



<http://www.orientjchem.org>

ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (1): Pg. 185-190

Synthesis, Characterisation and Antibacterial Studies of Transition Metal Complexes Derived from S-benzyl- β -N-(2-hydroxy-5-bromophenyl) Methylendithiocarbazate

MANMEET SINGH* and RAJNEESH SAXENA

Department of Chemistry, S.M. College, Chandausi (India).
E-mail: mssinghmanmeet@gmail.com

(Received: December 07, 2010; Accepted: January 11, 2011)

ABSTRACT

The Complexes of Ti(iii), V(iii), Mn(iii), Co(iii), Ru(iii), Ru(ii), MoO(v), Fe(iii), MoO₂(vi) and UO₂(vi) with S-benzyl- β -N-(2-hydroxy-5-bromophenyl) methylendithiocarbazate have been synthesized and characterised by melting points, molar conductance, magnetic susceptibility, electronic and IR spectral studies. The complexes of Ti(iii), V(iii), Mn(iii), Ru(iii) & MoO(v) are paramagnetic while all other complexes are diamagnetic. Based on these studies octahedral geometry have been proposed for all the complexes. The ligand and its metal complexes have been screened for antimicrobial activities.

Key words: Triazin, Octahedral, Antimicrobial activities and Transition metal.

INTRODUCTION

The importance of schiff base ligands and their complexes with transition metals have enhanced especially due to their biological applications. Metal chelates of certain multidentate schiff bases have been used for the purification of metals because of their high volatility and solubility in non polar solvents^{1,2}. The metal complexes with schiff bases find various industrial and biological applications. A few reports^{3,4} have appeared on the synthesis of triorganotin (iv) complexes of schiff bases derived from S-benzyl and S-methylendithiocarbazates. New chelated transition metal and uranium compounds with schiff bases

derived from S-benzylidithiocarbazate and o-hydroxyacetophenone, 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde are reported in this paper.

EXPERIMENTAL

Materials

All chemical used were of A.R. or equivalent grade. The metal salts used were TiCl₃, VCl₃, MnCl₃, CoCl₃, RuCl₃, RuCl₂, FeCl₃, MoO(v), MoO₂(vi) and UO₂(vi). TiCl₃ was prepared in the layer while all other salts were used as such. The solvents were carefully purified throughly dried and still before used.

Preparation of the ligands

O-hydroxyacetophenone, S-benzylthiocarbamate (HyAcSBDTC-H₂) was prepared using hydrazine hydrate, O-hydroxyacetophenone, carbon disulphide and benzyl chloride. The yellow crystals thus obtained melted at 152°C.

Preparation of new complexes

The metal salt was dissolved in benzene and added slowly to the benzene solution of the ligand. The mixture was refluxed for 2 hours when a solid product was obtained which was filtered, washed with hexane and dried in vacuo.

METHODS

The microanalyses for C, H & N was carried out at CDRI, Lucknow. Metals and sulphur were estimated gravimetrically in the lab. The molar conductance was measured by digital conductivity meter (HPG System, G-3001) in DMSO at room temperature. Magnetic susceptibility was determined by Gouy's balance using CuSO₄·5H₂O as calibrant. The electronic spectra was recorded at Beckmann DV-spectrophotometer. IR spectra were recorded in KBr phase at CDRI, Lucknow.

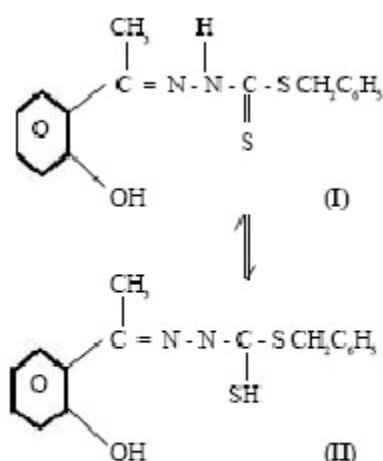
Antimicrobial activity

The antibacterial and antifungal activities

of Schiff bases and their corresponding metal chelates were evaluated by agar well diffusion method. The antimicrobial activity of all the synthesized compounds was evaluated by measuring the zone of growth of inhibition against the test organisms with zone reader (Hi antibiotic zone scale). The medium with DMSO as solvent was used as a negative control whereas media with ciprofloxacin (antibacterial) and griseofulvin (antifungal) were used as the positive controls. The ligands and their M(III) complexes were tested for their antibacterial activity against bacteria *E.coli*, *S.aureus*, *Paeruginosa* and *B.megaterium* and for antifungal activity against the fungi *K.fragilis*, *R.rubra*, *C.albicans* and *T.recsei*.

RESULTS AND DISCUSSION

The elemental analyses suggested 1:1 stitometry for all the synthesized complexes. The molar conductance values at 10⁻³ M dilution in DMSO suggested 1:1 electrolytic nature for all the complexes (Table 1). The values of effected magnetic moment for all the complexes of Ti(III), Mn(III) Co(III) Ru(III), Fe(III) & MoO(v) suggested paramagnetic nature whereas the complexes of Ru(II), MoO₂(VI) and UO₂(VI) are diamagnetic in nature. The schiff bases derived from S-benzylthiocarbamate have the structural formulae I or II.



Where X=H, R=CH₃ (HYAcSBDTC-H₂)

They have a thione (C = S) group and an adjacent imino proton; these conditions are most favourable for enthiolisation of the thione group to the more stable C-SH form (5). However, the IR spectra of the present ligands do not display ν_{SH} at 2570 cm^{-1} indicating the presence of thioketo form in the solid state and in solution. But, in the presence of metal ions the enthiolisation of the schiff bases is considerably enhanced. The IR spectrum of the

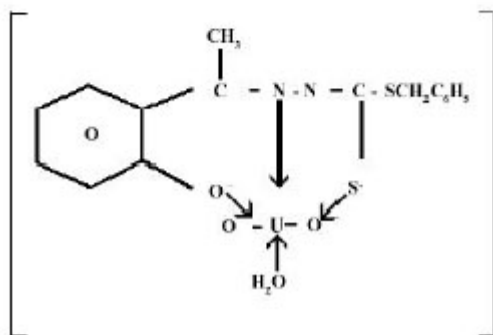
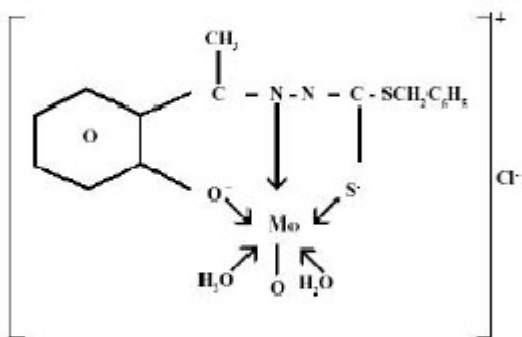
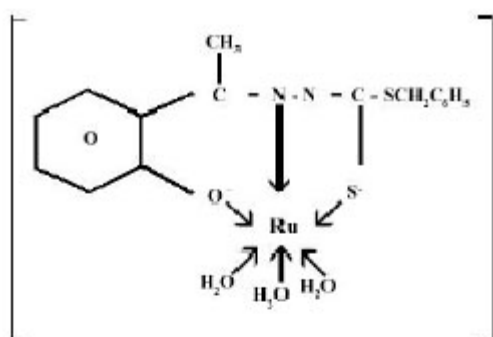
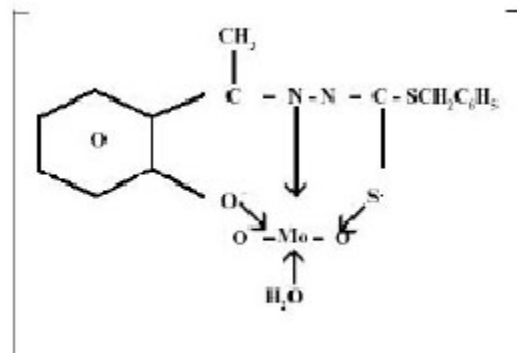
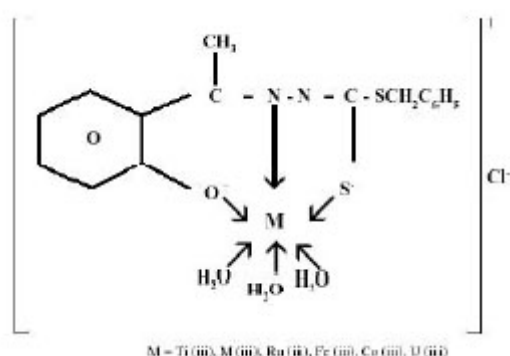
ligands (band positions in cm^{-1}) HyAcSBDTC- H_2 in nujol shows a strong ν_{N-H} band around 3160; in the chloro and bromo-derivatives, this band is seen around 3080. The ν_{O-H} mode is lowered and overlaps with RC-H mode. However, the spectra of the ligands in CCl_4 solution shows ν_{N-H} and ν_{O-H} bands at 3350-3320 and 3230-3200 respectively indicating hydrogen bonding in the solid state. The bands occurring at 1610, 1045-1030 and 940-920

Table 1: Elemental Analysis (%) found

Compounds	M.P. ($^{\circ}\text{C}$)	C	H	N	S	Cl
[Ti (C ₁₆ H ₂₀ O ₄ N ₂ S ₂)Cl]	(262)	42.48	4.36	6.15	14.10	7.84
Yellow		(42.52)	(4.42)	(6.20)	(14.17)	(7.86)
[V (C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	(324)	42.20	4.35	6.11	14.01	7.75
Light yellow		(42.24)	(4.40)	(6.16)	(14.08)	(7.81)
[Fe(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	(302)	41.72	4.30	6.00	13.90	7.66
Reddish brown		(41.78)	(4.35)	(6.09)	(13.92)	(7.72)
[Ru(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	(289)	38.00	3.91	5.51	12.60	6.95
Green		(38.05)	(3.96)	(5.55)	(12.68)	(7.03)
[Co (C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	(296)	41.45	4.26	6.01	13.77	7.59
Pinkish yellow		(41.51)	(4.32)	(6.05)	(13.83)	(7.67)
[Ru(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	(342)	40.88	4.19	5.91	13.59	-
Yellowish green		(40.93)	(4.26)	(5.97)	(13.64)	
[Mo [(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	(256)	38.52	3.55	5.57	12.79	7.07
Brown		(38.59)	(3.61)	(5.62)	(12.86)	(7.13)
[U(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	(311)	31.83	2.60	4.59	10.58	-
Brown		(31.89)	(2.65)	(4.65)	(10.63)	
[Mo(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	(267)	41.67	3.42	6.02	13.85	-
off White		(41.73)	(3.47)	(6.08)	(13.91)	
[Mn(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)Cl]	(271)	41.83	4.30	6.03	13.88	7.66
Brown		(41.87)	(4.36)	(6.10)	(13.95)	(7.74)

Table 2: Antimicrobial activities of transition metal complexes (Zone formation in mm)

Compounds	<i>S. typhi</i>	<i>S. aureus</i>	<i>K. pneumoniae</i>	<i>B. subtilis</i>	<i>S. flexneri</i>	<i>P. aeruginosa</i>
[Ti (C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	8	11	13	7	16	11
[V (C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	16	13	15	13	21	22
[Fe(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	17	16	13	16	27	19
[Ru(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	13	17	21	19	28	25
[Co (C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	19	21	25	22	17	28
[Ru(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	15	26	26	23	25	26
[Mo [(C ₁₆ H ₂₀ O ₄ N ₂ S ₂) Cl]	14	14	21	29	12	29
[U(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	11	18	10	15	8	14
[Mo(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)]	13	14	27	12	13	25
[Mn(C ₁₆ H ₂₀ O ₄ N ₂ S ₂)Cl]	15	22	29	18	21	16



in the ligand spectra have been assigned to $\nu\text{C}=\text{N}(6)$, $\nu\text{C}=\text{S}3$ and $\nu\text{N}-\text{N}$ respectively.

The spectra of chelated titanium derivatives show complete absence of $\nu\text{O}-\text{H}$ and $\nu\text{N}-\text{H}$ indicating the dibasic nature of the ligand. The $\text{VC}=\text{N}$ mode is lowered indicating its coordination with titanium⁷. The $\nu\text{C}-\text{S}$, $\nu\text{N}-\text{N}$ and $\nu\text{C}-\text{O}$ modes are observed at 1025- 1000, 970-920 and 1255-1240 respectively indicating complexation^{8,9} of the ligands.

The presence of coordinated water molecules has been suggested by the appearance of non ligand bands in the IR spectra of the complexes in the range of 3410-3420 cm^{-1} (νOH), 845-855 cm^{-1} (wagging) and 740-750 cm^{-1} (rocking) modes of coordinated water molecules. This was further supported by TGA. The thermiograms showed the loss of water molecules above 160°C.

The uranium complexes shows the Vasy ($\text{O}=\text{U}=\text{O}$) at 905 cm^{-1} and this band occurs in the usual range (870-950 cm^{-1}) observed for the majority of trans-UO_2 compounds. The MoO_2 complexes exhibits the Vsy ($\text{O}=\text{Mo}=\text{O}$) and Vasy ($\text{O}=\text{Mo}=\text{D}$) stretches at 945 and 905 cm^{-1} and these occur in the usual range (892-964 cm^{-1} ; 840-925 cm^{-1}) reported the majority of MoO_2 (ii) compounds.

The MoO_5 complex shows in non ligand band at 950 cm^{-1} due to $\text{Mo}=\text{O}$ band. The observed value of magnetic susceptibility was used to calculate the spin only value of magnetic moment, which came out to be 1.68 B.M. This value suggested paramagnetic nature of the complex and that Ti (iii) has not been oxidised to Ti (iv) during or after complexation. The electronic spectrum of the

complex has shown a single broad band at 19500 cm^{-1} which has been assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ for octahedral symmetry¹².

The spin only value for the magnetic moment of the complex calculated from the observed value of magnetic susceptibility come out to be 2.89 B.M. This is very close to the calculated value for d^2 ion like V^{+3} . The electronic spectrum of the complex showed band at 16000 cm^{-1} with a shoulder at 21000 cm^{-1} . The low energy band has been assigned to $3T_{1g} \rightarrow 3T_{2g}$ whereas the high energy band to $3T_{1g} \rightarrow 3T_{1g}$ (P) transitions respectively. These are characteristic of octahedral geometry¹³.

The μ_{eff} value for the complex is 5.20 B.M. which is in good agreement with manganese (iii) complexes. Mn (iii) has a 5D electronic ground state in pure octahedral symmetry. In the electronic spectrum of this complex exhibits two bands at 19000 and 13000 cm^{-1} assignable to ${}^5B_1 \rightarrow {}^5B_2$ and ${}^5B_1 \rightarrow {}^5E_g$ transition respectively and are characteristic of octahedral geometry¹⁴.

The room temperature magnetic susceptibility and the magnetic moment of the complex are 14518×10^{-6} cgs and 5.87 B.M. respectively. This value corresponds to Fe^{3+} (d^5) configuration and suggested paramagnetic nature for the complexes. The electronic spectrum of the complex exhibits three bands at 12730, 19650 and 25000 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ transitions respectively and are characteristic of octahedral symmetry¹⁵.

The ground state of Ru(iii) is ${}^2T_{2g}$ and the first doublet levels in order of increasing energy are ${}^2A_{2g}$ and ${}^2T_{1g}$ which arise from t_{2g} , e_g configuration. The electronic spectrum of the complex displays bands at 13650 cm^{-1} , 17500 cm^{-1} and 22550 cm^{-1} which may be assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$, ${}^2T_{1g} \rightarrow {}^4T_{2g}$ and ${}^2T_{2g} \rightarrow {}^2A_{1g}$, ${}^2T_{1g}$ transitions respectively. These are characteristic of Ru(iii) octahedral complexes¹⁶. The ruthenium(ii) complex is diamagnetic in nature. This has indicated the presence of ruthenium in the +2 oxidation state. The electronic spectrum of the complexes showed at single band at 23000 cm^{-1} . This band has been assigned to the charge transfer transition arising from the excitation of an electron

from metal t_{2g} level to the unfilled molecular orbital derived from π^* level of the ligand, in accordance with the assignments made for other similar octahedral Ru(ii) complexes¹⁷.

The magnetic susceptibility measurement has suggested diamagnetic nature for the complex as expected d^0 system. The electronic spectrum of dioxymolybdenum (vi) complex shows absorption bands of considerably high intensity at 35000 and 30000 cm^{-1} . These bands may be assigned to ligand-metal charge transfer transitions¹⁸.

The μ_{eff} for the complex calculated from the observed value of magnetic susceptibility is 1.76 B.M. at room temperature, which indicated the presence of Mo(V) state of the metal. The electronic spectrum of the metal chelate suggested octahedral geometry with a strong tetragonal distortion resulting from molybdenum-oxygen bond. The spectrum exhibits three absorption bands at 13500, 19600 and 25000 cm^{-1} assignable to the transitions ${}^2B_2 \rightarrow 2E$ ($d_{xy} \rightarrow d_{xz}$, d_{yz}), ${}^2B_2 \rightarrow 2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and ${}^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z^2}$) transitions respectively¹⁹.

The study of magnetic properties suggested that the complex is diamagnetic in nature as expected for f^0 system. The electronic spectrum of uranyl complex shows bands at 21750, 25200 and 37000 cm^{-1} consistent with vibronic structure of triatomic entity of UO_2 group. This complex has octahedral geometry²⁰.

The Co (iii) complex is diamagnetic in nature as expected for a low spin d^6 ion. The electronic spectrum of the cobalt (iii) complex displays bands at 15200, 21100 and 23400 cm^{-1} which may be assigned to ${}^1A_{1g} \rightarrow {}^3T_{2g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively. These are similar to those reported for other six coordinated Co (III) complexes²¹.

CONCLUSIONS

On the basis of studies performed octahedral geometry may be proposed for all the complexes with a distortion in case of oxomolybdenum (V) complex due to Mo = O moiety.

Antimicrobial activity

The in vitro biological screening effects of the investigated compounds were tested against six bacteria : Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa and Shigella flexneri. The measured zone of inhibition against the growth of various microorganisms is listed in (Table 2).

A comparative study of the ligands and their complexes indicates that most of the metal chelates exhibit higher antimicrobial activity than that of the free ligand and the control. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and chelation theory.

REFERENCES

1. A. Bansal and R.V. Singh, *Synth. React. Inorg. Met. - Org. Chem.*, **31**: 381 (2001).
2. Nedra Pal Singh, Vaibhav Pratap Tyagi and Bindiya Ratnam, *J. Chem. Pharm. Res.*, **2**(1): 473-477 (2010).
3. Srivastava T N, Chauhan A K S and Agarwal M, *Synth react inorg metal org Chem.* **10**: 29 (1980).
4. Pardhy S A, Gopinathan S, and Gopinathan C, *Indian J. Chem.* **19**: 130 (1980).
5. Mayer R, *Organosulphur Chemistry* (Interscience, New York), 219 (1967).
6. Kovacc J E, *Spectrochim Acta*, **23A**: 183 (1967).
7. Tandon J P and Prasad R N, *J. Inorg Nucl. Chem.*, **37**: 35 (1975).
8. Aggarwal R C and Singh S K *Indian J. Chem.* **7**: 810 (1969).
9. Bellamy, L J, *The infrared spectra of complex molecules* (Methuen London) 108 (1959).
10. Syamal A and Singh M M, *React Funct. Polym.*, **21**: 45, 149 (1993).
11. Syamal A and Maurya M R *Coord Chem. Rev.* **95**: 183 (1989).
12. Samik Gupta, S. Roy, T N Mandal, K. Das, S. Ray, R.J. Butcher and S K Kar, *J. Chem. Sci.*, **122**(2): 239-245 (2010).
13. Rahul Kumar Rastogi, Poonam Garg and Shamim Ahmad, *Asian Journal of Chemistry* **21**: 6144-6148 (2009).
14. Mahesh K. Singh, Samhita Bhaumik and Ram A. Lal, *J. Indian Chem. Soc.*, **84**: 418-426 (2007).
15. A Syaml, D Kumar, A K Singh, P K Gupta, Jaipal and L K Sharma, *Indian Journal of Chemistry*, **41A**: 1385-1390 (2002).
16. T. Daniel Thangadurai and K. Natarajan, *Indian Journal of Chemistry* **41A**: 741-745 (2002).
17. K.P. Balasubramanian, S. Manivannan and V. Chinnusamy, *J. Indian Chem. Soc.* **85**: 1075-1081 (2008).
18. A Syamal and M M Singh, *Indian Journal of Chemistry*, **32A**: 42-48 (1993).
19. A Syamal and M M Singh, *Indian Journal of Chemistry*, **32A**: 42-48 (1993).
20. D Kumar, A Syamal and AK Singh, *Indian Journal of Chemistry*, **42A**: 280-286 (2003).
21. Vinod K Sharma and Shipra Srivastava, *Indian Journal of Chemistry*, **45A**: 1368-1374 (2006).