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Synthesis of transition metal complexes of bidentate ligand and their antimicrobial studies

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ABSTRACT

The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) were prepared from bidentate Schiff base, 1-(2-Hydroxybenzamido)-2-(2-methylphenyl)-azomethin. The Schiff base ligand was synthesised from 2-hydroxy benzo hydrazide and acetophenone. These metal complexes were characterized by molar conductivity, magnetic susceptibility, thermal analysis, x-ray diffraction, FTIR, ¹H-NMR, UV-vis and mass spectroscopy. The analytical data of these metal complexes showed metal: ligand ratio (1:2). The physico-chemical study supports the presence of square planar geometry around Cu (II), Ni (II) and octahedral geometry around Co (II), Mn (II) and Fe (III) ions. The IR spectral data reveal that the ligand behave as bidentate with ON donor atom sequence towards central metal ion. The molar conductance values of metal complexes suggest their non electrolyte nature. The x-ray diffraction data suggests monoclinic crystal system for these complexes. Thermal behavior (TG/DTA) and kinetic parameters calculated by Coats-Redfern method are suggestive of more ordered activated state in complex formation. Antibacterial and antifungal activities of the ligand and its metal complexes were performed in vitro against *Staphylococcus aureus*, *Escherichia coli* and *Aspergillus Niger*, *Trichoderma* respectively.

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KEYWORDS

Bidentate Schiff base;
Thermal analysis;
XRD;
Antibacterial activity;
Antifungal activity;
Metal complexes.

INTRODUCTION

Hydrazones are a special group of compounds in the Schiff base family, characterized by the presence of (>C=N-N=C<). The presence of two interlinked nitrogens separate them from imines, oximes, etc. Compared to simple hydrazone Schiff bases, acyl, aroyl, and hetero-aroyl Schiff bases have additional donor sites like >C=O, making them more flexible and versatile.

This versatility has made hydrazones good polydentate chelating agents that can form a variety of complexes with various transition and inner transition metals. A number of hydrazone derivatives have interesting bioactivity towards anti-bacterial, anti-fungal^[1], anti-convulsant^[2], anti-inflammatory^[3], anti-malarial^[4,5], analgesic^[5], anti-platelets^[6], anti-tuberculosis^[7], and anti-cancer activities^[8]. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides, and plant growth regulators

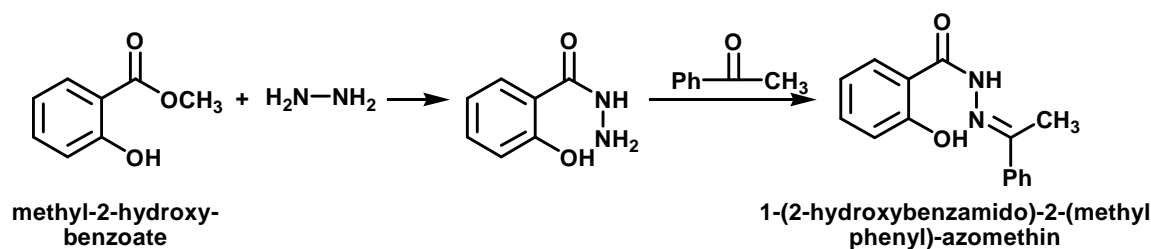


Figure 1 : Synthesis of ligand

and are used as plasticizers, stabilizers and antioxidant initiators for polymerization. Hydrazone derivatives are used in analytical chemistry as selective metal extracting agents as well as in the spectroscopy for the determination of certain transition metals^[9].

It was thought worth while that the metal complexes formed by the combination of transition metal ion with a potent hydrazone ligand should be more biologically active than the metal salts or the ligand individually. Therefore, we report here the synthesis and characterization of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) complexes with 1-(2-Hydroxybenzamido)-2-(2-methylphenyl)-azomethin. The anti-fungal and anti-bacterial properties of the ligand and its metal complexes were also tested.

EXPERIMENTAL

Apparatus and reagents

All chemicals used were of the analytical grade (AR) and of highest purity. Methyl-2-hydroxybenzoate, hydrazine and acetophenone were purchased from E-Merk (AR grade) and were used for synthesis of ligand. AR grade metal chlorides of S.D.Fine chemicals were used for complex preparation. Spectral grade solvents were used for spectral measurements. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CHNS analyzer. IR spectra for ligands and metal complexes were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets in the range of 4000-400 cm⁻¹. ¹H-NMR spectra of the ligand was measured in CDCl₃ using TMS as an internal standard. The TG/DT analysis was recorded on Perkin Elmer TA/SDT-2960 with heating rate 10°C/min. XRD was recorded on Philips 3701 employing CuK_α radiation (λ=1.541Å) in the range 20° to 90°. The UV-vis spectra of the complexes were recorded on Jasco UV-530 Spectrophotometer. Magnetic susceptibility measure-

ments were carried out on Guoy balance at room temperature using Hg [Co(SCN)₄] as a calibrant. Molar conductance was measured on Elico CM-180 conductometer using 1 mM solution in dimethyl sulphoxide.

Synthesis of ligand

Step 1

For the synthesis of ligand, 50ml ethanolic solution of 0.001mol (0.168g.) of methyl salicylate was taken in round bottomed flask and to this 0.001 mol (0.108g.) of hydrazine in ethanol was added slowly under stirring. The resulting mixture was refluxed for about 3-4h. It was naturally cooled to room temperature. After cooling, the solid residue was washed several times with hot ethanol and used for further study. (Yield: 80%).

Step 2

Above synthesised intermediate 0.001mol was refluxed with 0.001mol of acetophenone in super dry ethanol for 4 h. The precipitate thus formed was filtered, dried in vacuum in presence of CaCl₂ and recrystallised in ethanol (yield: 72%) (Figure 1).

Preparation of complexes

To a hot solution of ligand (0.02 mol) in chloroform, methanolic solution (25mL) of metal chloride (0.01mol) was added under constant stirring. The pH of the reaction mixture was adjusted to 7.5-8.5 by adding 10% alcoholic ammonia solution and refluxed for about 5h. The precipitated solid metal complex was filtered and washed with hot methanol, followed by petroleum ether, ethyl acetate and dried over CaCl₂ in vacuum desiccator (yield 65%).

RESULT AND DISCUSSION

All the complexes are coloured solids, air stable

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TABLE 1 : Physical characterization, analytical and molar conductance data of compounds

Compound	F. W.	M.P. / Decomp. Temp. °C	Color	Molar conduc. Mho cm ² mol ⁻¹	Found(Calculated)			
					C	H	N	M
H ₂ L	254.00	194°C	White	---	70.25(70.93)	5.00(5.15)	10.80(11.02)	
[CuL]	570.28	>300°C	Orange	09.10	63.00(63.18)	4.20(4.59)	9.40(9.82)	11.00(11.14)
[NiL]	565.23	280°C	Light reddish	16.20	63.00(63.74)	4.25(4.63)	9.50(9.91)	10.00(10.38)
[CoL(H ₂ O)]	601.50	>300°C	Orange	30.15	59.30(59.90)	4.90(5.02)	4.50(9.31)	9.90(9.79)
[MnL(H ₂ O) ₂]	597.50	>300°C	Brown	19.05	60.40(60.30)	4.80(5.06)	9.40(9.37)	9.25(9.19)
[FeL(H ₂ O) ₂]	598.41	>300°C	Brown	20.17	60.10(60.21)	5.15(5.05)	9.50(9.36)	9.40(9.33)

and are having good solubility in polar solvents DMF and DMSO. The elemental analysis show 1:2 (metal: ligand) stoichiometry for all the complexes. Micro analytical data and molar conductance values are given in TABLE 1. The metal contents in complexes were analyzed by gravimetric analysis^[10]. All the complexes show low conductance which indicates their non-electrolytic nature. The magnetic measurement studies suggest that the Cu(II), Co(II), Mn(II) and Fe(III) complexes exhibit paramagnetic whereas the Ni (II) shows diamagnetic behavior.

¹H-NMR spectra

¹H-NMR spectra of synthesised ligand was recorded in CDCl₃. It shows following signals at 2.3 δ (s, 3H, N=C-CH₃), 4.8 δ (s, 1H, -C-N-H), 7.08 δ (dd, 2H, Ar-H), 7.22 δ (dd, 3H, Ar-H), 7.43 δ (s, 3H, Ar-H), 7.55 δ (dd, 2H, Ar-H) and 10.23 δ (s, 1H, Ar-OH).

Mass spectra of the ligands

Mass spectral data confirms the structure of the ligand H₂L (Figure 1) as indicated by the peaks corresponding to their molecular masses.

FT-IR spectra

The FT-IR spectrum of the free ligand shows four characteristic bands at 3260-3300, 3434, 1650 and 1607 cm⁻¹ assignable to ν(-N-H), free (-O-H) stretching phenolic moiety, amide carbonyl (-C=O) and azomethine (-C=N), stretching modes respectively. The absence of a weak broad band in 3260-3300 cm⁻¹ region, noted in the spectra of the metal complexes indicates deprotonation of bonded (-NH) group during the complexation and subsequent coordination of the oxygen of amide carbonyl to metal ion enolization^[11].

This is further supported by the upward shift in phe-

nolic (-OH) to the extent of 30-50 cm⁻¹ on complexation. The ν(C=N) band is shifted to lower wave number with respect to free ligand, indicating that the nitrogen of the azomethine group is coordinated to the metal ion, which was further confirmed by observation of the red shift in the ν(N-N) stretching frequency from 923 cm⁻¹ to 953 cm⁻¹ regions^[12,13]. This is further supported by upward shift in ν(C-N) to the extent of 10-50 cm⁻¹^[14]. New bands observed in the complexes at 1621 and 1625 cm⁻¹ are attributed to the >C=N-N=C< group^[15]. The spectra of metal chelates showed new bands in the 457-540 and 407-478 cm⁻¹ regions which can be assigned to ν(M-O) and (M-N) vibrations respectively^[16]. The spectra of Co(II), Mn(II) and Fe(III) showed a strong band at 3150-3600 cm⁻¹ region, suggesting the presence of coordinated water in these metal complexes^[17]. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840 cm⁻¹ region^[17]. The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence co-ordination takes place via oxygen of amide and nitrogen of azomethine group of ligand molecule.

Electronic absorption spectra and magnetic measurements

The electronic spectra of Cu(II) complex in DMSO show bands at 10570, 12547, 27472 cm⁻¹ assignable to a ²B_{1g} → ²A_{1g} transition and charge transfer respectively. The electronic spectral data coupled with observed magnetic moment 1.7 B.M. suggest square planar geometry for Cu(II) complex^[18,19]. Ni(II) complex display three bands at 12706, 18903 and 23584 cm⁻¹ assignable to ¹A_{1g} → ¹T_{2g} transition and two charge transfers respectively. These electronic transitions along with diamagnetic nature, suggest square planar geom-

TABLE 2 : Magnetic and electronic absorption spectral data of compounds

Compound	Magnetic moment μ_{eff} (B.M.)	Frequency in cm^{-1} ($\text{e}^{-1}\text{Lmol}^{-1}\text{cm}^{-1}$)	Band assignment	Geometry
[C ₁₅ H ₁₃ N ₂ O ₂]	1.7	32894	INCT ^a	Square planar
		33898	INCT	
		34246	$d_{xy} \rightarrow d_{x^2-y^2}$	
		10570	${}^2B_{1g} \rightarrow {}^2A_{1g}$	
[C ₃₀ H ₂₆ N ₄ O ₄ Cu]	Dia.	12547	INCT	Square planar
		27472	INCT	
		12706	${}^1A_{1g} \rightarrow {}^1T_{2g}$	
[C ₃₀ H ₂₆ N ₄ O ₄ Ni]	2.6	18903	INCT	Square planar
		23584	INCT	
		12335	${}^4T_{1g} \rightarrow T_{2g}$ (F)	
[C ₃₀ H ₂₆ N ₄ O ₄ Ni]	5.9	16119	${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F)	Octahedral
		27933	INCT	
		16611	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
		24390	${}^6A_{1g} \rightarrow {}^4T_{2g}$	
[C ₃₀ H ₃₀ N ₄ O ₆ Co]	5.8	26881	INCT	Octahedral
		13793	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
		19960	(⁴ D) ${}^6A_1 \rightarrow {}^4T_1$	
[C ₃₀ H ₃₀ N ₄ O ₆ Mn]	5.8	32467	INCT	Octahedral

TABLE 3 : The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	n	Method	E _a (kJmol ⁻¹)	Z _i S ⁻¹	ΔS# (JK ⁻¹ mol ⁻¹)	ΔG# (kJmol ⁻¹)	Correlation coefficient (r)
CO(II)	I	1.5	HM	11.29	0.8200	-155.24	21.43	0.9996
			CR	17.31	0.4858	146.87	20.88	0.9658
	II	1.5	HM	22.91	0.5306	-161.22	43.13	0.9908
			CR	10.70	0.0927	145.06	41.11	0.9966

etry for Ni(II) complex^[21,22]. The Co(II) complex exhibits three bands at 12335, 16119 and 27933 cm^{-1} assignable to ${}^4T_{1g} \rightarrow T_{2g}$ (F), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F) transitions and charge transfer respectively. These transitions and observed magnetic moment 4.7 B.M. indicate high spin octahedral geometry of the complex^[22,23]. Fe(III) complex exhibit bands at 13793, 19960 and 32467 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_1$ (D), ${}^6A_{1g} \rightarrow {}^4T_1$ transitions and charge transfer respectively. The observed magnetic moment 5.85 B.M along with electronic transitions corresponds to octahedral geometry.^[25,26] In case of Mn(II) complex, the observed magnetic moment 5.7 B.M and the spectral bands at 16611, 24390 and 26881 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$

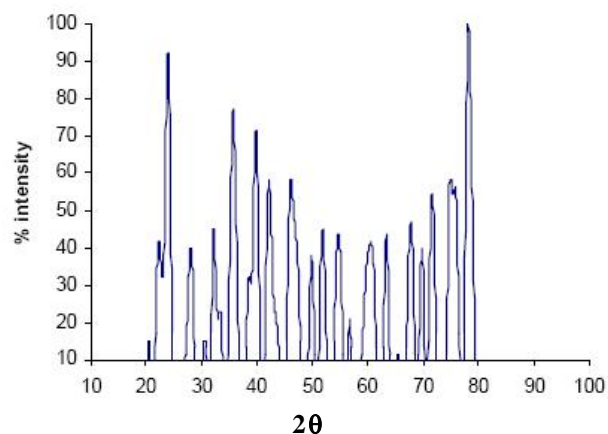


Figure 2 : X-ray diffractograms of Fe (III) complex

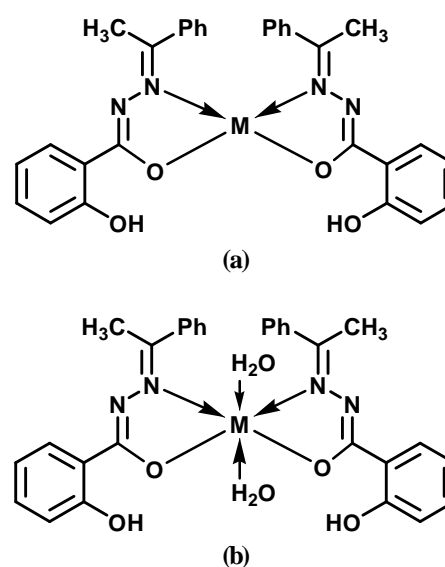


Figure 3 : The proposed structure of the complexes. (a) when M = Cu (II) and Ni (II), (b) when M = CO (II), Mn (II) and Fe (III)

and charge transfer respectively, indicates octahedral geometry for the Mn(II) complex^[25,27]. The calculated values of ligand field splitting energy (10Dq), Racah interelectronic repulsion parameter (B), covalent factor (β), ratio ν_2/ν_1 and ligand field stabilization energy (LFSE) (TABLE 2) support the proposed geometry for all the as-synthesised metal complexes.

X-ray diffraction study

The X-ray diffractogram of a representative metal complex of Fe(III) was scanned in the range 5-100° at wavelength 1.54 Å (Figure 2). The diffractogram and associated data depict 2θ value for each peak, relative intensity and interplanar spacing (d-value). The diffractogram of Fe(III) complex showed fifteen reflections with maxima at 2θ (23.07°) corresponding to d

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TABLE 4 : Antibacterial activity of compounds

Test compound	inhibition zone (mm)			
	<i>E. Coli</i>		<i>Staphylococcus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
<i>Ciproflaxin</i>	29	32	31	35
[C ₁₅ H ₁₃ N ₂ O ₂] (H ₂ L)	07	10	11	13
[C ₃₀ H ₂₆ N ₄ O ₄ Cu]	13	13	15	18
[C ₃₀ H ₂₆ N ₄ O ₄ Ni]	12	12	12	16
[C ₃₀ H ₃₀ N ₄ O ₆ Co]	12	13	13	16
[C ₃₀ H ₃₀ N ₄ O ₆ Mn]	10	12	11	14
[C ₃₀ H ₃₀ N ₄ O ₆ Fe]	10	12	11	14

value 3.855Å°. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10 % have been indexed by using computer programme^[27]. The above indexing method also yields Miller indices (hkl), unit cell parameters and their volume. The unit cell of Fe(III) complex yielded value of lattice constants, a = 10.05Å°, b = 4.08Å°, c = 7.28Å° and unit cell volume V = 435.91(Å°)³. In concurrence with these cell parameters of Fe(III) complex, the condition such as a ≠ b ≠ c and α = γ = 90° ≠ β required for the compounds to be monoclinic was tested and found to be satisfactory for Fe(III) complex. The above value indicate that the metal complex show monoclinic crystal system. Experimental density value of the complex was determined by using specific gravity method^[28] and found to be 2.32 gcm⁻³ for Fe(III) complex. On the basis of these studies, probable structures for the complexes under study have been proposed.

Thermal analysis

The simultaneous TG/DT analysis of a representative metal complex Co(II) was studied from ambient temperature to 1000°C in nitrogen atmosphere using α-Al₂O₃ as reference. The thermogram of Co(II) metal complex shows mass loss 5.7 % (calcd.5.98 %) in the range 150-230°C. An endothermic peak in this region ΔT_{max} = 112°C, corresponds to removal of two coordinate water molecules^[29,30]. The anhydrous complex then show slow decomposition from 240-500C, with 54.23 % (calcd.55.05 %) mass loss. A broad exotherm ΔT_{max} = 265°C in DTA may be attributed to removal of noncoordinated part of the ligand. The second step decomposition from 550~800°C, with mass loss of 22.01

TABLE 5 : Anti-fungal activities of compounds yield of Mycelial dry weight in mg (% inhibition)

Test compound	<i>Aspergillus Niger</i>		<i>Trichoderma</i>	
	250 ppm	500 ppm	250 ppm	500 ppm
	79	79	70	70
[C ₁₅ H ₁₃ N ₂ O ₂] (H ₂ L)	60 (23)	24 (70)	39 (43)	18 (73)
[C ₃₀ H ₂₆ N ₄ O ₄ Cu]	39 (49)	10 (87)	20 (71)	02 (97)
[C ₃₀ H ₂₆ N ₄ O ₄ Ni]	42 (46)	13 (84)	22 (69)	03 (96)
[C ₃₀ H ₃₀ N ₄ O ₆ Co]	49 (37)	16 (80)	31 (54)	04 (94)
[C ₃₀ H ₃₀ N ₄ O ₆ Mn]	52 (33)	18 (77)	34 (51)	08 (89)
[C ₃₀ H ₃₀ N ₄ O ₆ Fe]	53 (32)	18 (77)	35 (50)	12 (83)

% (calcd.22.82 %) corresponds to decomposition of coordinated part of ligand. A broad endotherm ΔT_{max} = 754°C in DTA is observed for this step. The mass of final residue corresponds to stable CoO, 16.01 % (calcd.16.62 %).

Kinetic calculations

The kinetic and thermodynamic parameters viz n (order of reaction), energy of activation (E_a), pre-exponential factor (z), entropy of activation (ΔS) and free energy change (ΔG) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method^[31] and Coats-Redfern integral method^[31]. The data is given in TABLE 3. The results show that the values obtained by two methods is comparable. The calculated value of energy of activation of the complex is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the metal complex^[32,33]. The negative value of entropy of activation indicates that the activated complex is more ordered than the reactant and that the reactions is slow. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

Antimicrobial activity

The antimicrobial activity of the ligand and its complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus* and *Escherichia coli* by paper disc plate method^[34]. The compounds were tested at the concentration 0.5 mgmL⁻¹ and 1 mgmL⁻¹ in DMF and compared with known antibiotics viz ciproflaxin.

(TABLE 4). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method^[35] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (TABLE 5). From TABLE 4 and 5, it is clear that the inhibition by metal chelates is higher than that of a ligand and metal salts. The results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes^[34,35]. Such enhanced activity of metal chelates is due to increased lipophilic nature of the metal ions in complexes^[36]. The increase in activity with concentration is due to the effect of metal ions on the normal process.

Investigation of antifungal activity of the ligand and its metal complexes revealed that all metal chelates are more fungi toxic than their parent ligand TABLE 5. The antifungal activity of the ligand is found to enhance several times on being coordinated with metal ions. Comparison of activities of the ligand and its metal chelates showed that the copper complex is approximately found to be two times more active as the ligand, against *Aspergillus Niger* and activity of ligand against *Trichoderma* is found to increase after chelation and antibacterial studies that the metal chelates have higher activity than the corresponding free ligand and control against the same microorganism under identical experimental conditions.

As a result, metal complexes of Cu(II), Ni(II) and Co(II) shows good antibacterial and antifungal activity, where as Mn (II) and Fe (III) complexes shows comparatively less activity.

CONCLUSION

In the light of above discussion we have proposed square-planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II), Mn(II) and Fe(III) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, ON bidentate, coordinating via amide oxygen and azomethin nitrogen as illustrated in figure 2. The complexes are biologically active and are having enhanced antimicrobial activities compared to free ligand. TG/DT study reveals thermal stability of metal complexes. The XRD analysis suggests monoclinic crystal system for Fe (III) complex.

REFERENCES

- [1] C.Loncle, J.M.Brunel, N.Vidal, M.Dherbomez, Y.Letourneux; Eur.J.Med.Chem., **39**, 1067 (2004).
- [2] S.G.Ku, Cu Kgu Zel, A.Mazi, F.Sahin, S.O'ztu Rk, J.Stables; Eur.J.Med.Chem., **38**, 1005, (2003).
- [3] R.Todeschini, A.L.P.de Miranda, K.C.M.da Silva, S.C.Parrini, E.J.Barreiro; Eur.J.Med.Chem., **33**, 189 (1998).
- [4] P.Melnyk, V.Leroux, C.Sergheraert, P.Grellier; Bioorg.Med.Chem.Lett., **16**, 31 (2006).
- [5] P.C.Lima, L.M.Lima, K.C.M.da Silva, P.H.O.Le'da, A.L.P.de Miranda, C.A.M.Fraga, E.J.Barreiro; Eur.J.Med.Chem., **35**, 187 (2000).
- [6] C.Cunha, J.M.Figueiredo, J.L.M.Tributino, A.L.P.Miranda, H.C.Castro, R.B.Zingali, C.A.M.Fraga, M.C.B.V.de Souza, V.F.Ferreira, E.J.Barreiro; Bioorg.Med.Chem., **11**, 2051 (2003).
- [7] K.K.Bedia, O.Elc'in, U.Seda, K.Fatma, S.Nathaly, R.Sevim, A.Dimoglo; Eur.J.Med.Chem., **41**, 1253 (2006).
- [8] N.Terzioglu, A.Gu'rsoy; Eur.J.Med.Chem., **38**, 781 (2003).
- [9] P.B.Sreeja, A.Sreekanth, C.R.Nayar, M.R.Pra-thapachandra Kurup, A.Usman, I.A.Razak; S.Ch-antrapromma, H.K.Fun; J.of Molecular Structure, **5**, 645(2), 221-226 (2003).
- [10] A.I.Vogel; 'A Text Book of Qualitative Inorganic Analysis', 3rd, Ed., Logmans, London, 540 (1975).
- [11] R.S.Baliger, V.K.Revankar; J.Serb.Chem.Soc., **71**(12), 1301-1310 (2006).
- [12] F.Hueso-Urena, N.A.Illan-Cabeza, M.N.Moreno-Carretero, A.L.Penans- Chamorro; Acta Chem. Solv., **47**, 481 (2000).
- [13] K.K.Narang, A.Aggarwal, H.K.Fun; J.Inorg. Chim.Acta, **9**, 137 (1974).
- [14] S.Chandra, M.Tyagi, M.Refat; J.Ser.Chem.Soc., **74**(8-9), 907-915 (2009).
- [15] E.R.Blout, M.Fields, R.Karplus; J.Am.Chem.Soc., **70**, 194 (1948).
- [16] R.Natrajan, K.Antonyasamy, C.Thangaraja; Transition Met.Chem., **28**, 29-36 (2003).
- [17] A.S.Munde, A.N.Jagdale, S.M.Jadhav, T.K.Chon-dhekar; J.of the Korean Chemical Society, **53**(4), (2009).
- [18] R.Natrajan, K.Antonyasamy, C.Thangaraja; Transition Met.Chem., **28**, 29 (2003).
- [19] N.Raman, Y.Pitchaikaniraja, A.Kulandaisamy; Proc.Indian Acad.Sci.(Chem.Sci.), **113**, 183 (2001).

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- [20] K.M.Reddy, M.B.Halli, A.C.Hiremath; J.Indian Chem.Soc., **17**, 118 (1994).
- [21] M.Mokhles Abd-Elzaher; J.Chin.Chem.Soc., **48**, 153 (2001).
- [22] A.B.P.Leve; Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 275 (1968).
- [23] K.C.Satpathy, A.K.Panda, R.Mishra, I.Pande; Transition Met.Chem., **16**, 410 (1991).
- [24] M.N.Patel, V.J.Patel; Synth.React.Inorg.Met.Org. Chem., **19**, 137 (1989).
- [25] L.Sacconi; Transition Met.Chem., **61**, 943 (1968).
- [26] J.R.Carvajal, T.Roisnel; 'Winplotr, A Graphic Tool for Powder Diffraction', Laboratoire Leon Brillouin (cea/enrs) 91191 gif suryvette cedexFrance, (2004).
- [27] D.P.Shoemaker, C.W.Garland; 'Experiments in Physical Chemistry', 5th Edn., McGraw-Hill International Edition, New York, 17-27 (1989).
- [28] N.S.Bhave, R.B.Kharat; J.Inorg.Nucl.Chem., **42**, 977 (1980).
- [29] V.K.Revankar, V.B.Mahale; Indian J.Chem.A, **28**, 683 (1979).
- [30] H.H.Horowitz, G.Metzger; Anal.Chem., **35**, 1464 (1963).
- [31] A.W.Coats, I.P.Redfern; Nature, **20**, 68 (1964).
- [32] A.M.El-Awad; J.Therm.Anal.Cal., **61**, 197 (2000).
- [33] A.Impura, Y.Inoue, I.Yasumori; Bull.Chem.Soc.Jpn., **56**, 2203 (1983).
- [34] P.S.Mane, S.G.Shirodkar, B.R.Arbad, T.K.Chondhekar; Indian J.Chem., **40**, 648 (2001).
- [35] R.P.Venketeswar, N.A.Venkata; Indian J.Chem.A, **42**, 896 (2003).
- [36] L.Mishra, V.K.Singh; Indian. J.Chem.A, **32**, 446 (1993).