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Synthesis, Characterization and Antibacterial Studies of Oxovanadium (IV) and Copper(II) Schiff Base Complexes Derived from Benzoin and Anthranilic Acid-A Tridentate Ligand

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ABSTRACT

Oxovanadium VO(IV) and Cu(II) complexes with a tridentate Schiff base derived from benzoin and 2-aminobenzoic acid have been synthesized and characterized. The nature of the bonding and geometry of the complexes have been deduced from elemental analysis, spectral (UV, FTIR, ESR) analysis, magnetic susceptibility measurements, molar conductivity measurements and thermal analysis. The magnetic moments and electronic spectra of the complexes indicate octahedral geometry for both the complexes having molecular formula $[VO(L(H_2O)_2)]$ and $[CuL(H_2O)_3]$. Both the complexes were found to be non-electrolytic in nature. The IR spectra reveals the involvement of azomethine nitrogen (-C=N-) oxygen atoms from hydroxyl group and carboxylate ion are coordinated to the metal, with coordinated water. The thermal decomposition of the complexes yields the oxides of metal as the stable residue. The ESR spectra of both the complexes in dimethyl sulfoxide (DMSO) at 77K were recorded and their salient features are reported. The metal complexes have been screened for their antibacterial activity against organisms like *Escherichia coli*, *Staphylococcus aureus*, *Serratia sp*, *Pseudomonas aeruginosa* and *Bacillus cereus* by disc diffusion method and the results revealed that the complexes are more potent than the ligand.

Keywords: Schiff base, Benzoin, Anthranilic acid, Oxovanadium (IV), Copper (II) antibacterial studies

INTRODUCTION

The field of Schiff bases complexes is fast developing because of the wide variety of possible structures for ligands, depending on the aldehyde and amine used. Many Schiff bases and their complexes have been widely studied because of their applications in industrial [1], biological, clinical, analytical [2] and pharmacological [3] area. They play an important role in both synthetic and structural research because of their preparative accessibility and structural diversity [4]. From the literature survey it was revealed that most of the Schiff bases were bidentate or tetradentate [5,6] with four nitrogens (MN_4) or two nitrogens and two oxygens (MN_2O_2) as donors. The tridentate Schiff bases and their studies were found to be rare.

The Schiff base formed from benzoin and 2-aminobenzoic acid (anthranilic acid) acting as a tridentate ligand with an azomethine (-C=N-) nitrogen and two oxygens from hydroxyl group and carboxylic acid group are the coordinating sites resulted into MNO_2 chromophore. The Co(II) complex [7] in 1977 and Fe^{2+} , Ni^{2+} complexes [8] in 2012 of this ligand were reported in various journals with IR, molar conductance and coordinated water analysis only. In this paper we report the synthesis and structural characterization (microanalytical data, FTIR, UV-Vis, ESR, magnetic susceptibility, molar conductance and thermal analysis) of oxovanadium(IV) and copper(II) complexes of the Schiff base derived from benzoin and anthranilic acid.

EXPERIMENTAL

Benzoin, anthranilic acid, $VOSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$, ethyl alcohol, etc. were purchased from Merck and used as such without any further purification. The elemental analysis (C,H,N,S) were performed using EL elemental analyser at Central Electrochemical Research Institute (CECRI). The FT infrared spectra were recorded in the range $4000-400\text{ cm}^{-1}$ on a Shimadzu FTIR 8400S spectrometer using KBr pellet techniques. Electronic (UV-VIS) spectra were recorded on a Shimadzu UV-spectrophotometer in the range $200-1100\text{ cm}^{-1}$ using dimethyl sulfoxide (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 10 K/min. The ESR spectra of various Schiff base complexes were recorded on a JES-X₃ series in the scan range of 2300-4300 Gauss at LNT. The magnetic susceptibility measurements of the complexes were carried out using Guoy balance. The molar conductance was measured on ELICO-CM180 using DMSO as the solvent at room temperature. The antibacterial studies were carried out with disc diffusion method.

Synthesis of Schiff bases

From benzoin and anthranilic acid

The ligand was synthesized by using the reported procedure [7,8]. To the ethanolic solution of benzoin (4.24 g, 0.02 mol) an ethanolic solution of 2-aminobenzoic acid (2.74 g, 0.02 mol) was added, followed by the addition of anhydrous sodium acetate (3 g) and the mixture was refluxed for an hour. The hot solution was poured into ice cold water where upon grayish white precipitate of the Schiff base separated, suction filtered, washed with water, recrystallized from rectified spirit and dried *in vacuo* [7,8]. Their scheme of preparation is shown in Figure 1.

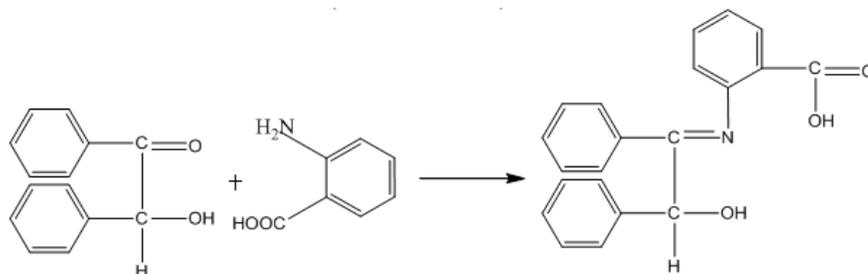


Figure 1: Schematic representation of synthesis of tridentate ligand BA

Synthesis of oxovanadium (IV) and copper(II) complexes

$\text{VO SO}_4 \cdot 5\text{H}_2\text{O}$ (2.53 g, 0.01 mol in 20 ml ethanol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.70 g, 0.01 mol in 20 ml ethanol) were used for the synthesis of oxovanadium (IV) and copper(II) complexes respectively with 3.31 g of the ligand dissolved in 20 ml ethanol followed by drop wise addition of ammonia until the metal chelate separated, which was then suction filtered washed with ethanol and ether, and dried *in vacuo*. The crystals were recrystallized from rectified spirit and dried [8].

RESULTS AND DISCUSSION

Microanalysis and molar conductance studies

The elemental analysis data given in Table 1 suggests that the synthesized compounds have 1:1 (metal:ligand) stoichiometry with coordinated water having molecular formula $[\text{VO}(\text{BA}) \cdot (\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{BA}) \cdot (\text{H}_2\text{O})_3]$, where BA is the tridentate ligand synthesized from benzoin and anthranilic acid. These complexes have molar conductance in the range 12-13.5 $\text{S cm}^2 \text{mol}^{-1}$ representing its non-electrolytic nature.

Table 1: Physical characterization, analytical and molar conductance data

Compound	Mol. Wt.	Colour	Yield	Elemental Analysis (%) Found (Calc.)				$\Lambda_m \text{ S cm}^2 \text{ mol}^{-1}$
				C	H	N	M	
$\text{C}_{21}\text{H}_{17}\text{NO}_5(\text{BA})$	331.34	Grayish white	80%	75.86 (76.11)	4.051 (5.171)	4.051 (4.225)	-	-
$[\text{VO}(\text{BA}) \cdot (\text{H}_2\text{O})_2]$	432.30	Dark green	75%	58.88 (58.34)	4.695 (4.136)	3.290 (3.379)	15.95 (16.15)	12
$[\text{Cu}(\text{BA}) \cdot (\text{H}_2\text{O})_3]$	444.92	Dark brown	75%	55.11 (56.68)	4.500 (4.75)	3.112 (3.14)	14.02 (13.83)	13.5

Infrared analyses

Coordination to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine group and lowers the $\nu_{\text{C}=\text{N}}$. The spectrum of the free Schiff base ligand BA shows $\text{C}=\text{N}$ bands at region 1595 cm^{-1} and shifts to lower frequency in the complexes showing the involvement of the coordination of $\text{C}=\text{N}$ - in bond formation [9-12]. It was further supported by M-N peak at $410\text{-}420 \text{ cm}^{-1}$ in the complexes [13,14].

The frequency corresponding to ν_{COO} present in the ligand 1491 cm^{-1} is shifted to lower wave number in the complexes, indicating the bond formation through the carboxylate COO^- anion. It was further supported by M-O peak at $500\text{-}598 \text{ cm}^{-1}$ in the complexes [13,14]. An absorption band at 976 cm^{-1} in case of $[\text{VO}(\text{BA}) \cdot (\text{H}_2\text{O})_2]$ corresponds to $\nu_{\text{V}=\text{O}}$ [17] which was found to be absent in the IR spectrum of the ligand. The appearance of new peaks in the range $3379\text{-}3509 \text{ cm}^{-1}$ due to water in the complex indicates the presence of coordinated water molecules [15-19]. The IR spectral data was presented in Table 2.

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

Compound	ν_{OH}	$\nu_{\text{C}=\text{N}}$	ν_{COO^-}	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{V}=\text{O}}$
$\text{C}_{21}\text{H}_{17}\text{NO}_5(\text{BA})$	-	1595	1491	-	-	-
$[\text{VO}(\text{BA}) \cdot (\text{H}_2\text{O})_2]$	3379-3416	1514	1471	420	500	976
$[\text{Cu}(\text{BA}) \cdot (\text{H}_2\text{O})_3]$	3509	1569	1472	410	528	-

UV-VIS electronic spectra and magnetic susceptibility measurement

The free ligand shows absorption maxima appearing around 38461 and 31250 cm^{-1} due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively. The electronic spectrum of $[\text{VO}(\text{BA}) \cdot (\text{H}_2\text{O})_2]$ shows peaks at 13333 , 18500 , 27932 cm^{-1} assigned to be ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions respectively supporting the octahedral structure of the complex and confirmed by its magnetic moment of 1.71 BM [20]. The electronic spectrum of Cu(II) complex shows peaks at 13513 , 19083 , 24038 cm^{-1} corresponding to ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{1g}$, ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$, ${}^2\text{E}_g \rightarrow {}^2\text{B}_{1g}$ transition respectively.

Its magnetic moment was found to be 1.80 BM supporting a distorted octahedral environment [18] around the Cu(II) ion. The UV-Vis electronic spectra and magnetic susceptibility measurement data was presented in Table 3.

Table 3: UV-Visible Spectral Data and magnetic moments of the complexes

Compound	Absorption max (cm ⁻¹)	Assignments	μ (BM)
C ₂₁ H ₁₇ NO ₃ (BA)	38461 31250	n→π* π→π*	
[VO(BA).(H ₂ O) ₂]	13333 18500 27932	² B ₂ → ² E ₁ ² B ₂ → ² B ₁ ² B ₂ → ² A ₁	1.71
[Cu(BA).(H ₂ O) ₃]	13513 19083 24038	² A _{1g} → ² B _{1g} ² B _{2g} → ² B _{1g} ² E _g → ² B _{1g}	1.80

Thermal studies

From the thermogram of the complex [Cu(BA).(H₂O)₃] (Figure 2) it was observed that the compound is thermally stable up to 150°C indicated by a horizontal plateau. After 150°C the first stage of decomposition takes place and progresses till 300°C with a mass loss of about 73% and second stage was seen in the range 300-690°C with a mass loss of 10.5%. The total mass loss observed was 83.5% with a residual mass of 16.5%. The first and second stage of decomposition was due to the loss of three water molecules and breaking of the tridentate Schiff base from the complex, leaving CuO, as the stable residue above 690°C. The calculated value of the residue, 17.42% is in good agreement with the observed value of 16.5%.

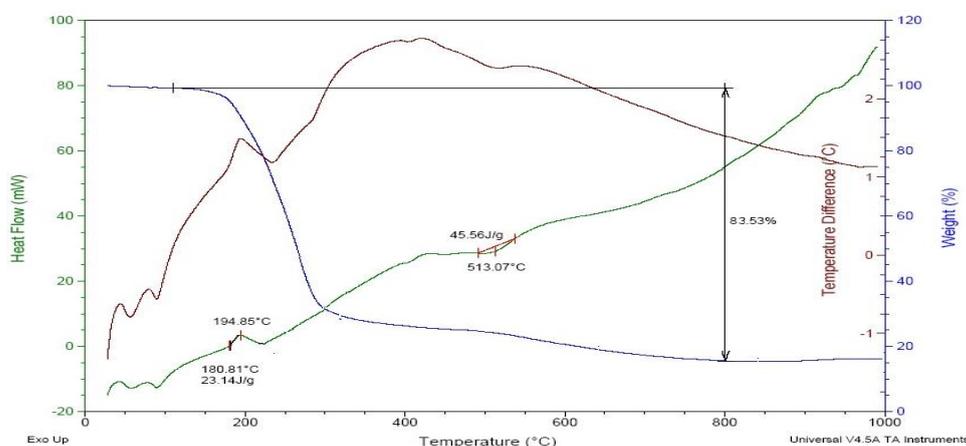


Figure 2: TG/DTA curve of [Cu(BA).(H₂O)₃] in static air

The TG curve of [VO(BA).(H₂O)₂] in static air atmosphere is given in Figure 3. The first stage of decomposition is seen starting at 50°C and progressing till 100°C. The weight loss during this stage was 8.1%. This was due to the loss of two water molecules from the complex. The calculated value of 8.32% is in good agreement with this. The second stage of decomposition starts at 100°C and progressing till 330°C with a mass loss of 54.02% and third stage is seen initiating immediately at 330-750°C with a mass loss of 17.98% leaving behind a residual percentage of 19.9%. During the second and third stage of decomposition the breaking of the tridentate Schiff base from the complex takes place leaving behind a stable residue V₂O₅. The calculated value of 20.9% is in good agreement with the theoretical value.

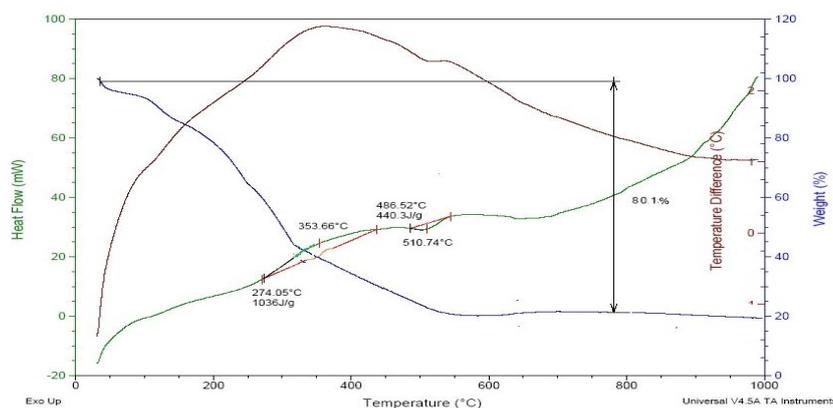
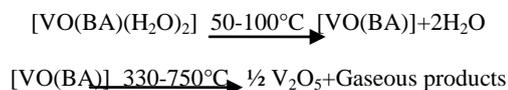


Figure 3: TG/DTA curve of [VO(BA).(H₂O)₂] in static air

ESR spectroscopy

The X-band ESR spectrum of the oxovanadium complexes were recorded in DMSO solution at liquid nitrogen temperature (Figure 4). In the frozen state, in the spectrum we expect two types of resonance components, one set due to parallel while the other set due to perpendicular features, due to the interaction between the electron and the vanadium nuclear spin ($I=7/2$) [19,21]. But it was found that the spectrum was not well resolved to calculate the spectral parameters and hence the $g_{(av)}$ value was calculated and found to be 1.9661.

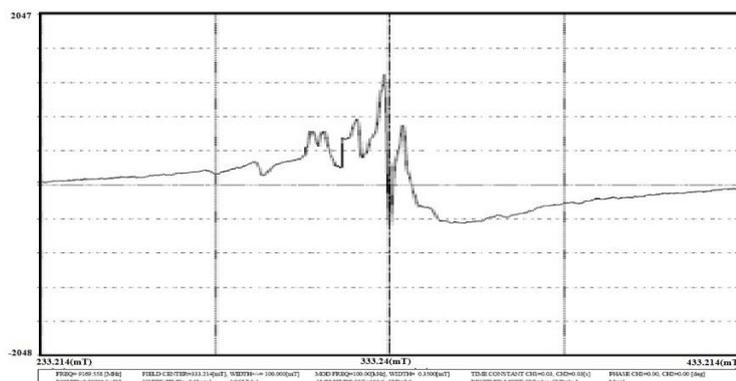


Figure 4: ESR Spectrum of [VO(BA).(H₂O)₂] at LNT

ESR spectrum of Cu(II) complex given in Figure 5 shows four well resolved peaks in the low field region corresponds to $g_{||}$ (2.3683), g_{\perp} (2.0443) and g_{iso} (2.1523). The trend $g_{||}(2.3683) > g_{\perp}(2.0443) > g_e(2.0023)$ observed for the complex suggests that the unpaired electrons is in $d_{x^2-y^2}$ orbital of Cu(II) ion. It was also supported by the value of the exchange interaction G estimated from expression:

$$G = \frac{g_{||} - 2.0023}{g_{\perp} - 2.0023}$$

If $G > 4.0$ the local axes are aligned parallel or slightly misaligned. If $G < 4.0$ significant exchange coupling is possible and the misalignment is appreciable. The observed value of $G = 8.71$ suggests that the unpaired electron is present in $d_{x^2-y^2}$ orbital [22-24] and is slightly misaligned. These parameters also support distorted octahedral geometry for Cu(II) complex.

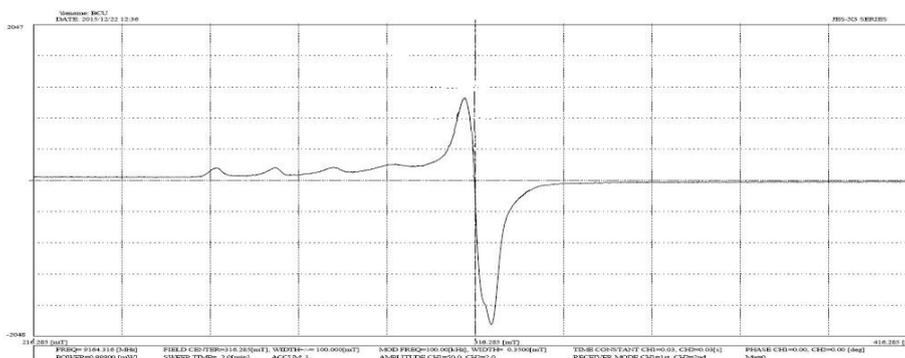


Figure 5: ESR Spectrum of [Cu(BA).(H₂O)₃] at LNT

Antibacterial studies

The ligands and the complexes were assayed for their antimicrobial activities against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Serratia* (sp.) and *Bacillus cereus* by the disc diffusion method [25,26]. 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 overtones concept and chelation theory. According to overtone's concept of cell permeability the lipid membrane that surrounds the cell favour 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 delocalization of π electrons in the chelate ring increases and enhances the penetration of the complexes into lipid membranes. The antibacterial data are presented in Table 4.

Table 4: 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 ₂₁ H ₁₇ NO ₅ (BA)	9	15	8	9	8	++
[VO(BA).(H ₂ O) ₂]	12	13	12	13	11	+++
[Cu(BA).(H ₂ O) ₃]	9	7	10	12	10	++

CONCLUSION

In this work the synthesis and characterization of tridentate Schiff base ligands derived from benzoin and anthranilic acid and its interaction with metals is reported. The metal complexes formed were non-electrolytic in nature. The synthesized systems were characterized by microanalysis, molar conductance values, FTIR, ESR, UV spectroscopy and TG analysis. The analytical and spectral data suggests an octahedral geometry for the complexes. The antibacterial screening tests were also performed against bacteria which indicate that the complexes exhibit good antibacterial activity than the ligands. Based on the above results the structures of coordination compounds under investigation are formulated in Figure 6.

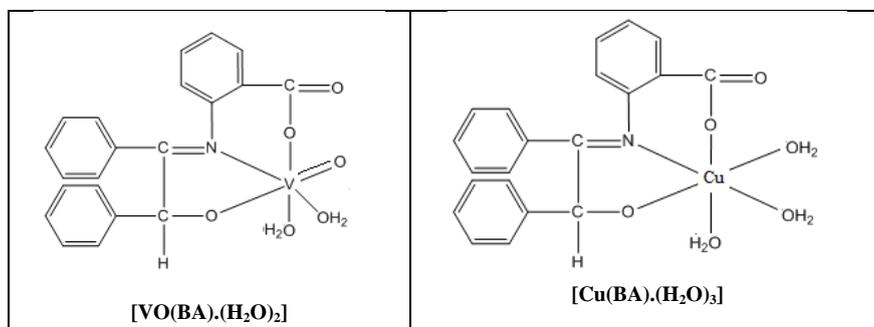


Figure 6: The proposed structure of complexes

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REFERENCES

- [1] R. Bu. Xiu, F.L. Mintz, X.Z. You, R.X. Wang, Q. Yue, Q.J. Meng, Y.J. Lu, D.V. Derveer, *Polyhedron.*, **1996**, 15, 4885-4891
- [2] N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy, *J. Chem. Sci.*, **2003**, 115(3), 161-167.
- [3] Z.H. Chohan, S.K.A. Sherazi, *Metal-Based Drugs.*, **1997**, 4(6), 327-332.
- [4] Bimal kumar, B.K. Rai, Nisha Ambastha, *Orien. J. Chem.*, **2011**, 27, 1173-1178.
- [5] M. Yoshizawa, *J. Am. Chem. Soc.*, **2005**, 127, 2798.
- [6] S.A. Zerkocski, C.T. Seto, G.M. Whitesiders, *J. Am. Chem. Soc.*, **1991**, 114, 5473.
- [7] B.B. Mahaptra, B.K. Mahaptra, S. Guru, *J. Inorg. Nucl. Chem.*, **1977**, 39, 2291-2291.
- [8] Y.K. Gupta, S.C. Agarwal, S.P. Madnawat, *Ultra Scientist.*, **2012**, 24(2), 370-374.
- [9] V.B. Rana, D.P. Singh, P. Singh, M.P. Teotia, *Trans. Met. Chem.*, **1982**, 174.
- [10] S. Chandra, K.K. Sharma, *Trans. Met. Chem.*, **1983**, 8(1).
- [11] W.U. Malik, R. Bembi, R. Singh, *Inorg. Chem. Acta.*, **1983**, 68, 223.
- [12] P. Bora, H.S. Yadav, *Iranian J. Sci. Tech.*, **2013**, 37, 310.
- [13] K. Nakomato, Wiley-NY, USA, **1963**, 234-241.
- [14] K.S. Patel K.S. M.O. Agwara, *J. Sci.*, **1990**, 24, 107.
- [15] G.M. Gehad, M.M. Omar, M.M. Ahmed, *Hindy Science Direct*, **2005**.
- [16] B.G. Kalagouda, C.H. Vidydhara, A.P. Siddapa, R.P. Basavaraj, *Metal. Based Drugs.*, **2014**.
- [17] R.B. Xiu, E.A. Mintz, X.Z. You, *Polyhedron.*, **1996**, 15, 4585.
- [18] C. Sulekh, J. Deepali, K.S. Amit, S. Pratiba, *Molecules*, 14010174.
- [19] A.L. Sharma, I.O. Singh, M.A. Singh, H.R. Singh, *Trans. Met. Chem.*, **2001**, 26, 532.
- [20] R.C. Maurya, H. Singh, S. Pandey, T. Singh, *Indian J. Chem.*, **2001**, 40, 1053.
- [21] T.F. Yen, *Electron Spin Resonance of Metal Complexes*, Plenum Press, NY, USA, **1969**.
- [22] B.J. Hathaway, A.A.G. Tomilnson, *Coord. Chem. Rev.*, **1970**, 5.
- [23] I.M. Procler, B.J. Hathaway, D.E. Billing, P. Nicholas, *J. Chem. Soc. A.*, **1986**, 1678.
- [24] M.S. Suresh, V. Prakash, *Int. J. Phys. Sci.*, **2010**, 5(9), 1443-1449.
- [25] N. Raman, S. Ravichandran, C. Thangaraja, *J. Chem. Sci.*, **2004**, 116(44), 214-219.
- [26] Z. Shirin, R.M. Mukherje, *Polyhedron.*, **1992**, 11, 2625.