

Synthesis, Physiochemical, Thermal, Catalytic and Electrical Studies of Mn(III) VO(IV), MoO₂(VI) and UO₂(VI) Complexes with Unsymmetrical Schiff Base Ligand

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Abstract: The solid complexes of Mn(III), VO(IV), MoO₂(VI) and UO₂(VI) with unsymmetrical dibasic tetradentate ONNO donor Schiff base derived from the condensation of salicylaldehyde, *o*-hydroxy acetophenone and ethylene diamine have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, IR and reflectance spectra. The thermal dehydration and decomposition of these complexes were studied kinetically using the Horowitz-Metzger method. The solid state electrical conductivity of complexes has been measured in the temperature range 313 K ≤ T ≤ 403 K and the complexes exhibited semiconducting behavior. Scanning electron micrograph has also been reported and suggested homogeneous phase material. Complexes were used for the catalytic oxidation of styrene.

Keywords: Unsymmetrical Schiff base, Tetradentate, Electrical conductivity, Catalytic oxidation

Introduction

Schiff base are an important class of ligands in coordination chemistry and find extensive application in different fields¹. Schiff bases derived from the salicylaldehyde are well known as polydentate ligands coordinating in neutral forms^{2,3}. Oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to form transition metal complexes with unusual configuration, structural liability and sensitivity to molecular environments^{4,5}. Their metal complexes find wide applications as antibacterial, antiviral, antimalarial agents^{6,7}, homogeneous and heterogeneous catalysts^{8,9} and magnetic materials¹⁰. A literature survey reveals that the Schiff base derived from salicylaldehyde, *o*-hydroxyacetophenone and ethylenediamine has not reported so far. In this article, we describe the synthesis and characterization of Mn(III), Vo(IV), MoO₂(VI) and UO₂(VI) complexes of *N*-(salicylidene)-*N*¹-(*o*-hydroxyacetophenone)-ethylenediamine.

Experimental

The metal contents in the complexes were analyzed by standard methods. The analysis of Carbon, Hydrogen and Nitrogen were performed on Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow, India. The infrared spectra of ligand and its complexes were obtained in KBr pellets on Perkin-Elmer spectrophotometer 597 at SAIF, Panjab University, Chandigarh, India. The room temperature magnetic susceptibility measurements of the resulting complexes were measured by Gouy's method. The paramagnetic susceptibilities were corrected for diamagnetism of ligand and metal ion. Thermograms of the complexes were recorded in the temperature range room temperature to 700 °C at the heating rate of 20 °C /min using a Mettler STA 409 simultaneous thermal analyzer at IIT Madras, Chennai India. Solid-state electrical conductivity of the complexes was measured in their compressed pellet forms using the conventional two-probe method. Diffuse reflectance spectra of complexes were recorded on Varian Cary 5E UV-NIR spectrophotometer at RSIC, IIT Madras, Chennai. SEM image of complexes were recorded at VNIT, Nagpur, India.

All chemicals used in the present work *viz.*, salicylaldehyde, *o*-hydroxyacetophenone, ethylenediamine, metal salts, solvents, *etc.*, were of A.R. grade. The unsymmetrical Schiff base *N*-(salicylidene)-*N'*-(*o*-hydroxyacetophenone) ethylenediamine (H₂L) was obtained by known method¹¹. Manganese(III) acetate dihydrate and dioxomolybdenum diacetate were prepared by known methods¹².

Preparation of metal complexes

Ligand is highly soluble in hot DMF (90-100 °C) to increase solubility of ligand; minimum amount of DMF was used. To a hot stirred solution of 2 mmol of ligand in DMF (10 mL) was added a solution of metal salts (2 mmol) (10 mL) in DMF and then reflux for 1 h. Then pH of the solution was adjusted to 7.5 using alcoholic ammonia and resulting solution was further refluxed for about 4 h. The colored solution was concentrated to ca 15 mL and then cooled to room temperature to give colored precipitation of the complex. The complexes thus separated out was filtered, washed with DMF and hot ethanol to give the analytically pure products and dried in desiccators over CaCl₂.

Antibacterial and antifungal study

The antibacterial activities of the ligand and the complexes have been carried out against the bacteria *Staphylococcus aureus*, *Bacillus Subtilis*, *Salmonella typhimurium* and *Escherichia coli* using nutrient agar medium by the disc diffusion method. Solutions of 100, 200 and 300 ppm of the compounds in DMSO were used for the studies. These discs were placed on the already seeded plates and incubated at 35 °C for 24 h. The diameter (mm) of the inhibition zone around each disc was measured after 24 h.

The antifungal activity was evaluated by the same disc diffusion method using potato dextrose agar medium containing starch 20 g. Dextrose 20 g and agar-agar powder 15 g dissolved in 1000 mL distilled water. Same concentrations of compounds were used. The organisms used were *Aspergillus oryzae* and *Fusarium species*. The fungicidal activity of the compounds was recorded after 7 days.

Catalytic oxidation study

Catalytic oxidation of styrene to corresponding epoxide by VO(IV) and UO₂(VI) complexes tested in presence of an aqueous solution of 30% H₂O₂ as an oxidant. These catalytic reactions were carried out in 50 mL reaction flask fitted with water condenser. A general

procedure was followed for all reactions. In a typical experiment, styrene (5.2 g, 30 mmol) and 30% H₂O₂ (1.7 g, 30 mmol) were mixed in 1:1 proportion in 5 mL of acetonitrile and the reaction mixture was heated at 60 °C with continuous stirring. An appropriate catalyst to be tested (0.3 g, 3 mmol) was added to the reaction mixture and heated at 60 °C under constant stirring for 4 h. After the completion of reaction, an organic layer was separated by separating funnel and analyzed using 19091Z.413E Agilent Gas Chromatography with HP-1 column having length 30 m and inner diameter 0.32 mm and FID detector.

Results and Discussion

The reaction of the ligand with the metal ions gave desired complexes. The newly synthesized Schiff base complexes are very stable at room temperature in solid state. The complexes are insoluble in common organic solvents and soluble in DMSO. The results of elemental analysis and physical properties of the compounds are presented in Table 1 and are in good agreement with the proposed Schiff base complexes. The elemental analysis suggests 1:1 metal: ligand ratio.

Table 1. Analytical and spectral data of compounds

Compound	Color	% of yield	Elemental Analysis (% Found/Calcd)				IR cm ⁻¹			
			C	H	N	M	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
[H ₂ L]	Yellow	90.80	72.30 (72.32)	6.88 (6.42)	9.35 (9.92)	-	1634	1283	-	-
[MnL(OAc) H ₂ O]	Brown	59.84	55.08 (55.35)	5.07 (5.10)	6.82 (6.80)	13.27 (13.34)	1598	1297	582	489
[VOL]	Silver Gray	62.35	58.52 (58.80)	4.59 (4.61)	8.08 (8.07)	14.61 (14.68)	1597	1299	567	464
[MoO ₂ L]	Pale Cream	61.28	49.76 (50.01)	3.90 (3.92)	6.89 (6.86)	23.43 (23.52)	1615	1330	520	473
[UO ₂ L]	Golden Brown	71.43	36.91 (37.09)	2.89 (2.91)	5.11 (5.09)	43.07 (43.28)	1599	1295	585	491

Electronic spectra

The Mn(III) ion(d⁴) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions. The diffuse reflectance spectrum of Mn(III) complex display absorption bands at 818, 609 and 445 nm corresponding to tetragonally distorted octahedral geometry. These bands may be assigned to ⁵B_{1g} → ⁵A_{1g}, ⁵B_{1g} → ⁵B_{2g}, and ⁵B_{1g} → ⁵E_g, transitions, respectively¹³. The VO(IV) complex display absorption bands at 782, 613 and 454 nm corresponding to ²B₂ → ²E₁, ²B₂ → ²B₁ and ²B₂ → ²A₁ transitions respectively for square pyramidal environment around V(IV) ion¹⁴. MoO₂(VI) complex display bands at 445 nm suggesting octahedral geometry¹⁵. UO₂(VI) complex shows bands at 802, 583 and 355 nm consistent with the vibronic structure of the triatomic entity of the UO₂(VI) group. The UO₂(VI) complex display weak band at 583 nm assignable to ¹Σ_{g+} → ³Π_u transitions¹⁶.

Infrared spectra

The characteristic vibrational frequencies have been identified by comparing the spectra of the complexes with that of the parent ligand and literature value of absorption of simple type of compound (Table 1). The Schiff base exhibits a medium broad band at 3052 cm⁻¹, which

may be due to the presence of intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen atom^{17,18}. The absence of this band in the spectra of complexes indicates the deprotonation of the phenolic group and coordination of the oxygen atom to metal ion. This is further supported by the shift of the $\nu(\text{C-O})$ (phenolic)¹⁹ band from 1283 cm^{-1} of the ligand to $1295\text{-}1330\text{ cm}^{-1}$ in the spectra of complexes, indicating the coordination of phenolic oxygen atom to the metal ion²⁰. The strong band observed at 1635 cm^{-1} due to $\nu(\text{C=N})$ stretch in ligand spectrum has been shifted to lower frequency by ca. $20\text{-}40\text{ cm}^{-1}$ upon coordination^{21,22}. The Mn(III) complex show two bands at 1656 and 1449 cm^{-1} corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$. The magnitude of the separation $\Delta\nu_{\text{COO}^-}$ between the frequencies of $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ in Mn(III) complex is much greater ($\Delta\nu_{\text{COO}^-} = 207\text{ cm}^{-1}$) than the ionic value ($\Delta\nu_{\text{COO}^-} = 158\text{ cm}^{-1}$). This indicates that acetate ligand coordinated as monodentate ligand²³. In the oxovanadium complex, strong band at 977 cm^{-1} is assigned to $\nu(\text{V=O})$ mode²⁴. $\text{MoO}_2(\text{VI})$ complex exhibit $\nu_{\text{sym}}(\text{O=Mo=O})$ and $\nu_{\text{asym}}(\text{O=Mo=O})$ bands at 944 and 902 cm^{-1} respectively in the present compound suggest a *cis*- MoO_2 structure because dioxomolybdenum(VI) compound having *trans*- MoO_2 structure is expected to exhibit only the $\nu_{\text{asym}}(\text{O=Mo=O})$ band since $\nu_{\text{sym}}(\text{O=Mo=O})$ is IR inactive²⁵. The uranyl complex exhibit a strong band at 940 cm^{-1} and the medium intensity band at 879 cm^{-1} assignable to $\nu_{\text{asym}}(\text{O=U=O})$ and $\nu_{\text{sym}}(\text{O=U=O})$ mode respectively²⁶. The bonding through oxygen and nitrogen is supported by the appearance of new bands in the region $520\text{-}585$ and $464\text{-}491\text{ cm}^{-1}$ which may be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations respectively²⁷.

Magnetic properties

The $\text{MoO}_2(\text{VI})$ and $\text{UO}_2(\text{VI})$ complexes are found to be diamagnetic in nature expected for octahedral geometry^{15,28}. The magnetic moment of $\text{VO}(\text{IV})$ complex was found to be 1.71 B.M. towards square pyramidal geometry²⁹. Mn(III) complex was found to be 4.76 B.M. which is expected for d^4 system³⁰.

Thermal properties

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies about the status of water molecules present in some of these complexes as well as to know their decomposition pattern. An analysis of the thermogram of the complexes of $\text{VO}(\text{IV})$, $\text{MoO}_2(\text{VI})$ and $\text{UO}_2(\text{VI})$ indicate that these complexes undergo one step decomposition after dehydration, while Mn(III) complex undergo two step decomposition after dehydration. The complexes of $\text{VO}(\text{IV})$, $\text{MoO}_2(\text{VI})$ and $\text{UO}_2(\text{VI})$ show mass loss up to $140\text{ }^\circ\text{C}$ indicating the presence of one lattice water molecule (% wt. loss obs/calcd: Mn(III): 4.98/4.18, $\text{MoO}_2(\text{VI})$: 3.96/4.23 and $\text{UO}_2(\text{VI})$: 3.49/3.17). There is further loss in weight up to $280\text{ }^\circ\text{C}$ indicating the presence of one coordinated water in Mn(III) complex (% wt. loss obs/calcd: Mn(III): 8.75/8.37). In all the complexes, rapid loss in weight has been observed around $300\text{ }^\circ\text{C}$ indicative of decomposition of free part of the coordinated ligand. A gradual increase in temperature above $600\text{ }^\circ\text{C}$ was accompanied by degradation of coordinated part of the ligand. The thermogravimetric analysis has proved to be useful analytical technique in evaluating thermodynamic activation parameters of the complexes upon thermal decomposition process, such as activation energy (E_a), frequency factor (Z), entropy change ($-\Delta S$) and free energy change (ΔF) by employing Horowitz-Metzger method³¹, which are shown in Table 2.

Table 2. Magnetic, Electrical conductivity and Thermal decomposition data of complexes

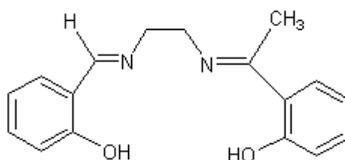
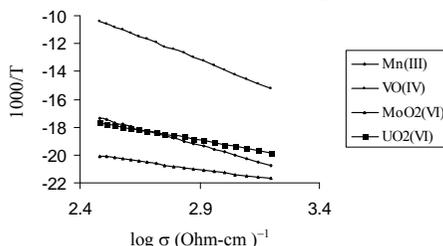
Complex	μ_{eff}	Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Half decomposition temp, $^{\circ}\text{C}$	Activation energy E_a kJmol^{-1}	Frequency Factor Z Sec^{-1}	Entropy change ($-\Delta S$) $\text{Jmol}^{-1}\text{K}^{-1}$	Free energy change (ΔF) kJmol^{-1}
[MnL(OAc)H ₂ O]	4.76	1.12×10^{-8}	238	15.20	109.42	210.38	65.27
[VOL]	1.71	8.38×10^{-6}	386	34.88	78.32	215.29	117.98
[MoO ₂ L]	Diamagnetic	1.23×10^{-9}	634	21.44	150.89	209.52	154.28
[UO ₂ L]	Diamagnetic	1.15×10^{-8}	301	16.03	141.13	209.25	79.03

Electrical properties

The DC electrical conductivity of the ligand and its complexes has been studied in the temperature range $313 \text{ K} < T < 403 \text{ K}$ using the two-probe technique Table 2. The value of the solid-state electrical conductivity of the complexes were found to be in the range of 10^{-9} to $10^{-6} \Omega^{-1}\text{cm}^{-1}$ and they are semiconductor in nature³², because their conductivity increases with increase in temperature and decreases upon cooling over the studied temperature range. The activation energy-temperature dependence follows the Arrhenius relation

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

Where σ_0 , E_a and k are conductivity constants, the activation energy and the Boltzman constant, respectively. The plots of $\log \sigma$ vs. $1000/T$ (Figure 2) for all the compounds are found to be linear over the entire temperature range. The activation energy of the compounds lies in the range 0.199-0.583.

**Figure 1.** *N*-(Salicylidene)-*N'*-(*o*-hydroxyacetophenone)-ethylenediamine (H₂L)**Figure 2.** Plot of $\log \sigma$ vs. $1000/T$

Surface analysis is used in understanding the surface features of the material. The Scanning electron micrograph (SEM) of metal complexes indicates the presence of well-defined crystals free from any shadow of the metal ion on their external surface. The morphology and particle size of the unsymmetrical Schiff base metal complexes have been

illustrated by SEM. Figure 3 depict the SEM photograph of the synthesized VO(IV) complex as representative example. There is a uniform matrix of the synthesized complexes in the pictograph, which leads to dealing with homogeneous phase material. VO(IV) complex is rock like shape morphology with 2-3.5 μm particle size and $\sim 2 \mu\text{m}$ pore size.

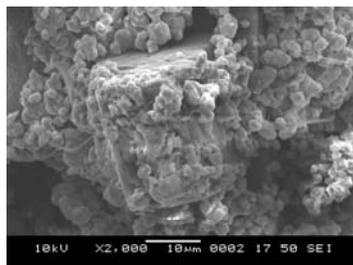


Figure 3. Scanning electron micrograph of [VOL]

Antimicrobial activity

The Schiff base and its metal complexes were evaluated for antimicrobial activity against two strain gram +ve bacteria (*Staphalococcus aureus*, *Bacillus subtilis*), gram -ve bacteria (*Salmonella typhimurium*, *Escherichia coli*) and fungus (*Aspergillus oryzae*, *Fusarium species*). The antimicrobial screening results are given in Table 3. These observations show that the majority of the compounds are more active than their respective Schiff bases. In some cases, Schiff bases and their complexes have similar activity against bacteria and fungi³³. Chelation may enhance or suppress the biochemical potential of bioactive organic species. The antibacterial screening shows that compounds [MnL(OAc)H₂O] and [UO₂L] exhibit the most activity. The fungicidal screening shows that compounds [VOL] and [MoO₂L] are most effective against *Fusarium species*.

Table 3. Antimicrobial activities of ligand and its complexes

Compound	Diameter of inhibition zone, mm (Concentration in ppm)																	
	Antibacterial Screening Data									Antifungal Screening Data								
	<i>Staphalococcus aureus</i>			<i>Bacillus Subtilis</i>			<i>Salmonella typhimurium</i>			<i>Escherichia coli</i>			<i>Aspergillus oryzae</i>			<i>Fusarium species</i>		
	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
LH ₂	9	17	6	6	8	9	7	7	9	8	12	17	-	-	-	6	-	8
[MnL(OAc)H ₂ O]	9	-	20	-	9	11	8	10	13	8	11	19	6	6	7	6	6	7
[VOL]	-	-	-	7	9	12	6	7	10	-	6	8	7	-	8	6	7	9
[MoO ₂ L]	-	6	8	-	8	11	-	7	10	-	7	9	-	7	-	6	8	10
[UO ₂ L]	-	-	7	-	5	6	6	8	11	-	6	8	-	-	-	8	10	13

Catalytic activity

The catalytic oxidation of organic substrates by transition metal complexes is an area of current interest, in view of this in the present paper the catalytic activity of VO(IV) and UO₂(VI) complexes for epoxidation of styrene to corresponding styrene oxide were carried out using H₂O₂ as an oxidant. These oxidation reaction yielded styrene oxide as a major product with minor amount of phenyl acetaldehyde as side product³⁴. Epoxidation of styrene resulted 6.20 and 19.20% conversion and 18.55 and 95.94% Selectivity for VO(IV) and UO₂(VI) complexes, respectively of styrene into styrene oxide (Figure 4). No significant side products were identified.

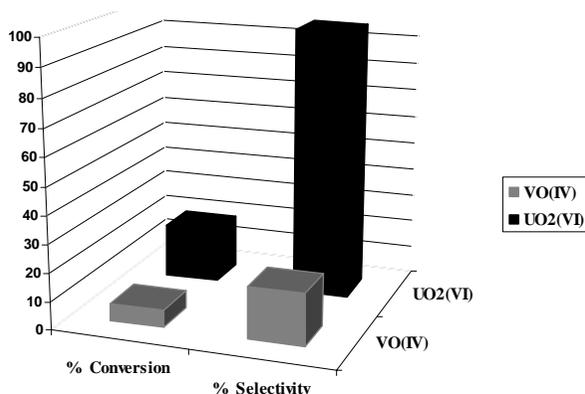


Figure 4. Catalytic study of complexes

Conclusion

Coordination chemistry of an unsymmetrical Schiff base ligand, obtained from the reaction of salicylaldehyde, *o*-hydroxy acetophenone and ethylene diamine, is described. Mn(III), VO (IV), MoO₂(VI) and UO₂(VI) complexes have been synthesized using above Schiff base ligand and characterized on the basis of analytical, magnetic and spectral data. The Schiff base coordinates through its azomethine nitrogens and phenolic oxygens to the metal ion and act as a tetradentate ligand. All the complexes except VO(IV) complex exhibits regular octahedral geometry. Thermal behavior, electrical conductivity and antimicrobial activity of all the complexes are investigated. All the complexes are semiconducting in nature. SEM image of the VO(IV) complex indicates homogeneous phase material. It has been suggested that chelation/coordination enhance or suppress the biochemical potential of bioactive organic species.

References

1. Tarafder M H, Saravanan N, Crouse K A and Ali A M, *Trans Met Chem.*, 2001, **26(6)**, 613-616; DOI:10.1023/A:1012047001167
2. Vukadin M L, Ljijanas V, Katalin M S and Valerijal C, *J Serb Chem Soc.*, 2003, **68(12)**, 919-927.
3. Sonmez M and Sekerci M, *Polish J Chem.*, 2002, **76(7)**, 907-914.
4. Garnovskii A D, Vasilchenko I S, Garnovskii D A and Kharisov B I, *J Coord Chem.*, 2009, **62(2)**, 151-204; DOI:10.1080/00958970802398178
5. Raman N, Raja S J and Sakthivel A, *J Coord Chem.*, 2009, **62(5)**, 691-709; DOI:10.1080/00958970802326179
6. Refat M S, El-Deen I M, Anwer Z M and El-Ghol S, *J Coord Chem.*, 2009, **62(10)**, 1709-1718; DOI:10.1080/00958970802684205
7. Ziegler J, Schuerle T, Pasierb L, Crystal Kelly, Ashraf Elamin, Kelly A Cole and David W Wright, *Inorg Chem.*, 2000, **39(16)**, 3731-3733; DOI:10.1021/ic000295h
8. Chittilappilly P S, Sridevi N and Yusuff K K M, *J Mol Catal A Chem.*, 2008, **286(1-2)**, 92-97; DOI:10.1016/j.molcata.2008.02.002
9. Arun V, Sridevi N, Robinson P P, Manju S and Yusuff K K M, *J Mol Catal A Chem.*, 2009, **304(1-2)**, 191-196; DOI:10.1016/j.molcata.2009.02.011
10. He X, Lu C Z and Wu C D, *J Coord Chem.*, 2006, **59(9)**, 977-984; DOI:10.1080/00958970500440553

11. Maldhure A K and Aswar A S, *J Indian Chem. Soc.*, 2009, **86**, 697-702.
12. Chen G J J, McDonald W and Newton W E, *Inorg Chem.*, 1976, **15(11)**, 2612-2615; DOI:10.1021/ic50165a008
13. Singh N K, Singh D K and Singh J, *Indian J Chem Sec A*, 2001, **40**, 1064.
14. Rupini B, Mamatha R, Mogili R, et al., *J Indian Chem Soc.*, 2007, **84**, 630.
15. Nair M L H and Siji V L, *J Indian Chem Soc.*, 2009, **86**, 448.
16. Dash D C, Mohapatra R K, Ghosh S and Naik P, *J Indian Chem Soc.*, 2009, **86**, 123.
17. Sarkar A R and Mandal S, *Synth React Inorg Met-Org Chem.*, 2000, **30(8)**, 1477-1488; DOI:10.1080/00945710009351847
18. Hankare P P, Patil R K and Chavan S S, Jagtap A H and Battase P S, *Ind J Chem Sec A*, 2001, **40**, 1326-1329.
19. Gupta K C and Sutar A K, *J Mol Catal A: Chem.*, 2007, **272(1-2)**, 64-74; DOI:10.1016/j.molcata.2007.03.025
20. Maurya M R, Khurana S and Rehder D, *Eur J Inorg Chem.*, 2001, 773.
21. Aranha E P, Dos Santos M P, Romera S and Dockal E R, *Polyhedron*, 2007, **26(7)**, 1373-1382; DOI:10.1016/j.poly.2006.11.005
22. Vafazadeh R and Kashfi M, *Bull Korean Chem Soc.*, 2007, **28(7)**, 1227; DOI:10.5012/bkcs.2007.28.7.1227
23. El-Saied F A, Ayad M I, Issa R M and Aly S A, *Pol J Chem.*, 2000, **74(7)**, 919.
24. Mandlik P R, Aswale S R and Aswar A S, *J Indian Chem Soc.*, 2002, **79**, 690.
25. Syamal A and Maurya M R, *Coord Chem Rev.*, 1989, **95(2)**, 183-238; DOI:10.1016/0010-8545(89)80026-8
26. Selbin J, *Angew Chem.*, 1996, **5**, 712.
27. Khandar A A, Netaji K and Rezvani Z, *Molecule*, 2005, **10**, 302.
28. Halli M B and Qureshi Z S, *Ind J Chem Sec A*, 2004, **43**, 2347.
29. Pessoa J C, Kiss T, João Costa Pessoa, Teresa Duarte M, Fátima Minas da Piedade M, Tamás Jackush, Margarida M C A Castro, Carlos F G C Geraldes and Fernando A, *Eur J Inorg Chem.*, 2005, **4**, 732-744; DOI:10.1002/ejic.200400481
30. Kureshy R I, Khan N H, Abdi S H R et al., *Polyhedron*, 1999, **18**, 1775.
31. Horowitz H H and Metzger G, *Anal Chem.*, 1963, **35(10)**, 1464-1468; DOI:10.1021/ac60203a013
32. Bansod A D, Mahale R G and Aswar A S, *Russian J Inorg Chem.*, 2007, **52(6)**, 879-883; DOI:10.1134/S0036023607060113
33. Bolos C A, Nikolov G S, Ekateriniadou L et al., *Russian J Inorg Chem.*, 2007, **52(6)**, 882.
34. Maurya M R, Kumar U, Correia I, Pedro A and João C P, *Eur J Inorg Chem.*, 2008, **4**, 577-587; DOI:10.1002/ejic.200700662