Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(7):1535-1540

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and characterization of adducts of Bis(*o*-isobutyldithiocarbonato) oxovanadium(IV) with substituted pyridines and their biological studies

Neerupama*, Pooja Sharma, Deepshikha Khajuria and Renu Sachar

Department of chemistry, University of Jammu, Babasaheb Ambedkar Road, Jammu, India

---

ABSTRACT

A series of adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines have been synthesized by treating Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines in acetone in equimolar ratios. Analytical results show that the adducts have 1:1 stoichiometry with general formula VO(O-isobulyldithiocarbonato)$_2$L where L = 2 and 3-bromopyridine; 4-acetylpyridine; 3-hydroxypyridine; 2–methoxypyridine; 2-amino-3-methylpyridine; 2-amino-4-methylpyridine; 2-amino-5-methylpyridine). The addition complexes have been characterized by elemental analysis, conductivity measurements, magnetic susceptibility measurements, infrared and electronic spectral studies. These studies suggest a distorted octahedral structure and paramagnetic nature of the adducts. Antifungal activity of some adducts have been carried out against the fungal strain Sclerotium rolfsii.

Keywords: Oxovanadium(IV), O-isobutyldithiocarbonate, Sclerotium rolfsii

---

INTRODUCTION

Xanthates are one of the interesting member of the 1,1-dithiolate family. Xanthates are widely used as fungicides, pesticides, chelating agents for the removal of heavy metal ions from toxic wastes; precursors for metal- organic chemical vapour deposition (MOCVD) and synthesis of semiconductor nanoparticles[1,2]. These have been extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections [3]**.** Metal xanthates are weel known agents in the flotation of minerals of transition metals such as copper, zinc, cobalt and nickel and in the separation and quantitive determination of large number of cations [4,5]. The use of cellulose xanthate for the column for the separation of alcohols by chromatographic method is one of excellent application of metal xanthate [6]. Xanthate also finds application as catalysts in RAFT polymerization. S-2(ethylpropionate)-(O-ethylxanthate) and newly synthesized (S)-2(ethyl isobutyratye)-(O-ethylxanthate) were used as reversible addition fragmentation chain transfer (RAFT) agents for radical polymerization of N-vinylpyrrolidine (NVP**)** [7,8]. Xanthates have recently been shown to inhibit the replication of both DNA and RNA viruses in vitro. The antiviral activity was exerted only under acidic pH conditions. Unexpectedly, it was found that certain xanthate derivatives exhibit beneficial antimicrobial and antiviral effects [9]**.**

EXPERIMENTAL SECTION

Preparation of Potassium salt of O-isobutyldithiocarbonate

Potassium salt of isobutyl xanthate was prepared by the method reported in literature [10]. Into a 500 ml round bottomed flask, fitted with a reflux condenser, was placed 42 g (0.75 mol) of potassium hydroxide pellets and 192.71 g (234.72 ml, 2.6 mol) of isobutyl alcohol. The reaction mixture was heated under reflux for 1 hour. The mixture was then cooled and liquid from the residual solid was decanted off into another dry 500 ml flask. To this flask, was added 52 g (45 ml, 0.75 mol) of carbon disulphide slowly with constant shaking. The residual solid mass was filtered (after cooling in ice) on a sintered glass funnel at the pump. It was washed with three 25 ml portions of ether. The resulting potassium O-isobutyldithiocarbonate (potassium salt of isobutyl xanthate) was dried in a vacuum dessicator over anhydrous calcium chloride. It was then recrystallized from absolute ethanol.

Preparation of bis(O-isobutyldithiocarbonato)oxovanadium(IV)

The saturated aqueous solutions of hydrated vanadyl sulfate (1.63 g, 0.01 mol) and potassium O-isobutyldithiocarbonate (3.76 g, 0.02 mol) were prepared separately and then mixed with constant stirring. Dark green precipitates were formed which were filtered immediately and were dried in a vacuum desiccator over anhydrous calcium chloride. The composition of the complex was established to be $VO[S_2C(O-C_4H_9)]_2$ by the elemental analysis.

Preparation of 1:1 adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines

The 1:1 addition complexes of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines were prepared by stirring $VO[S_2C(O-C_4H_9)]_2$ (0.927 g, 0.0026 mol) in acetone with substituted pyridines [2-bromopyridine=0.410 g ; 3-bromopyridine= 0.410 g; 4-acetylpyridine=0.314; 3-hydroxypyridine=0.247 g; 2-methoxypyridine= 0.287 g; 2-amino-3-methylpyridine=0.2511 g ; 2-amino-4-methylpyridine=0.2511 g ; 2-amino-5-methylpyridine= 0.2511 g (0.0026 mol)] for 30 min. The contents of the reaction mixture were allowed to stand for 20–24 h and the green obtained was washed with the solvent used in their preparation and dried over calcium chloride at room temperature.

METHODS

Carbon, Hydrogen, Nitrogen and Sulfur were determined on elemental analyzer (elemental vario EL III, carlo Erba 1108). Molar conductance was determined on the millimolar solution in DMF using century CC 601 Conductivity Bridge. Infrared spectra of the complexes over the region 4,000–200 cm21 were recorded using KBr pellets on Infrared spectrophotometer (Perkin Elmer FT-IR). The electronic spectra of the adducts were recorded in DMF on systronics 119 UV–visible spectrophotometer. Magnetic moments were determined at room temperature by VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance and magnetic moments of the adducts isolated are presented in Tables.

RESULTS AND DISCUSSION

I. Preliminary investigation

The adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) are microcrystalline solids and are characterised by various physic-chemical techniques. These adducts are insoluble in common organic solvents such as benzene, acetone, toluene, 1,4-dioxane, nitrobenzene, ethanol etc. However these adducts are soluble in dimethylformamide and dimethylsulfoxide. The elemental analysis reveals that the adducts isolated have 1:1 stoichiometry depending upon the molar ratios of metal and ligand taken for their preparation **(Table 1).**

II. Physico-chemical investigation

The structures of the isolated complexes were established from their molar conductance measurements, magnetic susceptibility measurements, electronic and infrared spectral data. The results of these investigations are tabulated and discussed.

1. Molar conductance measurement

The molar conductance value of their millimolar solutions in DMF are found in the range of 3.48-7.54 $ohm^{-1}mole^{-1}cm^2$.These values are lower than the values which can be expected for uni-univalent electrolytes in these solvents suggesting that these complexes are neutral and non-ionic in character **(Table 2).**

2. Magnetic measurements

The VO^{2+} cation, being d^1 ion, possesses a spin only magnetic moment value of 1.73 B.M corresponding to one unpaired electron [11]. The adducts of (O-isobutyldithiocarbonato) oxovanadium (IV) exhibit magnetic moments in the range 1.79-2.13 B.M and the values of magnetic moments are presented in **(Table 2).** The values are in accordance with the paramagnetic nature of these adducts due to the presence of unpaired electron. It also suggests that the adducts of oxovanadium(IV) have octahedral geometry and are monomeric in nature. The higher value of magnetic moment may be due to the orbital contribution.

Table 1:- Analytical data of 1:1 adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridine

S. No	NAMEOF THE ADDUCT *FORMULA*	MOL. Wt.	% YIELD	COLOUR	%age (Found)				%age (Calculated)			
					C	H	N	S	C	H	N	S
1	Bis(O-isobutydithiocarbonato) (2-bromopyridine)oxovanadium(IV)	522.84	75	Green	33.91	3.88	2.11	23.91	34.42	4.20	2.67	24.47
2	Bis(O- isobutydithiocarbonato) (3-bromopyridine)oxovanadium(IV)	522.84	85.4	Green	33.80	3.74	2.30	23.80	34.42	4.20	2.67	24.47
3	Bis(O- isobutydithiocarbonato) (2-methoxypyridine)oxovanadium(IV)	473.94	83.5	Green	39.71	4.70	2.16	26.85	40.51	5.20	2.95	27.00
4	Bis(O- isobutydithiocarbonato) (4-acetylpyridine) oxovanadium(IV)	485.94	77.2	Green	40.90	4.68	2.25	25.70	41.98	5.14	2.88	26.34
5	Bis(O- isobutydithiocarbonato) (3-hydroxypyridine)oxovanadium(IV)	459.94	88	Green	38.61	4.81	2.91	26.14	39.13	5.00	3.04	27.82
6	Bis(O isobutydithiocarbonato) (2-amino-3-methylpyridine)oxovanadium(IV)	472.94	72.2	Green	39.97	4.87	4.13	26.85	40.59	5.49	5.92	27.06
7	Bis(O- isobutydithiocarbonato) (2-amino-4-methylpyridine)oxovanadium(IV)	472.94	70.5	Green	39.85	4.98	4.97	26.75	40.59	5.49	5.92	27.06
8.	Bis(O- isobutydithiocarbonato) (2-amino-5-methylpyridine)oxovanadium(IV)	472.94	80	Green	39.74	4.75	4.79	26.15	40.59	5.49	5.92	27.06

Table 2:- Molar conductance and magnetic data of 1:1 adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines

S.No	NAME OF THE ADDUCT	MOLAR CONDUCTANCE (Ohm^{-1} mol^{-1} cm^2)	MAGNETIC DATA	
			μ_{eff}(B.M)	TEMPERATURE (K)
1	Bis(O-isobutydithiocarbonato)(2-bromopyridine)oxovanadium(IV)	5.75	1.84	300
2	Bis(O- isobutydithiocarbonato)(3-bromopyridine)oxovanadium(IV)	6.19	1.81	300
3	Bis(O- isobutydithiocarbonato)(2-methoxypyridine)oxovanadium(IV)	7.35	1.76	300
4	Bis(O- isobutydithiocarbonato)(4-acetylpyridine)oxovanadium(IV)	5.78	1.76	300
5	Bis(O- isobutydithiocarbonato)(3-hydroxypyridine)oxovanadium(IV)	3.75	1.85	300
6	Bis(O -isobutydithiocarbonato)(2-amino-3-methylpyridine)oxovanadium(IV)	5.35	1.78	300
7	Bis(O- isobutydithiocarbonato)(2-amino- 4-methylpyridine)oxovanadium(IV)	6.25	1.79	300
8.	Bis(O- isobutydithiocarbonato)(2-amino- 5-methylpyridine)oxovanadium(IV)	3.90	1.80	300

III. Spectral studies

1. Infrared spectra

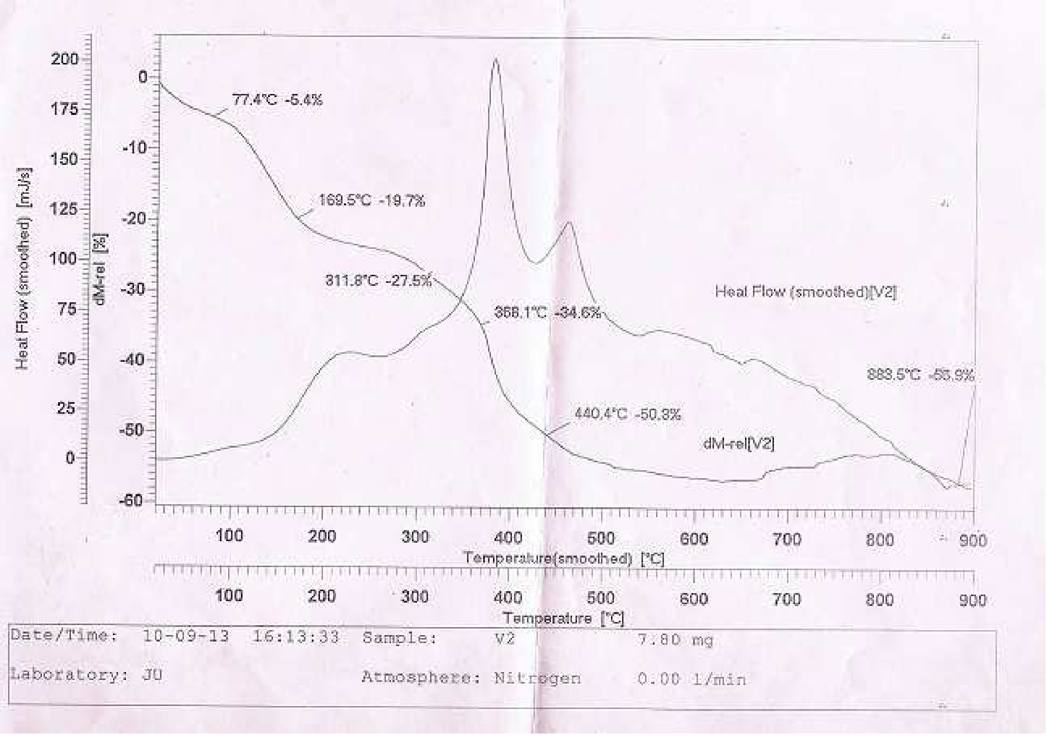
IR spectra of oxovanadium(IV) complexes exhibit characteristic band due to V=O stretching vibration. VO moiety has a double bond character between V and O and any change in the electron density on the vanadium ion is expected to alter the V=O stretching frequency also. The infrared spectra of the adducts of oxovanadium(IV) xanthates exhibit a strong band in the range 996-960cm^{-1} which is attributed to the terminal V=O bond. These values are within the range observed for monomeric complexes containing VO^{2+} cation [12-14]. A comparison of the infrared spectral data of five coordinated oxovanadium(IV)xanthates with their corresponding adducts reveal that V=O band in the parent complexes (1000-990cm^{-1}) get displaced to lower frequencies (980-960cm^{-1}) in the corresponding adducts [13, 15-16]**.** This displacement can be attributed to the electronic donation of the base to the vanadium (N-V), which increases the electron density on the metal d-orbitals, and consequently the pπ-dπ donation from oxygen atom to vanadium is expected to be reduced [17-19]. In $VO(S_2COR)_2$, characteristic bands corresponding to C-O-C symmetric and asymmetric vibrations are observed in the region 1280cm^{-1} and 1147cm^{-1} respectively. On adduct formation as the electron density on vanadium ion increases(due to the donation of electrons by Lewis bases) the donation of electrons from xanthate ligand to metal ion decreases which in turns lowers the bond order of the C-O-C bond that is reflected by the shift in characteristic bands due to symmetric and asymmetric vibrations of the C-O-C group to lower frequencies **(Table 3).**

2. Electronic spectra

The electronic spectra of the adducts of oxovanadium(IV)xanthates with substitutedpyridine, prepared in the present work, were recorded in dimethylformamide. The electronic spectra data of the adducts of oxovanadium(IV)bis(O-isobutyldithiocarbonate) show three bands in the range 12255-15935 cm^{-1}, 15925-19043 cm^{-1} and 22550-29265 cm^{-1} and are assigned to $e \leftarrow b_2$, $b_1 \leftarrow b_2$ and $a_1 \leftarrow b_2$ transitions respectively are presented in **(Table 3)** These bands are characteristic of oxovanadium(IV) complexes in octahedral environment [20-22].

IV. Thermogravimetrical Analysis

The TGA Graph of Bis(O-isobutyldithiocarbonato)(3-bromopyridine)oxovanadium(IV) shows a stepwise loss of weight with the rise of temperature. The first step is observed at 311.8 °C which may be due to loss of 3-bromopyridine (calculated=30.2 %, Found=27.5%). Another significant loss of weight was observed at 883.5 °C which is due to loss of two xanthate moieties (calcutated = 56.9 % , Found = 56.9 %). This is followed by gradual loss of weight till the resultant weight corresponding to formation of V_2O_5 as a stable product at 883 ° C. **(Figure 1)**



Date/Time: 10-09-13 16:13:33 Sample: V2 7.80 mg
Laboratory: JU Atmosphere: Nitrogen 0.00 l/min

Fig 1: TGA of the adduct bis(O-isobutyldithiocarbonato)(3-bromopyridine)oxovanadium(IV)

Table 3: Electronic and Infrared spectral data of 1:1 adducts of bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines

S.No.	Name of the adduct	Electronic spectral data (cm^{-1})			Infrared Spectral data (cm^{-1})			
		ν1	ν2	ν3	ν(C-S)	ν(C-O)	ν(V=O)	ν(V-S)
1.	Bis(O-isobutydithiocarbonato)(2-bromopyridine)oxovanadium(IV)	12165	17750	23700	1029	1134	982	409
2.	Bis(O- isobutydithiocarbonato)(3-bromopyridine)oxovanadium(IV)	12599	17454	24986	1031	1130	978	406
3.	Bis(O- isobutydithiocarbonato)(2-methoxypyridine)oxovanadium(IV)	13853	18450	26350	1040	1147	961	411
4.	Bis(O- isobutydithiocarbonato)(4-acetylpyridine) oxovanadium(IV)	13786	18220	25697	1056	1130	974	405
5.	Bis(O-isobutydithiocarbonato)(3-hydroxypyridine)oxovanadium(IV)	14796	17854	25980	1032	1145	970	410
6.	Bis(O isobutydithiocarbonato)(2-amino-3-methylpyridine)oxovanadium(IV)	13678	16640	25100	1029	1158	975	413
7.	Bis(O- isobutydithiocarbonato)(2-amino-4-methylpyridine)oxovanadium(IV)	14350	15987	24986	1055	1140	961	420
8.	Bis(O- isobutydithiocarbonato)(2-amino-5-methylpyridine)oxovanadium(IV)	14372	15680	25346	1035	1152	971	415

IV. Biological studies:

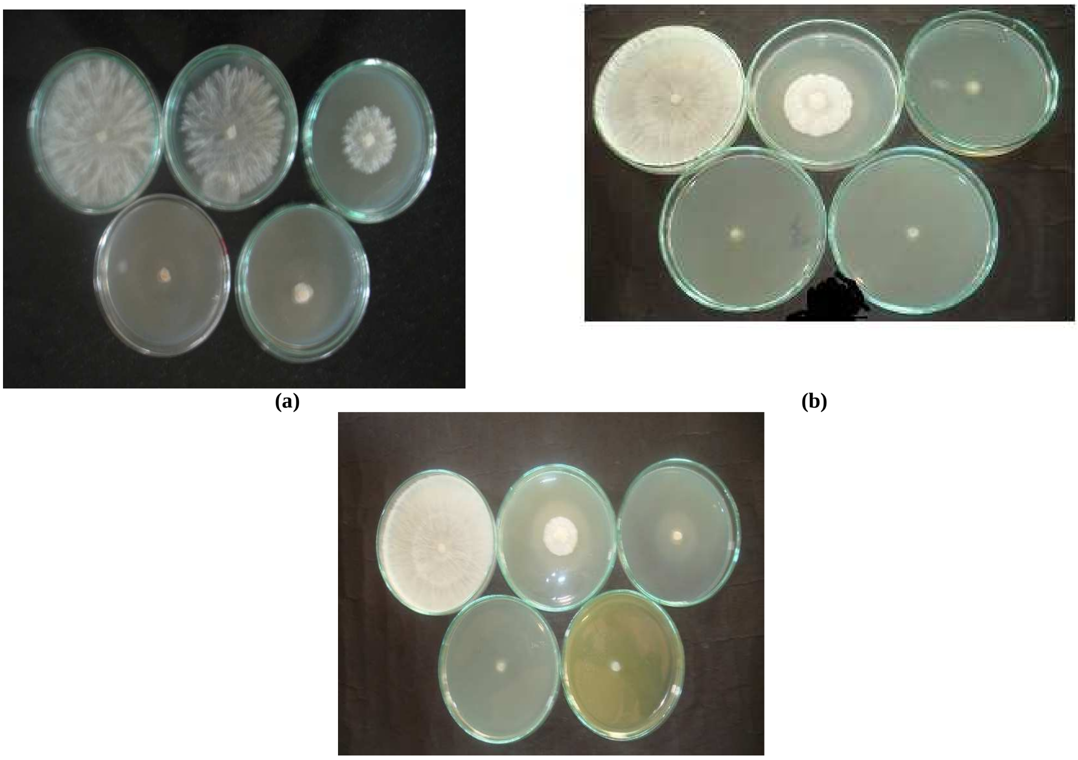
The antifungal activity of the adducts was tested by **Poisoned food technique** against the pathogenic fungus *Sclerotium rolfsii*. The linear growth of the fungus in controlled manner was recorded at different concentration of the adducts. The growth inhibition of Sclerotium rolfsii over control was calculated **(Table 4).** It is found that on increasing the concentration of the adducts, the colony diameter of the fungus decreases and hence percent inhibition increases**(Figure 2)** [23]. The growth inhibition of Fungus over control was calculated as:

$$\% \text{ inhibition (I)} = C\text{-}T/C \times 100$$

where I = percent inhibition,C = mean growth of fungus(in mm) in control and T = mean growth of fungus(in mm) in treatment.

Table 4:-Invitro evaluation against *Sclerotium Rolfsii*, Mean Colony Diameter =90 mm

S.No.	Name of the adducts	Concentration (ppm)	Colony diameter (mm)	% inhibition (I) = [(C-T)/C]×100
1.	Bis(O-isobutydithiocarbonato) (2-bromopyridine)oxovanadium(IV)	50 100 150 200	60 30 10 2	33.33 66.67 88.89 97.78
2.	Bis(O-isobutydithiocarbonato) (2-methoxypyridine)oxovanadium(IV)	50 100 150 200	50 26.50 11.20 4.10	44.44 70.56 87.56 95.44
3.	Bis(O-isobutydithiocarbonato) (3-hydroxypyridine)oxovanadium(IV)	50 100 150 200	35 20 10.50 3.2	6.11 77.78 88.33 96.44



(a) **(b)**

(c)

Figure 2:- Antifungal activity of

(a) Bis(O-isobutyldithiocarbonato)(2-bromopyridine)oxovanadium(IV)
(b)Bis(O-isobutyldithiocarbonato)(2-methoxypyridine)oxovanadium(IV)
(c)Bis(O-isobutyldithiocarbonato)(3-hydroxypyridine)oxovanadium(IV)

CONCLUSION

On the basis of above studies it has been found that 1:1 adducts of Bis(O-isobutyldithiocarbonato)oxovanadium(IV) with substituted pyridines are paramagnetic and observed magnetic moment values suggest a distorted octahedral geometry around vanadium ion. These complexes also show considerable antifungal activities.

Acknowledgements

We acknowledgement The department of Plant Pthology, SKUAST for carrying out antifungal studies.

REFERENCES

[1] DC Onwudiwe; PA Ajibade, *Int. J. Mol. Sci*., **2011**, 1, 1964-1978.
[2] J Park; M Song; W Jung ; WY Oung , *Bull Kor. Chem. Soc.*, **2012**, 3, 3383.
[3] JJ Santanaa; RM Souto, *AIDS Research and Human Retro-viruses*., **2012**, 4, 1, 71-81.
[4] AP Chandra; L Puskar; DJ Simpson; AR Gerson, *Inter. J. of Min. Proc*., **2012**, 114, 16-26.
[5] SA Kondratev; VI Rostovtsev; VV Fomenko; YS Kargapolov, *J. of Min. Sci*., **2010**, 46(5), 569-574.

[6] JW Spanyer; JP Phillips, *Anal. Chem.*, **1956**, 28, 253–253.
[7] J Schmitt; N Blanchard, *J. Polym. Chem.*, **2011**, 2, 2231-2238.
[8] S Perrier; P Takolpuckdee, *J. Poly. Sci. Part A.*, **2005**, 43, I 22, 5347–5393
[9] W Friebolin; G Schilling; M Zoller; E Amtamnn, *J. Med. Chem.*, **2005**, 48(25), 7925.
[10] BS Furniss, AJ Hannaford, PWG Smith and AR Tatchell, *Vogel's Text Book of Practical Organic Chemistry*, Pearson Education, London, UK, 5th edition, **1989.**
[11] BJA Jeragh; AE Dissouky, *Trans. Met Chem.*, **2004**, 29(6), 579-585.
[12] KP Callahan; P J Durand, *Inorg. Chem.*, **1980**, 19 (11), 3211–3217.
[13] N Sharma; V Kumar; R Sharma; M. Kumari; SS Kanwar, *Bull. Chem. Soc. Jpn.*, **2011**, 84 (8), 855–861.
[14] V Malik; G Solanki; V Singh, *Ori. J. Chem.*, **2009,** 25(4), 1041-1046.
[15] H Han; L Lu; Q Wang; M Zhu; C Yuan; SX Fu, *Dalton Trans.*, **2012,** 41(36), 11116-11124.
[16] PB Sreeja, MRP Kurup, *Spectrochimica Acta Part A., Molecular and Biomolecular Spect.***,** **2005**, 61, 2331–2336
[17] YJ Jang; U Lee; BK Koo, *Bull. Korean Chem. Soc.*, **2005,** 26, 72**.**
[18] S Bhattacharya; T Ghosh, *Trans. Met Chem.*, **2002**, 27(1), 89-94.
[19] EB Seena; N Mathew; M Kuriakose; MRP Kurup, *Polyhedron*, **2008**, 27(5), 1455–1462.
[20] Y Kurt; BCM Acikgoz; E Tuzun; G Atun and B Ulkuseven, *Polyhedron*, **2013,** 65, 2867–2872.
[21] S Parihar; S Pathan; RN Jadeja; A Patel; VK Gupta, *Inorg Chem.*, **2012**, 16, 1152-1161.
[22] MR Maurya, *Coordination Chemistry Reviews.*, **2003,** 237, 163–181.
[23] YL Nene; PN Thapliyal, Fungicides in Plant Disease Control III Edn., **1993**, 691.