem. Soc. Jpn.*, 37, (1), 8, (1964)
- [24]. B.B Kanl and K. B. Pandeya, *J. Inorg. Nucl. Chem.*, 40, 1035, (1989)
- [25]. Y. Nishida and S. Kida, *Inorg. Nucl. Chem., Lett.*, 7, 325, (1971).
- [26]. Kumar L, Chandra S *Trans Met Chem* 31:368(2006).
- [27]. Maany. H, Abdel-Hamid S, EL- Shafi O, EI-Asmy A. *Trans Met Chem* 31:522(2006)

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