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## Synthesis, characterization and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand

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**Abstract:** Complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with an asymmetric tetradentate Schiff base ligand derived from dehydroacetic acid, 4-methyl-*o*-phenylenediamine and salicylic aldehyde were synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV–Vis, IR, <sup>1</sup>H-NMR spectroscopy, X-ray diffraction analysis of powdered samples and thermal analysis, and screened for antimicrobial activity. The IR spectral data suggested that the ligand behaves as a dibasic tetradentate ligand towards the central metal ion with an O NNO donor atoms sequence. From the microanalytical data, the stoichiometry of the complexes 1:1 (metal:ligand) was found. The physico-chemical data suggested square planar geometry for the Cu(II) and Ni(II) complexes and octahedral geometry for the Co(II), Mn(II) and Fe(III) complexes. The thermal behaviour (TGA/DTA) of the complexes was studied and kinetic parameters were determined by Horowitz–Metzger and Coats–Redfern methods. The powder X-ray diffraction data suggested a monoclinic crystal system for the Co(II), Mn(II) and Fe(III) complexes. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and fungicidal activity against *Aspergillus niger* and *Trichoderma viride*.

**Keywords:** dehydroacetic acid; asymmetrical tetradentate Schiff base; transition metal complexes; thermal analysis; powder X-ray diffraction; antimicrobial activity.

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## INTRODUCTION

Schiff bases are most widely used as chelating ligands in coordination chemistry.<sup>1</sup> They are also useful in catalysis and in medicine as antibiotics, antiallergic and antitumor agents.<sup>2</sup> The metal complexes of Schiff bases derived from heterocyclic compounds have been the centre of attraction for many workers in recent years.<sup>3-7</sup> Tetradentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds.<sup>8</sup> Many symmetrical bis-tetradentate Schiff bases of 1,2-diamines with *o*-hydroxyaldehydes/ketones have been prepared and studied intensively. However, much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1,2-diamines and different aldehydes/ketones. In particular those derived from aromatic 1,2-diamines have been under-investigated.<sup>9</sup> It is worthwhile to mention that as symmetrical Schiff bases of this type are difficult to obtain and not easy to isolate.<sup>10</sup>

One of the oxygen heterocyclic compounds 3-acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione (dehydroacetic acid or DHA) was reported to be an excellent chelating agent and to possess promising fungicidal, bactericidal, herbicidal and insecticidal activities.<sup>11-14</sup> It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems.<sup>15</sup> A search of the literature revealed that no work has been done on transition metal complexes of the asymmetrical Schiff bases derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde. The synthesis of an asymmetrical tetradentate Schiff base formed by the condensation of 4-methyl-*o*-phenylenediamine, dehydroacetic acid and salicylic aldehyde (Fig. 1) is reported. The complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with this ligand were also prepared in the solid state and characterized by different physico-chemical methods.

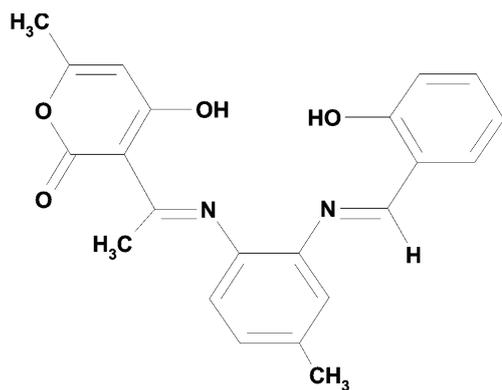


Fig. 1. Structural formula of the prepared asymmetrical ligand.

## EXPERIMENTAL

Dehydroacetic acid (purity  $\geq 99\%$ ) for synthesis was obtained from Merck, Germany, and used as supplied. 4-Methyl-*o*-phenylenediamine and salicylic aldehyde of A.R. grade, obtained from Acros Organics and Sisco, respectively, were used for the synthesis of the li-

gand. A.R. grade hydrated metal chlorides from S. D. Fine Chemicals were used for the preparation of the complexes. The C, H and N contents were determined on a Perkin Elmer (2400) CNS analyzer. The IR spectra were recorded on an FTIR spectrometer, Perkin Elmer Company using KBr pellets. The  $^1\text{H-NMR}$  spectrum of the ligand was measured in  $\text{CDCl}_3$  using TMS as the internal standard. The TG/DTA curves and XRD patterns were recorded on a Perkin Elmer TA/SDT-2960 and a Philips 3701, respectively. The UV-Vis spectra of the complexes were recorded on a Shimadzu UV-1601 spectrometer. The magnetic susceptibility measurements of the metal chelates were determined on a Gouy balance at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. The molar conductance of the complexes was measured on an Elico CM 180 conductivity meter using  $10^{-3}$  M solutions in DMF. The microorganisms were collected from the Biotechnology Department, Milind College of Science, Aurangabad and the strains were maintained on nutrient agar at  $4^\circ\text{C}$ .

#### Synthesis

The asymmetric tetradentate Schiff base ligand was synthesized via a stepwise approach.<sup>16</sup> In the first step, the mono-Schiff base compound was prepared by refluxing 50 mL solution of 1.0 mmol (0.168 g) of dehydroacetic acid and 1.0 mmol (0.12 g) 4-methyl-*o*-phenylenediamine in super dry ethanol for about 3 h. The thus-formed mono-Schiff base was then refluxed with 1.0 mmol (0.12 g) salicylic aldehyde to prepare the asymmetric ligand viz. 4-hydroxy-3-(1-{{2-[(2-hydroxybenzylidene)amino]-4-methylphenyl}imino}ethyl)-6-methyl-2H-pyran-2-one ( $\text{H}_2\text{L}$ ). The thus-formed asymmetric Schiff base was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol (yield: 70 %).

To a hot methanolic solution (25 ml) containing 1.0 mmol (0.38 g) of the ligand, a methanolic solution (25 ml) of a metal chloride (hydrate) (1.0 mmol) 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 3 h. The precipitated solid metal complex was filtered off under hot conditions and washed with hot methanol, petroleum ether ( $40\text{--}60^\circ\text{C}$ ) and dried over anhydrous  $\text{CaCl}_2$  in a vacuum desiccator (yield: 50–60 %).

#### Antimicrobial activity

The antimicrobial activity of the ligand and metal complexes were tested *in vitro* against bacteria *Staphylococcus aureus* and *Escherichia coli* by the paper disc plate method.<sup>17</sup> The compounds were tested at the concentration 0.50 and  $1.0\text{ mg mL}^{-1}$  in DMF and compared with known antibiotics viz. ciprofloxacin. For fungicidal activity, the compounds were screened *in vitro* against *Aspergillus niger* and *Trichoderma viride* by the mycelia dry weight method,<sup>18</sup> using glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with the control.

### RESULTS AND DISCUSSION

The physical characteristics, microanalytical, and molar conductance data of the ligand and its metal complexes are given in Table I. The analytical data of the complexes revealed 1:1 mole ratio (metal:ligand) and corresponds well with the general formula  $[\text{ML}]$  ( $\text{M} = \text{Cu}(\text{II})$  and  $\text{Ni}(\text{II})$ ) and  $[\text{ML}(\text{H}_2\text{O})_2]$  ( $\text{M} = \text{Co}(\text{II})$ ,  $\text{Mn}(\text{II})$  or  $\text{Fe}(\text{III})$ ). The magnetic susceptibilities of the  $\text{Cu}(\text{II})$  and  $\text{Ni}(\text{II})$  complexes at room temperature were found to be consistent with square-planar geometry and those of the  $\text{Co}(\text{II})$ ,  $\text{Mn}(\text{II})$  and  $\text{Fe}(\text{III})$  complexes with high-spin octahedral structures having two water molecules coordinated to the metal ion. The

presence of two coordinated water molecules was confirmed by TG/DT analysis. The metal chelate solutions in DMF showed low conductivity, supporting the non-electrolyte nature of the complexes.

TABLE I. Physical characterization and analytical and molar conductance data of the prepared compounds

Compound F.	W.	M.p. °C	Colour	$\Lambda$ S cm <sup>2</sup> mol <sup>-1</sup>	Found (Calcd.), %			
					C	H	N	
[C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ] (H <sub>2</sub> L)	376.42	178	Yellow	–	70.12 (70.20)	5.40 (5.36)	7.38 (7.44)	–
[Cu(C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> )]	437.974	>300	Green	20.13	60.58 (60.28)	3.90 (4.11)	6.50 (6.39)	14.23 (14.51)
[Ni(C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> )]	433.13	>300	Red	28.70	61.24 (60.95)	4.52 (4.16)	6.20 (6.46)	13.60 (13.55)
[CoC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	469.35	245	Reddish brown	18.20	56.50 (56.25)	4.88 (4.69)	6.25 (5.97)	12.95 (12.56)
[MnC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	465.36	255	Brown	17.55	56.25 (56.73)	5.00 (4.73)	6.35 (6.02)	12.04 (11.81)
[FeC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	466.27	>300	Brown	42.63	56.30 (56.62)	4.26 (4.72)	5.75 (6.01)	12.00 (11.98)

#### <sup>1</sup>H-NMR spectrum of the ligand

The <sup>1</sup>H-NMR spectra of the free ligand in CDCl<sub>3</sub> at room temperature showed the following signals at  $\delta$  (ppm): 2.15 (3H, s, C<sub>6</sub>-CH<sub>3</sub>), 2.45 (3H, s, phenyl-CH<sub>3</sub>), 2.55 (3H, s, N=C-CH<sub>3</sub>), 5.82 (1H, s, C<sub>5</sub>-H), 6.9–7.4 (8H, m, phenyl), 11.1 (1H, s, phenolic OH), 8.60 (1H, s, N=C-H) and 15.80 (1H, s, enolic OH of the DHA moiety).

#### IR spectra

The IR spectrum of the free ligand showed characteristic bands at 3100–3400, 1703, 1662, 1362, and 1223 cm<sup>-1</sup>, assignable to  $\nu$ (OH) (intramolecular hydrogen bonded),  $\nu$ (C=O) (lactone carbonyl),  $\nu$ (C=N) (azomethine),  $\nu$ (C-N) (aryl azomethine) and  $\nu$ (C-O) (phenolic) stretching modes, respectively.<sup>19</sup> The absence of a weak broad band in the 3100–3400 cm<sup>-1</sup> region, noted in the spectra of the metal complexes, indicates deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by the upward shift of  $\nu$ (C-O) (phenolic)<sup>18</sup> by 35–70 cm<sup>-1</sup>. On complexation, the  $\nu$ (C=N) band is shifted to lower wave numbers with respect to the free ligand, suggesting that the nitrogen of the azomethine group is coordinated to the metal ion. This is supported by the upward shift in  $\nu$ (C-N) by 15–55 cm<sup>-1</sup>.<sup>20</sup> The IR spectra of the metal chelates showed new bands in the 542–580 and 460–513 cm<sup>-1</sup> regions, which can be assigned to  $\nu$ (M-O) and  $\nu$ (M-N) vibrations, respectively.<sup>21</sup> The IR spectra of Co(II),

Mn(II) and Fe(III) complexes show a strong band in the 3200–3600  $\text{cm}^{-1}$  region, indicating the presence of coordinated water in these complexes. The presence of coordinated water was further confirmed by the appearance of a non-ligand band in the 830–840  $\text{cm}^{-1}$  region, assignable to the rocking mode of water.<sup>22</sup> The presence of coordinated water was also established and supported by TG/DT analysis of these complexes. Hence, coordination occurred via the phenolic oxygen and the azomethine nitrogen of the ligand molecule.

#### Magnetic measurements and electronic absorption spectra

The magnetic and electronic spectral data are given in Table II. The electronic absorption spectrum of the Cu(II) complex in DMSO solution shows three bands at 17813, 26525 and 30487  $\text{cm}^{-1}$ , assignable to the transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and two intra-ligand charge transfer bands. These data and the magnetic moment value of 1.72  $\mu_B$  suggest square-planar geometry around Cu(II).<sup>21,23</sup> The electronic absorption spectrum of the Ni(II) complex in DMSO solution consisted of two bands at about 17985 and 26595  $\text{cm}^{-1}$  assignable to the transition  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  and a charge transfer transition, respectively. These data, the diamagnetic nature and red colour of the complex are in accordance with square-planar geometry for the Ni(II) complex.<sup>24,25</sup> The electronic absorption spectrum of the Co(II) complex in DMSO solution had three bands at 10869, 19157 and 26954  $\text{cm}^{-1}$ , which may be attributed to the transitions  ${}^4T_{1g} \rightarrow T_{2g}(F)$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$  and charge transfer, respectively. Together with the magnetic moment value of 4.70  $\mu_B$ , a high-spin octahedral geometry for the Co(II) complex<sup>26,27</sup> was proposed. The octahedral geometry was further supported by the ratio  $\nu_2/\nu_1 = 1.762$ ,

TABLE II. Magnetic and electronic absorption spectral data (in DMSO) of the compounds

Compound	$\mu_{\text{eff}} / \mu_B$	$\nu / \text{cm}^{-1}$	B and assignment	Geometry
[C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ] (H <sub>2</sub> L) –		31347	INCT <sup>a</sup>	–
		40816	INCT	
[Cu(C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> )] 1.72		17813	${}^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
		26525	INCT	
		30487	INCT	
[Ni(C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> )] Dia	magnetic	17985	${}^1A_{1g} \rightarrow {}^1T_{2g}$	Square-planar
		26595	INCT	
[CoC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] 4.70		10869	${}^4T_{1g} \rightarrow T_{2g}(F)$	Octahedral
		19157	${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$	
		26954	INCT	
[MnC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] 5.77		16051	${}^6A_{1g} \rightarrow {}^4T_{1g}$	Octahedral
		23640	${}^6A_{1g} \rightarrow {}^4T_{2g}$	
		29411	INCT	
[FeC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] 5.79		12694	${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4D)$	Octahedral
		18761	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
		31250	INCT	

<sup>a</sup>Intra-ligand charge transfer band

which is close to the value expected for octahedral geometry. The electronic absorption spectrum of the Mn(II) complex in DMSO solution contained three bands at 16051, 23640 and 29411  $\text{cm}^{-1}$ , assignable to the transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and charge transfer, respectively. The electronic transitions together with a magnetic moment value  $5.77 \mu_B$ , which is close to the spin-only value ( $5.92 \mu_B$ ) suggests high spin octahedral geometry for the Mn(II) complex.<sup>26,28</sup> The electronic absorption spectrum of Fe(III) complex shows three weak bands at 12694, 18761 and 31250  $\text{cm}^{-1}$ , which may be assigned to the transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4D)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and charge transfer, respectively. The electronic transitions together with the magnetic moment value of  $5.79 \mu_B$  suggested high-spin octahedral geometry for the Fe(III) complex.<sup>26,29</sup>

#### Thermal analysis

The simultaneous TG/DTA analysis of the Cu(II), Ni(II), Co(II) and Mn(II) metal complexes was studied from ambient temperature to 1000 °C under a nitrogen atmosphere using  $\alpha\text{-Al}_2\text{O}_3$  as the reference. The TG curve of the Cu(II) and Ni(II) complexes exhibited no mass loss up to 270 °C, indicating the absence of coordinated water<sup>20</sup> and the high thermal stability of the complexes. On the TG curve of Cu(II) complex, the first step of decomposition from 295 to 352 °C, with a mass loss 21.75 % (calcd. 22.83 %), accompanied by an exothermic peak with  $t_{\text{max}} = 309$  °C on the DTA curve, may be attributed to the removal of the non-coordinated part of the ligand. The second step, from 485 to 650 °C with mass loss 49.30 % (calcd. 49.10 %), corresponds to the decomposition of the coordinated part of the ligand. An exothermic peak with  $t_{\text{max}} = 505.7$  °C on the DTA curve was observed for this step. The mass of the final residue corresponded to stable CuO, 20.85 % (calcd. 18.37 %).

The TG curve of the Ni(II) complex shows a two-step decomposition. The first step from 360 to 410 °C with a mass loss of 24.50 % (calcd. 23.08%), accompanied by an endothermic peak with  $t_{\text{max}} = 319$  °C on the DTA curve, may be attributed to the decomposition of the non-coordinated part of the ligand. The second step, from 460 to 835 °C with a mass loss of 50.24 % (calcd. 49.43 %), corresponds to the removal of the coordinated part of the ligand. For this step, a broad endothermic peak in the DTA was observed. The mass of the final residue 12 % (calcd. 17.05 %) does not correspond to any stoichiometry of the end product, as the residue obtained is not close to that expected for metal oxide.

The thermogram of the Co(II) complex shows a mass loss of 7.5 % (calcd. 7.6 %) in the temperature range 190–216 °C and an endothermic DTA peak in this region,  $t_{\text{min}} = 207$  °C, indicates the loss of two coordinated water molecules.<sup>30,31</sup> The anhydrous complex first showed decomposition from 240–550 °C, with a 21 % (calcd. 21.32 %) mass loss and a broad exothermic peak with  $t_{\text{max}} = 255$  °C in the DTA, which may be attributed to the removal of the non-coordinated part of the ligand. The second step of the decomposition from 545–

–860 °C, with a mass loss of 54.0 % (calcd. 54.58%) corresponds to the decomposition of the coordinated part of the ligand. A broad endothermic peak in the DTA was observed for this step. The mass of the final residue corresponded to stable CoO, 13.85 % (calcd. 15.09 %).

The TG curve for the Mn(II) complex showed a first mass loss of 7.30 % (calcd. 7.73 %) in the temperature range 190–200 °C and an endothermic peak in this region with  $t_{\min} = 195.7$  °C, indicating the removal of two coordinated water molecules. The anhydrous complex exhibited a single-step decomposition from 240 to 900 °C, with a 62 % mass loss and a broad endothermic peak in the DTA.

#### Kinetic calculations

The kinetic and thermodynamic parameters *viz.* the order of the reaction ( $n$ ), the energy of activation ( $E_a$ ), the pre-exponential factor ( $Z$ ), the entropy of activation ( $\Delta S^\ddagger$ ) and the Gibbs energy change ( $\Delta G^\ddagger$ ), together with the correlation coefficient ( $r$ ) for the non-isothermal decomposition of the metal complexes, were determined by the Horowitz–Metzger (HM) approximation method<sup>32</sup> and the Coats–Redfern integral method.<sup>33</sup> The obtained data are given in Table III. The results showed that the values obtained by two methods are comparable. The calculated values of the activation energy of the complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex.<sup>34,35</sup> The negative activation entropy value indicates that the activated complexes were more ordered than the reactant and that the reactions were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer electronic transitions.

TABLE III. The kinetic parameter of degradation of the metal complexes calculated by the Horowitz–Metzger (HM) and Coats–Redfern (CR) methods

M(II) complex	Step	$n$	Method	$E_a$ kJ mol <sup>-1</sup>	$Z$ s <sup>-1</sup>	$\Delta S^\ddagger$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$r$
Cu(II) I	I	1.01	HM	267.95	$1.8 \times 10^{27}$	271.67	248.67	0.9948
			CR	264.73	$1.94 \times 10^{23}$	195.28	250.86	0.9948
	II	1.42	HM	97.15	$1.9 \times 10^6$	-133.07	110.39	0.9982
			CR	93.34	$6.06 \times 10^5$	-142.73	113.55	0.9951
Ni(II) I	I	0.85	HM	136.36	$8.7 \times 10^{11}$	-22.99	138.18	0.9909
			CR	132.82	$2.1 \times 10^9$	-73.47	138.68	0.9890
	II	1.05	HM	47.17	68.1	-219.38	71.92	0.9977
			CR	46.37	41.04	-223.60	71.59	0.9892
Co(II) I	I	1.1	HM	12.53	0.7368	-253.36	30.90	0.9855
			CR	12.52	0.8983	-251.71	30.77	0.9912
	II	0.95	HM	37.16	4.290	-242.78	65.91	0.9995
			CR	33.34	4.756	-241.93	62.93	0.9995
Mn(II) –		0.65	HM	16.13	0.325	-263.26	43.83	0.9982
			CR	18.87	1.090	-253.16	45.51	0.9836

### Powder X-ray diffraction analysis

The X-ray diffractograms of the Co(II), Mn(II) and Fe(III) complexes were scanned in the range 5–100° at a wavelength of 1.543 Å. The diffractograms and associated data depict the  $2\theta$  value for each peak, the relative intensity and inter-planar spacing ( $d$ -values). The X-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10 % were indexed using a computer programme.<sup>36</sup> This indexing method also yields the Miller indices ( $hkl$ ), the unit cell parameters and the unit cell volume. The unit cell of Co(II) complex yielded values of lattice constants:  $a = 8.9706$  Å,  $b = 8.6441$  Å and  $c = 4.7755$  Å, and a unit cell volume  $V = 369.2291$  Å<sup>3</sup>. The unit cell of the Mn(II) complex yielded values of lattice constants:  $a = 24.5882$  Å,  $b = 4.4656$  Å,  $c = 5.8676$  Å, and a unit cell volume  $V = 627.2087$  Å<sup>3</sup>. The unit cell of the Fe(III) complex yielded values of lattice constants:  $a = 7.0696$  Å,  $b = 14.8954$  Å,  $c = 5.3504$  Å, and a unit cell volume  $V = 830.4539$  Å<sup>3</sup>. In concurrence with the cell parameters, conditions such as  $a \neq b \neq c$  and  $\alpha = \gamma = 90^\circ \neq \beta$  required for a monoclinic sample were tested and found to be satisfactory. Hence, it can be concluded that the Co(II), Mn(II) and Fe(III) complexes were monoclinic crystal systems. The experimental density values of the complexes were determined using the specific gravity method<sup>37</sup> and found to be 2.1908, 2.5002, and 2.0522 g cm<sup>-3</sup> for the Co(II), Mn(II) and Fe(III) complexes, respectively. Using the experimental density values,  $\rho$ , the molecular weight of the complexes,  $M$ , Avogadro's number,  $N$ , and the volume of the unit cell,  $V$ , the number of molecules per unit cell,  $n$ , were calculated using the equation  $\rho = nM/NV$  and they were found to be one for Co(II) and two for the Mn(II) and Fe(III) complexes. With these values, the theoretical densities were computed and found to be 2.1824, 2.4637 and 2.0645 g cm<sup>-3</sup> for the respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error.<sup>38</sup>

### Antimicrobial activity

The results of the *in vitro* antimicrobial activity of the ligand and metal complexes against the bacteria *Staphylococcus aureus* and *Escherichia coli*, determined by the paper disc plate method,<sup>17</sup> are presented in Table IV, in which the activity of a known antibiotic *viz.* ciprofloxacin is included for comparison. The results of the *in vitro* fungicidal activity of the compounds against *Aspergillus niger* and *Trichoderma viride* determined by the mycelia dry weight method<sup>18</sup> with glucose nitrate media, are given in Table V, in which the results of the control are also presented. From Tables IV and V, it is clear that the inhibition by the metal chelates was higher than that of the free ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes.<sup>17,18</sup> The inhibition of growth (%) of both fungi due to metal com-

plexes decreased in the order Cu (II) > Ni (II) > Co (II) > Mn (II) > Fe (II). Such enhanced activity of metal chelates is due to the lipophilic nature of the metal ions in the complexes.<sup>39</sup> The increase in activity with concentration is due to the effect of metal ions on the normal metabolic function of the cell. The action of compounds may involve the formation of hydrogen bonds with the active centre of cell constituents, resulting in interference with the normal function of the cell.<sup>40</sup>

TABLE IV. Antibacterial activity of the compounds

Test compound	Inhibition zone, mm			
	<i>E. coli</i>		<i>S. aureus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciprofloxin	29	32	31	35
[C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ] (H <sub>2</sub> L)	10	12	12	15
[CuC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ]	15	18	16	19
[NiC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ]	12	16	14	16
[CoC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	13	16	15	17
[MnC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	11	12	12	15
[FeC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	11	13	14	15

TABLE V. Yield of mycelial dry weight in mg and inhibition in % (in parentheses)

Test compound	<i>A. niger</i>		<i>T. viride</i>	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
[C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ] (H <sub>2</sub> L)	60 (24)	22 (72)	38 (46)	17 (76)
[CuC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ]	38 (52)	09 (89)	19 (73)	01 (99)
[NiC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> ]	40 (49)	12 (85)	20 (71)	02 (97)
[CoC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	49 (38)	14 (82)	25 (64)	04 (94)
[MnC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	45 (43)	16 (80)	28 (60)	07 (90)
[FeC <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]	52 (34)	17 (78)	32 (54)	09 (87)

### CONCLUSIONS

Based on the physicochemical and spectral data discussed above, square-planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II), Mn(II) and Fe(III) complexes are proposed. It is assumed that the ligand behaves as dibasic, ONNO tetradentate, coordinating *via* the phenolic oxygen and the imino nitrogen as illustrated in Fig. 2. The complexes are biologically active and showed enhanced antimicrobial activities compared to the free ligand. A thermal study revealed that the complexes are thermally stable. An XRD study suggested the monoclinic crystal system for the Co(II), Mn(II) and Fe(III) complexes.

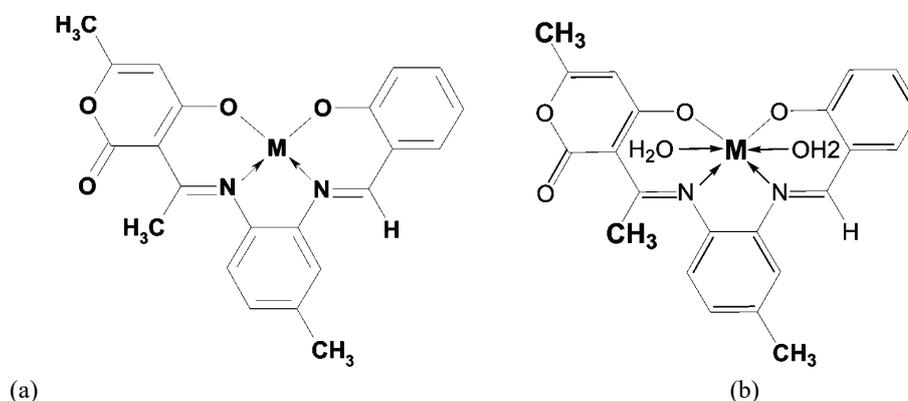


Fig. 2. The proposed geometry of the complexes; a)  $M(II) = Cu(II)$  or  $Ni(II)$  and b)  $M = Co(II)$ ,  $Mn(II)$  or  $Fe(III)$ .

## ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И ТЕРМИЧКА СТУДИЈА НЕКИХ ПРЕЛАЗНИХ  
МЕТАЛНИХ КОМПЛЕКСА СА АСИМЕТРИЧНИМ ТЕТРАДЕНТАТНИМ  
ШИФОВИМ БАЗАМА

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Синтетисани су комплекси  $Cu(II)$ ,  $Ni(II)$ ,  $Co(II)$ ,  $Mn(II)$  и  $Fe(III)$  са асиметричним тетраденатним Шифовим базама изведеним из дехидросирћетне киселине, 4-метил-о-фенилендиаминa и салицил-алдехида и окарактерисани елементалном анализом, кондуктометријом, магнетном суцептибилношћу, UV-Vis, IR, <sup>1</sup>H-NMR спектрима, рендгенском дифракционом анализом праха, термичком анализом и тестирани на антимикуробну активност. IR спектрални подаци сугерисали су да се лиганд понаша као двобазни тетраденатни лиганд према централном металном јону са ONNO секвенцијом донорних атома. Из микроанализе нађена је стехиометрија комплекса 1 : 1 (метал:лиганд). Физичко-хемијски подаци сугерисали су квадратно-планарну геометрију за  $Cu(II)$  и  $Ni(II)$  комплексе и октаедарску геометрију за комплексе  $Co(II)$ ,  $Mn(II)$  и  $Fe(III)$ . Термичко понашање (TGA/DTA) комплекса је проучавано и кинетички параметри су одређени Horowitz-Metzger и Coats-Redfern методама. Лиганд и његови метални комплекси су тестирани на антибактеријску активност према *Staphylococcus aureus* и *Escherichia coli* и антифунгалну активност према *Aspergillus niger* и *Trichoderma viride*. Рендгенски дифракциони подаци праха указали су на моноклинични кристални систем за  $Co(II)$ ,  $Mn(II)$  и  $Fe(III)$  комплексе.

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## REFERENCES

1. Y. Shibuya, K. Nabari, M. Kondo, S. Yasu e, K. Maeda, F. Uchida, H. Kawaguchi, *Chem. Lett.* **37** (2008) 78
2. B. J. Gangani, P. H. Parsania, *Spectrosc. Lett.* **40** (2007) 97

3. B. Sindhuku mari, G. Rij uulal, K. Mohanan , *Synth. React. Inorg., Met.-Org. Nano-Met. Chem.* **39** (2009) 24
4. M. Thankamony, K. Mohanan, *Indian J. Chem.* **46A** (2007) 247
5. N. Raman, J. Dhavethu Raju, A. Sakthivel, *J. Chem. Sci.* **119** (2007) 303
6. D. Wang, Y. Yang, Y. Yang, T. Zhao, X. Wu, S. Wang, Y. Hou, W. Chen, *Chin. Sci. Bull.* **51** (2006) 785
7. K. Shivakumar, Shashidhar, M. B. Halli, *Russ. J. Phys. Chem.* **82** (2008) 2269
8. S. A. Sadeek, M. S. Refat, *J. Korean Chem. Soc.* **50** (2006) 107
9. N. T. S. Pan, D. H. Brown, H. Adams, S. E. Spey, P. St yring, *J. Chem. Soc. Dalton Trans.* **9** (2004) 1348
10. S. F. Tan, K. P. Ang, *Transition Met. Chem.* **13** (1988) 64
11. D. Surya Rao, B. L. Subha Rao, V. T. John, M. C. Ganork ar. *Nat. Acad. Sci. Lett.* **1** (1978) 402
12. D. Surya Rao, C. Sadasiva Reddy, V. T. John, M. C. Ganorkar. *Curr. Sci.* **49** (1980) 511
13. B. Schleiffenbaum, O. Spertini, F. Tedder Thomas, *J. Cell. Biol.* **119** (1992) 229
14. V. G. Stanley, S. Woldesenbet, G. Cassandra, *Poult. Sci.* **75** (1996) 42
15. A. Levai, J. Jeko, *Monatsh. Chem.* **137** (2006) 339
16. M. A. Qayyoom, P. Hanumanthu, C. V. Ratnam, *Indian J. Chem.* **21B** (1982) 883
17. P. S. Mane, S. G. Shirodkar, B. R. Arbad, T. K. Chondhekar, *Indian J. Chem.* **40** (2001) 648
18. S. F. Tan, K. P. Ang, H. L. Jatchandran, *Transition Met. Chem.* **9** (1984) 390
19. P. Venketeswar Rao, A. Venkata Narasaiah, *Indian J. Chem.* **42A** (2003) 896
20. D. C. Dash, A. K. Panda, P. Je na, S. B. Patjoshi, A. Mahapatra, *J. Indian Chem. Soc.* **79** (2002) 48
21. R. Natrajan, K. Antonysamy, C. Thangaraja, *Transition Met. Chem.* **28** (2003) 29
22. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 3<sup>rd</sup> ed., Wiley Interscience, New York, 1970, pp. 159, 167, 214
23. N. Raman, Y. Pitchaikaniaraja, A. Kulandaisamy, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 183
24. K. M. Reddy, M. B. Halli, A. C. Hiremath, *J. Indian Chem. Soc.* **17** (1994) 118
25. M. Mokhles Abd-Elzaher, *J. Chin. Chem. Soc.* **48** (2001) 153
26. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968, p. 275
27. K. C. Satpathy, A. K. Panda, R. Mishra, I. Pande, *Transition Met. Chem.* **16** (1991) 410
28. L. Sacconi, *Transition Met. Chem.* **61** (1968) 943
29. M. N. Patel, V. J. Patel, *Synth. React. Inorg., Met.-Org. Chem.* **19** (1989) 137
30. N. S. Bhave, R. B. Kharat, *J. Inorg. Nucl. Chem.* **42** (1980) 977
31. V. K. Revankar, V. B. Mahale, *Indian J. Chem.* **28A** (1979) 683
32. H. H. Horowitz, G. Metzger *Anal. Chem.* **35** (1963) 1464
33. A. W. Coats, I. P. Redfern, *Nature* **20** (1964) 68
34. A.M. El-Awad, *J. Therm. Anal. Calorim.* **61** (2000) 197
35. A. Impura, Y. Inoue, I. Yasumori, *Bull. Chem. Soc. Jpn.* **56** (1983) 2203
36. J. R. Carvajal, T. Roisnel, *Winplotr, A Graphic Tool for Powder Diffraction*, Laboratoire Leon Brillouin (ceal/cnrs) 91191 Gif sur Yvette Cedex, France, 2004
37. D. P. Shoemaker, C. W. Garland, *Experiments in Physical Chemistry*, 5<sup>th</sup> ed., McGraw-Hill International Edition, New York, 1989
38. M. B. Deshmukh, S. Dhongade-Desai, S. S. Chavan, *Indian J. Chem.* **44** (2005) 1659
39. L. Mishra, V. K. Singh, *Indian J. Chem.* **32A** (1993) 446
40. N. Dharamraj, P. Viswanathamurthi, K. Natarajan, *Transition Met. Chem.* **26** (2001) 105.