

**INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN
CHEMISTRY AND PHARMACEUTICAL SCIENCES**

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

www.ijcrfps.com

DOI:10.22192/ijcrfps

Coden: IJCROO(USA)

Volume 4, Issue 1 - 2017

Research Article



DOI: <http://dx.doi.org/10.22192/ijcrfps.2017.04.01.003>

Synthesis and spectral characterization of oxovanadium complexes derived from benzoin, O-phenylenediamine and ethylenediamine and their antibacterial activities

N.Gayathri and M.S.Suresh *

Department of Chemistry, Government Arts College, Udthagamandalam-643002,
The Nilgiris, Tamil Nadu, India.

*Corresponding Author: mssgacooty@gmail.com sanjeevigk@gmail.com

Abstract

Two square pyramidal vanadyl complexes have been synthesized using tetradentate Schiff bases, by the condensation of benzoin and o-phenylenediamine/ethylenediamine in the ratio 2:1. These complexes were characterised using elemental analysis, FTIR, UV-Visible, ESR spectroscopic methods, magnetic susceptibility, molar conductivity measurements and thermal analysis. These complexes have the general formula $[VO(L)]$, where L - tetradentate Schiff bases were found to be non-electrolytic in nature. The infrared spectra reveals that two azomethine nitrogens ($-C=N-$) and two oxygen atoms from the ligands are coordinated to oxovanadium(IV) resulted in $VO(N_2O_2)$ chromophore. The electronic spectra suggested that they were square pyramidal in shape. The thermal decomposition of one the compound $VO(BOP)$ shows that it was thermally unstable. The eight line hyperfine splitting in ESR spectra indicates that a single vanadium is present in the molecule and both are paramagnetic. The metal complexes have been screened for their antibacterial activity against organisms like *E.coli*, *S.aureus*, *Serratia sp*, *P.aeruginosa* and *B.cereus*, and the complexes have more activity than the ligand.

Keywords: Benzoin, o-phenylenediamine, ethylenediamine, oxovanadium complexes, antibacterial studies

Introduction

A ketone or an aldehyde when condensed with a primary amine, schiff base, a compound containing azomethine group $R-C=N-$ is obtained, which on interaction with metal ions yield stable chelates with special properties. They have applications in biological, biochemical, anticancer, analytical and catalytic fields and possess antimicrobial activity. Also tetradentate Schiff bases containing N_2O_2 donor atoms are very important chelating ligands for designing medicinally and catalytically useful metal chelates⁽¹⁻⁴⁾. Vanadium is found to be very important element because it exhibit variety of insulin mimetic properties⁽⁵⁾. It decreases the insulin requirements of diabetic rats and supplementation of vanadium in the diet at subtoxic level leads to variety of metabolic changes including disturbances in the sulphur metabolism and cholesterol synthesis⁽⁶⁻⁸⁾.

From the literature survey it was revealed that the synthesis of both these tetradentate Schiff bases from benzoin and ethylenediamine/o-phenylenediamine, with N_2O_4 system, and their metal complexes (Co^{2+} , Ni^{2+} , Cu^{2+} and Mn^{2+}) were reported by H.N.Aliyu et.al^(9,10). But these complexes were characterized by IR, specific conductance, colour and its solubility only, and also their interaction with oxovanadium(IV) was not reported. As a continuation of our studies to synthesise oxovanadium complexes of Schiff bases, the present manuscript describes the synthesis of square pyramidal oxovanadium(IV) complexes of these ligands and their characterisation using elemental analysis, FTIR, UV-Vis, ESR spectroscopic methods, molar conductance, magnetic susceptibility measurements and thermal analysis.

Experimental

Benzoin, o-phenylene diamine, ethylene diamine, vanadylsulphate, ethylalcohol, etc. were purchased from Merck and used as such without any further purification. The elemental analysis (CHNS) were performed using EL elemental analyser at Central Electrochemical Research Institute (CECRI). The FT infrared spectra were recorded in the range 4000-400 cm^{-1} on a Shimadzu FTIR 8400S spectrometer using KBr pellet techniques. Electronic (UV-VIS) spectra were recorded on a Shimadzu UV-spectrophotometer in the range 200- 1100 cm^{-1} using DMSO solvent. The thermal analyses were carried out using universal V4.5A Thermal analysis instrument in an atmosphere of static air with a heating rate of 10K/min. The ESR spectra of various Schiff base complexes were recorded on a JES-X₃ series in the scan range of 2300-4300 Gauss. The molar conductance was measured on ELICO-CM180 using

DMSO as the solvent at room temperature. The magnetic susceptibility measurements of the complexes were carried out using a Guoy balance method. The antibacterial studies was carried out with disc diffusion method.

Synthesis of schiff bases

a) From Benzoin and O-Phenylenediamine (BOP)

To the ethanolic solution of benzoin (4.42g, 0.02mol in 20ml ethanol) an ethanolic solution of o-phenylene diamine (1.08g, 0.01mol in 20ml ethanol) was added, followed by the addition of sodium acetate (4g), and the mixture was refluxed for an hour. The hot solution was poured into ice cold water and yellow precipitate of the Schiff base separated out. It was filtered, washed with water, dried and recrystallised from ethanol^(9,11). Their scheme of preparation is shown in Figure 1

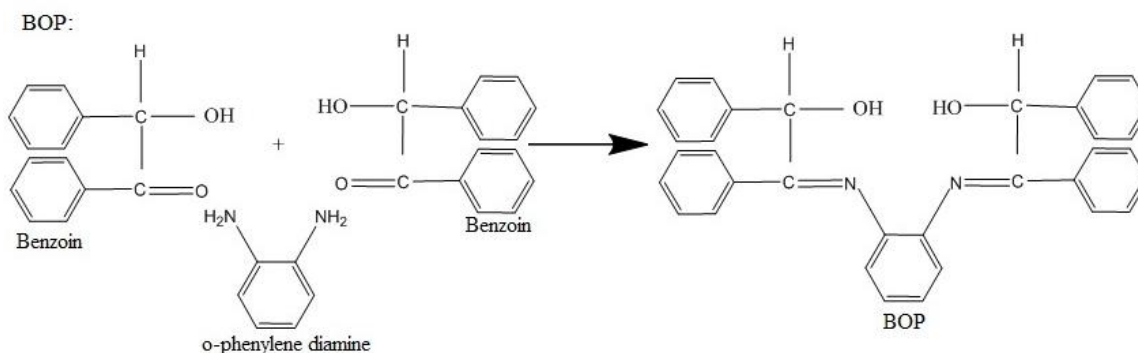


Figure 1: Schematic representation of synthesis of tetradentate ligand BOP

b) From Benzoin and Ethylenediamine (BED)

The same method was adopted for ethylenediamine^(10,11) complex also in which (4.48g,

0.01mol) ethylenediamine dissolved in 20ml alcohol was used instead of o-phenylenediamine. Its scheme is represented in Figure 2.

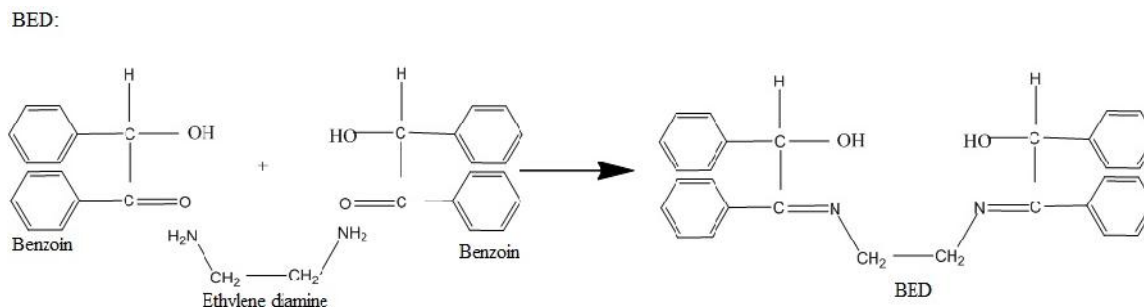


Figure 2: Schematic representation of synthesis of tetradentate ligand BED

A solution of the Schiff base was prepared by dissolving 4.96g, (0.01mol) in 50mL ethanol. To this solution an ethanolic solution of VOSO_4 (2.53g,0.01mol) was added followed by dropwise addition of ammonia. The dark green coloured complex was precipitated out, separated, filtered and washed several times with distilled water and hot ethanol. The same method was used for other complex with a solution containing 4.48g,0.01 mol of the ligand BED in 20ml ethanol⁽¹¹⁾.

The Analytical data (Table 1) suggests that the synthesized complexes have the molecular formula $[\text{VO}(\text{BOP})]$ and $[\text{VO}(\text{BED})]$ where BOP and BED are the tetradentate Schiff bases (1:1 metal to ligand stoichiometry). These complexes are stable, non-hygroscopic and dark green in colour. They have molar conductance in the range of 11-12.5 $\text{S cm}^2\text{mol}^{-1}$ indicating that they are non-electrolytic in nature. The physical, analytical and conductivity data are presented in Table 1

Table 1:Physical characterisation, analytical and molar conductance data.

Compound	Mol.Wt	Colour	Yield	Elemental Analysis (%) Found (Calc)				Λ_m $\text{S cm}^2\text{mol}^{-1}$
				C	H	N	M	
$\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2(\text{BOP})$	496.56	Yellow	75%	82.20 (82.23)	5.600 (5.683)	5.700 (5.638)	--	--
$[\text{VO}(\text{BOP})]$	561.48	Dark Green	65%	69.29 (72.72)	4.929 (5.026)	4.133 (4.986)	11.87 (11.92)	11
$\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2(\text{BED})$	448.52	Yellow	75%	80.11 (80.33)	6.300 (6.292)	6.200 (6.242)	--	--
$[\text{VO}(\text{BED})]$	513.44	Dark Green	65%	71.24 (70.17)	5.236 (5.496)	5.702 (5.453)	13.10 (13.03)	12.5

Infrared analyses

The O-H absorption observed in the region 3416-3379 cm^{-1} in benzoin was there in the ligand prepared from benzoin and o-phenylenediamine, but was missing in the vanadyl complex synthesized. It is due to the deprotonation of the O-H group of the ligand and coordination of oxygen to the metal. The band at 1680 cm^{-1} was observed in the new ligand (BOP) is assigned to C=N of azomethine group was shifted to lower frequency 1660 cm^{-1} . The lowering of this band supports coordination of N atoms of azomethine group to the VO^{2+} ⁽¹²⁻¹⁵⁾. It was further supported by M-N peak at 466 cm^{-1} and M-O peak at 580 cm^{-1} . The peak observed at 987 cm^{-1} was due to V=O .

In ethylenediamine-benzoin complex, also the absorption at 3415-3379 cm^{-1} due to O-H was found to be missing, due to deprotonation and coordination of oxygen to the metal. The azomethine C=N absorption at 1610 cm^{-1} in the free ligand was shifted to lower frequency 1585 cm^{-1} and new peaks at 449 cm^{-1} , 596 cm^{-1} were assigned to be M-N & M-O respectively. These data support the coordination of azomethine group to oxovanadium group^(16,17). The coordination of nitrogen atom of azomethine group to metal is expected to reduce the bond order of C=N group and hence decreases its stretching frequency (C=N). The IR data are presented in Table 2.

Table 2. Infra-red spectral data of the Schiff bases and its vanadyl complexes

Compound	OH	OH-bending	C=N	C-H	M-N	M-O	V=O
Benzoin	3416-3379	1388	-	3028,3084, 3059	-	-	-
$\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2$ (BOP)	3416- 3361	-	1680	3028,3084, 3059	-	-	-
$[\text{VO}(\text{BOP})]$	-	-	1660	3065	466	580	987
$\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$ (BED)	3415-3379	-	1610	3067-3037	-	-	-
$[\text{VO}(\text{BED})]$	-	-	1585	3060-3028	449	596	976

UV-VIS Electronic spectra and magnetic susceptibility measurements

The free ligands shows absorption maxima appearing around 35714 and 30769 cm^{-1} for BOP and 34482 and 26315 cm^{-1} for BED was due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively. But in the complex three higher energy bands appearing around 21008, 15151 and 11627 cm^{-1} assigned to

${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ for complex 1 and 21008, 16000 and 11235 cm^{-1} due to

${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ for complexes 2 respectively. These absorption bands are typical of square pyramidal⁽¹⁸⁻²²⁾ VO^{2+} species.

Table 3. UV-Visible Spectral Data and magnetic moments

Compound	Absorption Max (cm^{-1})	Assignments	μ (BM)
$\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2(\text{BOP})$	35714 30769	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	
$[\text{VO}(\text{BOP})]$	21008 15151 11627	${}^2B_2 \rightarrow {}^2A_1$ ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2E$	1.98 BM
$\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2(\text{BED})$	34482 26315	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	
$[\text{VO}(\text{BED})]$	21008 16000 11235	${}^2B_2 \rightarrow {}^2A_1$ ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2E$	1.99 BM

The magnetic moments of these complexes were seen to be in the range 1.98 - 1.99 BM which are also supporting the square pyramidal geometry of VO^{2+} complexes, a $3d^1$ system⁽²²⁾. The electronic spectral details and magnetic moments were presented in Table 3.

Thermal studies

From the thermogram (Figure 3) the o-phenylenediamine oxovanadium complex $[\text{VO}(\text{BOP})]$

was found to be thermally stable upto 50 $^{\circ}\text{C}$. When temperature increases, a mass loss of 20% was observed at the temperature range 50-90 $^{\circ}\text{C}$. The second stage of decomposition starts immediately at 90 $^{\circ}\text{C}$ and progressing till 175 $^{\circ}\text{C}$, with a mass loss of 21%. The third stage is seen starting at 175 $^{\circ}\text{C}$ and ends at 1000 $^{\circ}\text{C}$. But even at 1000 $^{\circ}\text{C}$ the decomposition does not stop and a horizontal plateau, for a stable residue was not obtained.

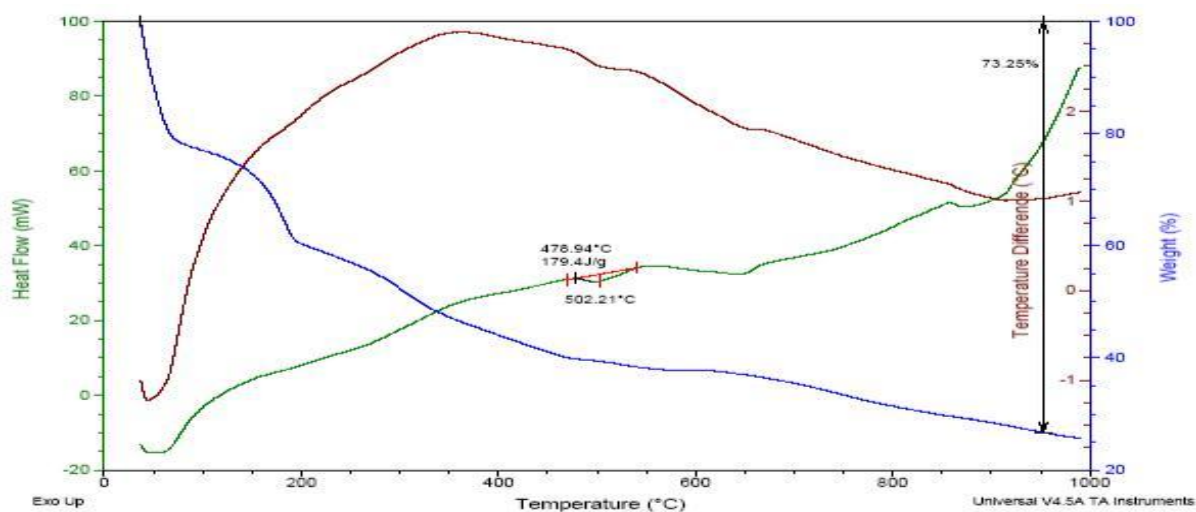


Fig 3: TG/DTA curve of $[\text{VO}(\text{BOP})]$ in Static Air

On heating, the loss of bulky Schiff base from the complex takes place in three different stages and finally V_2O_5 , a stable residue was expected, with a mass percentage of 15.70%. But even at 1000°C the mass percentage observed was only 25% , indicates that the decomposition is not yet completed.

ESR Spectroscopy

The X-band ESR spectra of both the complexes were recorded in DMSO at LNT (177K), given in Figure 4&5. In the frozen state, it shows two sets of eight lines which are due to parallel and perpendicular resonance feature of VO^{2+} . The eight line peaks are due to hyperfine splitting originating from the interaction of unpaired electrons with ^{51}V nucleus having a nuclear spin of

$I=7/2$. This confirms the presence of single oxovanadium(IV) in the complexes. The g_{\parallel} , g_{\perp} , $g_{(av)}$

$$g_{\parallel} = g_{\perp} \quad \text{-----} \quad (1)$$

$$g_{(av)} = 1/3(g_{\parallel} + 2 g_{\perp}) \quad \text{-----} \quad (2)$$

$$A_{(av)} = 1/3 (A_{\parallel} + 2 A_{\perp}) \quad \text{-----} \quad (3)$$

A_{\parallel} , A_{\perp} , and $A_{(av)}$ are calculated using the equation.

and represented in Table 4. It was found that $g_{\parallel} < g_{\perp}$ in both the complexes, is in good agreement with square pyramidal geometry. For ethylenediamine complex g -values are very close to spin only value of 2.0020 (free electron) suggesting little spin – orbit coupling⁽²³⁻²⁵⁾.

Table 4: ESR spectral data of the complexes

Complex	g_{\parallel}	g_{\perp}	$g_{(av)}$	A_{\parallel} (G)	A_{\perp} (G)	$A_{(av)}$ (G)
VO(BOP)	1.929	1.9570	1.9477	195.04	86.07	122.39
VO(BED)	1.963	2.0076	1.9929	197.19	73.17	114.50

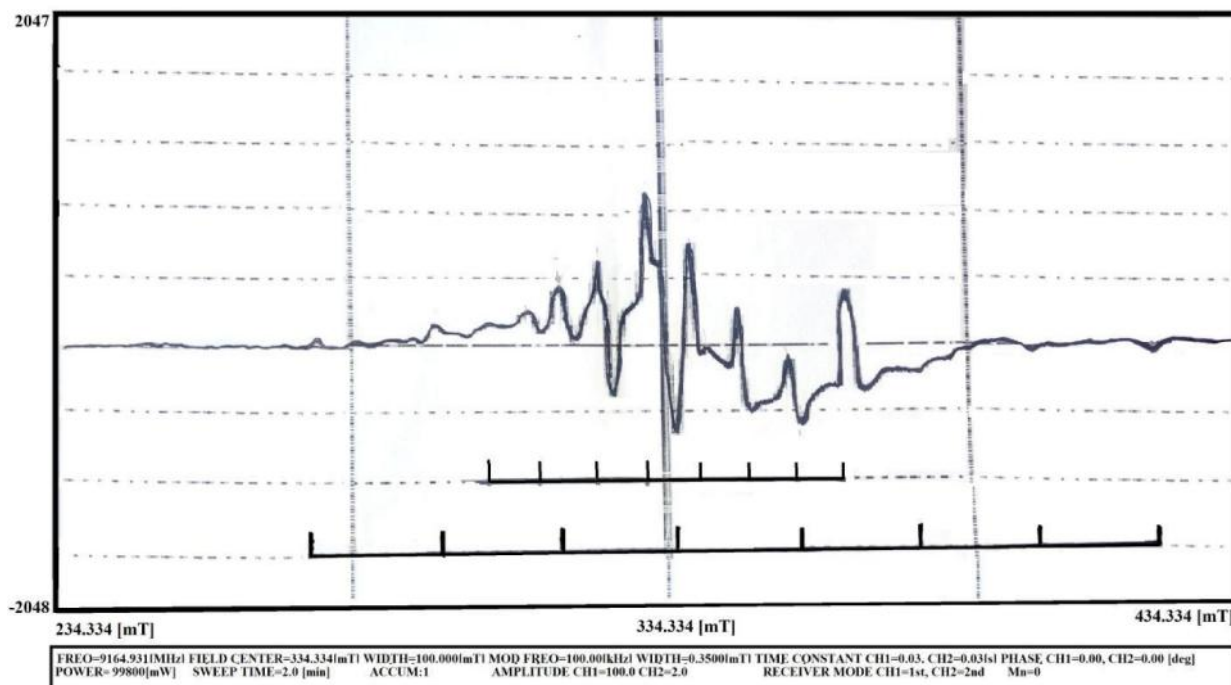


Figure 4: ESR Spectrum of VO(BOP) in LNT

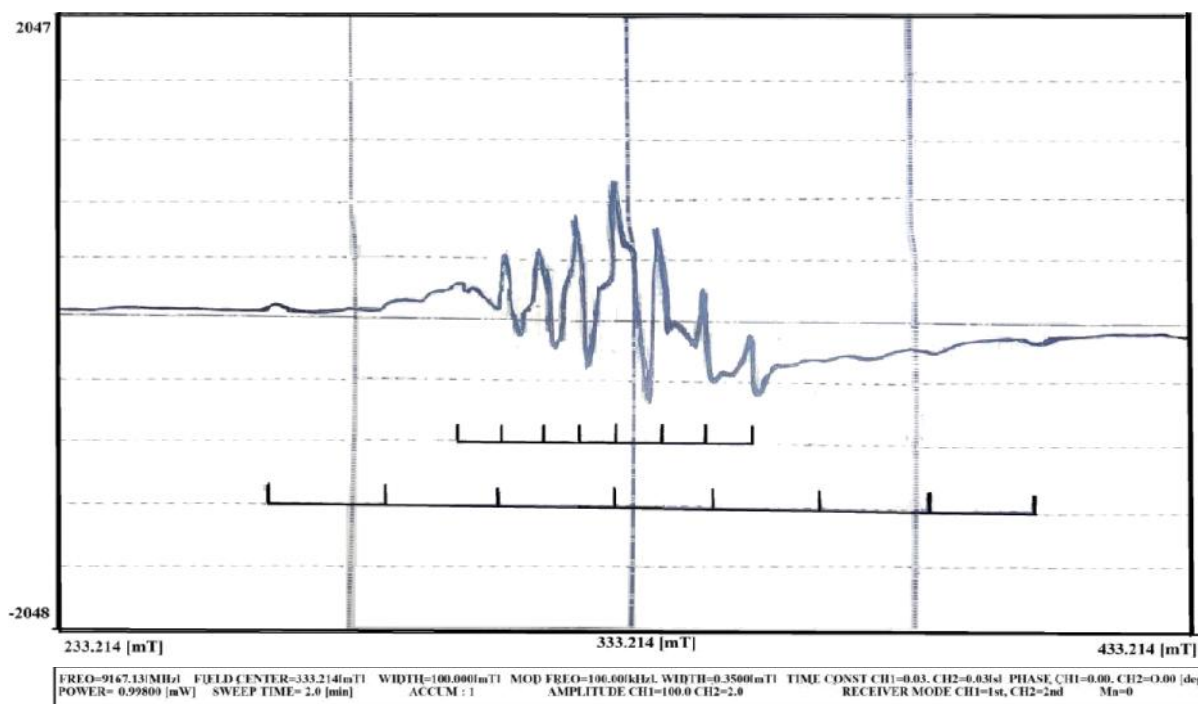


Figure 5: ESR Spectrum of VO(BED) in LNT

Antibacterial studies

The ligands and the vanadyl complexes were assayed for their antimicrobial activities against *E.coli*, *S.aureus*, *P.aeruginosa*, *Serratia* sp and *Bacillus cereus* by the disc diffusion method^(26,27). It was found that the complexes have better activity than the ligands explained by the theory of Tweedy. This is probably due to the greater lipophilicity nature of the complexes. Such increased activity of metal chelates can be explained on the basis of overtone concept and

chelation theory. According to overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of lipid soluble materials. On chelation, the polarity of metal ion will be reduced to a greater extent due to overlap of the ligand orbitals and partial sharing of positive charge of the metal ion with donor groups. Therefore the delocalisation of electrons in the chelate ring increases and enhances the penetration of the complexes into lipid membranes. The antibacterial data are presented in Table 5.

Table 5. Antibacterial activity data of the ligand and its complexes

Compound	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Serratia sp</i>	<i>Bacillus cereus</i>	Inference
C ₃₄ H ₂₈ N ₂ O ₂ (BOP)	9	10	7	8	12	++
[VO(BOP)]	13	14	13	13	13	+++
C ₃₀ H ₂₈ N ₂ O ₂ (BED)	7	10	8	9	-	++
[VO(BED)]	11	13	15	10	11	+++

Conclusion

In this work the synthesis and characterisation of tetradentate Schiff base ligands derived from benzoin with o-phenylene diamine (BOP) / ethylenediamine (BED) and its interaction with oxovanadium(IV) was reported.

The metal complexes formed were non-electrolytic in nature. The analytical and spectral data suggests that two azomethine N atoms and two oxygen atoms from

the ligand are coordinated to metal ions generating a square pyramidal environment. The antibacterial screening tests were also performed against bacteria which indicate that the vanadium complexes exhibit good antibacterial activity than the ligands. Based on the above results the structure of coordination compounds under investigation are formulated in Figure 6.

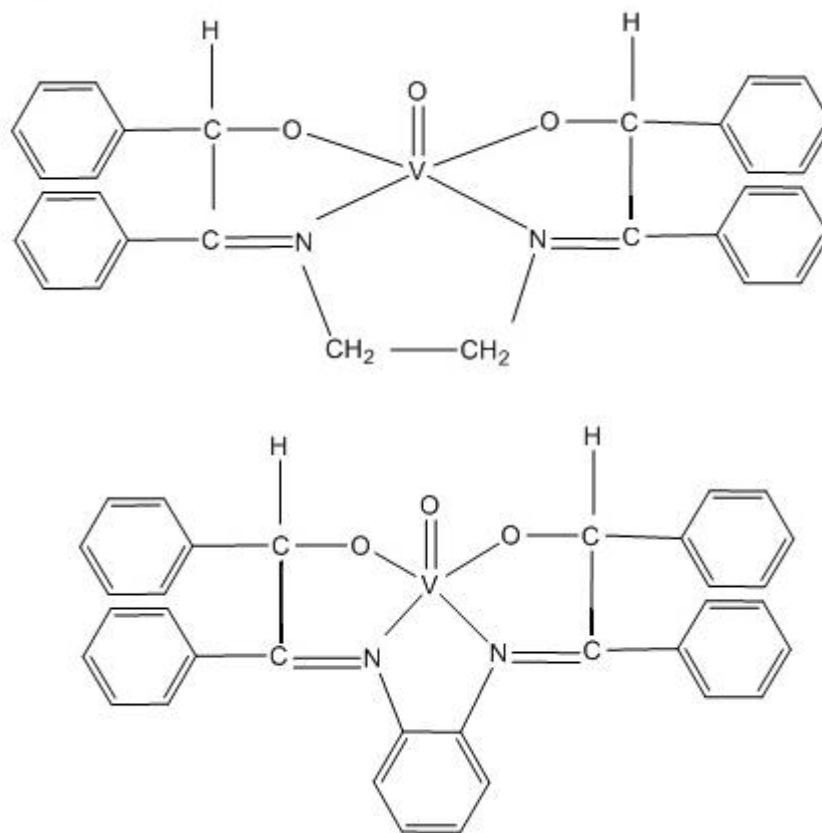


Figure 6: The proposed square pyramidal structure of complexes VO(BED)] & [VO(BOP)]


Acknowledgments

The authors are thankful to The Principal and The Head, Dept. of chemistry Govt. Arts College, Ooty, The Head, Dept of Pharmaceutical Chemistry, JSS College of Pharmacy, Ooty, The Head, SAIF, Pondicherry University, The Head, SAIF, CECRI, Karaikudi, The Head, SAIF, IIT-Chennai, The Head, SRMV, Coimbatore and Madurai Kamaraj University for recording the spectral data and performing the antibacterial studies.

References

1. K.Z.Ismail, A.El-Dissonky, A.Z.Shehaha, Polyhedron, **16**, 209, (1997).
2. K.B.Gudasi, R.V.Shenoy, R.S.Vadavi, M.S.Patila, S.A.Patila, Chem.Pharm.Bill, **53(a)**, 1077-1082, (2005).
3. L.Singh, A.Sharma, S.K.Sindhu, Asian.J.Chem, **11**,1445, (1999)
4. J.Kavitha, A.Kulandaisamy and P.Thillaiarasu, Bio Med Rx, **1(2)**, 13-16, (2013)
5. D.Rehder, Angrew Chem.Int.Ed.Engl, **30**, 148-167, (1991)
6. E.Friden, Scientific American, **227**, 52, (1972).
7. C.E.Heyliger, A.G.Tahilian, and J.H.McNeill, Science, **227**, 52, (1985)
8. Micheal W King., Introduction to cholesterol metabolism thermal biochemistry page, Org LLC, (1966-2013).
9. H.N.Aliyu, H.J.Abdullahi, African Scientist, **Vol.10**, No.4, (2009).
10. H.N.Aliyu, H.J.Abdullahi, Bayero Journal of pure and Applied Sciences, **2(2)**, 110- 112, (2009)
11. B.B.Mahapatra, B.K.Mahapatra, S.Guru, J.Inorganic Nuclear Chemistry, **Vol.40** pp.1179-1180, (1978)
12. V.B.Rana, D.P.Singh, P.Singh and M.P.Teotia, Transition Met.Chem,174, (1982)
13. S.Chandra, K.K.Sharma, Transition Met.Chem, **Vol.8(1)**, (1983)
14. W.U.Malik, R.Bembi and R.Singh, Inorg.Chem.Acta, **68**,223, (1983)
15. P.Bora, H.S.Yadav, Iranian J.of Sci & Tech, **37A3**, 310, (2013)

16. K.Nakomato K, Infrared Spectra of Inorganic and Coordination Compounds, Wiley- New York, 234-241, (1963)
17. K.S.Patel and M.O.Agwara, Nigerian Journal of Science, **24**,107, (1990)
18. A.B.P.Lever, Inorganic Electronic spectroscopy, 2nd Edn (Elsevier New York), (1968)
19. L.N.Sharada , M.C.Ganorkar, Indian J Chem, **27A**, 617, (1988)
20. R.L.Duta, A.Syamal, Elements of magnetochemistry, 2nd Edn (East West Press, New Delhi), (1992)
21. R.L.For mer & F.L.Urbach, Inorg Chem, **13**, 587, (1947).
22. A.Sarkara, S.Pal, Inorg.Chim.Acta, **361**, 2296-2304, (2008)
23. S.S.Dodwad, R.S.Dhamnaskar, P.S.Prabu, Polyhedron, **8**,1748, (1998).
24. S.N.Rao, D.D.Mishra, R.C.Maurya, N.N.Rao, Polyhedron, **16**,1828, (1997)
25. A.K.Yadava, .S.Yadav, R.Saxena, D.P.Rao, Eur.Chem.Bill, **4(7)**, 356-359, (2015)
26. N.Raman,N., S.Ravichandran,S., C.Thangaraja,C, J.Chem,Sci, **116(44)**, 214-219, (2004)
27. Z.Shirin, R.M.Mukherjee, Polyhedron, **11**, 2625, (1992)

Access this Article in Online	
	Website: www.ijcrpps.com
	Subject: Chemistry
Quick Response Code	
DOI: 10.22192/ijcrpps.2017.04.01.003	

How to cite this article:

N.Gayathri and M.S.Suresh. (2017). Synthesis and spectral characterization of oxovanadium complexes derived from benzoin, O-phenylenediamine and ethylenediamine and their antibacterial activities. Int. J. Curr. Res. Chem. Pharm. Sci. 4(1): 12-19.

DOI: <http://dx.doi.org/10.22192/ijcrpps.2017.04.01.003>