

# SYNTHESIS, CHARACTERISATION, THERMAL AND SEMICONDUCTING STUDIES OF 2-HYDROXY-5-METHYLACETOPHENONE-*s*-METHYLDITHIOCARBAZATE COMPLEXES

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The Schiff base, HMASMZ, was prepared by the condensation of 2-hydroxy-5-methylacetophenone with *s*-methylthiocarbazate and its complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) were synthesised. All the complexes were characterised on the basis of elemental analysis, magnetic measurements, infrared spectra, electronic spectra and thermogravimetric analysis. IR and <sup>1</sup>H-NMR spectral studies revealed that the Schiff base behaves like a dibasic and tridentate ligand coordinating through the deprotonated phenolic oxygen, azomethine nitrogen and thioenolic sulphur atoms to the metal ion. The d.c. electrical conductivity of all the complexes have been studied over a wide range of temperatures. Various kinetic parameters have been evaluated by using Freeman-Carroll, Sharp-Wentworth and Coats-Redfern methods.

## INTRODUCTION

Schiff base complexes of transition metal ions have been studied by many workers due to their interesting chemical, electrical, magnetic and biological properties and industrial importance.<sup>1,2</sup> The survey of the literature reveals that much work has been done on the Schiff bases of simple aldehydes or ketones<sup>3</sup> but such work on the substituted acetophenones is scanty. It was therefore thought of interest to prepare and characterize some complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and VO(IV) with the Schiff base HMASMZ.

## RESULTS AND DISCUSSION

All the synthesised coloured complexes are stable at room temperature and are non-hygroscopic. They are insoluble in water and common organic solvents but soluble in DMF and DMSO. Analytical data suggest 1:1 (metal : ligand) stoichiometry (Table 1) for these complexes.

Non-electrolytic nature of these complexes is indicated from low molar conductance values (3.35 to 6.53 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMF solutions.<sup>4</sup> The formulation of ligand is supported by analytical and spectral data. Its <sup>1</sup>H-NMR spectrum in CDCl<sub>3</sub> shows signals at 2.31, 2.332, 2.3940, 6.90–7.27, 10.0732, 11.2079 ppm (δ) corresponding to –CH<sub>3</sub>, Ar–CH<sub>3</sub>, –SCH<sub>3</sub>, phenyl protons, –NH and phenolic OH protons, respectively. The IR spectrum of ligand exhibits a band at 1622 cm<sup>-1</sup> due to ν(C=N) stretching vibrations.<sup>5</sup> The C=N band in all complexes shifted to lower frequency by 25–30 cm<sup>-1</sup> indicating the coordination of azomethine nitrogen to metal ion,<sup>6</sup> which is due to involvement of unshared pair of electrons on N atom in coordination to metal atom. The ligand shows a medium broad band at 2913 cm<sup>-1</sup>, assignable to intramolecularly hydrogen

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Table 1

Analytical, magnetic and electrical conductivity data of the complexes

Compounds	Elemental analysis % found (Calcd.)					$\mu_{\text{eff}}$ B. M.	$(\sigma)$ $\Omega^{-1}\text{cm}^{-1}$ (at 473 K)	Activation Energy (eV)
	M	C	H	N	S			
HMASMZ	---	51.92	4.95	10.50	24.95	----	$2.70 \times 10^{-6}$	0.39
$\text{C}^{11}\text{H}^{14}\text{ON}^2\text{S}^2$		(51.96)	(5.51)	(11.02)	(25.19)			
VO-L	15.40 (15.96)	40.05 (41.37)	3.75 (3.76)	7.83 (8.77)	19.03 (20.06)	1.60	$1.23 \times 10^{-9}$	0.92
Mn-L	15.48 (16.01)	37.38 (38.48)	3.15 (3.49)	7.13 (8.16)	17.95 (18.65)	5.70	$4.21 \times 10^{-10}$	0.50
Fe-L	15.54 (16.23)	37.96 (38.77)	3.03 (3.48)	7.99 (8.13)	17.90 (18.60)	4.82	$6.21 \times 10^{-11}$	0.40
CO-L	15.73 (16.98)	37.93 (38.04)	3.33 (3.45)	8.32 (8.06)	17.93 (18.44)	3.75	$4.52 \times 10^{-11}$	0.35
Ni-L	16.50 (16.88)	36.98 (37.98)	3.32 (3.45)	7.95 (8.05)	17.89 (18.41)	2.79	$3.73 \times 10^{-11}$	0.43
Cu-L	19.97 (20.07)	40.93 (41.70)	2.98 (3.79)	8.42 (8.84)	19.85 (20.22)	1.68	$4.08 \times 10^{-11}$	0.37
Zn-L	20.08 (20.60)	40.88 (41.58)	2.90 (3.78)	8.02 (8.82)	19.85 (20.16)	---	$3 \times 10^{-10}$	0.40
Cd-L	30.63 (30.84)	36.02 (36.22)	3.03 (3.29)	7.42 (7.68)	15.93 (15.56)	---	$9.52 \times 10^{-11}$	0.41

Where L = HMASMZ

bonded phenolic OH stretch.<sup>7</sup> This band disappears in the spectra of all complexes indicating the coordination of deprotonated oxygen with metal ion which is further confirmed by positive shift of 25–75  $\text{cm}^{-1}$  in ligand band at 1240  $\text{cm}^{-1}$  due to C–O phenolic stretch.<sup>8,9</sup> The absence of ligand absorption near 2600  $\text{cm}^{-1}$ , (–SH) indicates that at least in the solid state, it remains in the thioketo form (–C=N–NH–C=S).<sup>10</sup> However, in the solution the existence of thioketo and thioenol (–C=N–N=C–SH) tautomerism may exist. IR spectra of the complexes do not contain the  $\nu$ (–NH) band at 3127  $\text{cm}^{-1}$  of the ligand as this secondary amine N is involved in the thioenolisation and consequent deprotonation on coordination.<sup>11</sup> The thioamide (–NH–C=S) band at 823  $\text{cm}^{-1}$  of the ligand disappeared in all the complexes, indicating that thioenol sulphur is involved in bonding on deprotonation.<sup>12</sup> A strong band at 913  $\text{cm}^{-1}$  in VO(IV) complex is assigned to  $\nu$  (V=O) mode.<sup>13</sup> In the far IR region the additional bands observed around 500–600, 410–495 and 300–400  $\text{cm}^{-1}$  are assigned for M–O, M–N and M–S modes of vibrations, respectively.<sup>14</sup> The presence of strong and broad feature approximately at 3400–3500  $\text{cm}^{-1}$  in the spectra of the complexes may be assigned to  $\nu$ (–OH) stretching mode of water molecules.<sup>15</sup>

The electronic spectrum of Mn (II) complex exhibits weak bands at 15600, 19000 and 25995  $\text{cm}^{-1}$  assignable to the transition  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} {}^4\text{E}_g(\text{G})$ , respectively, suggesting octahedral stereochemistry around Mn(II) ion.<sup>16,17</sup> The calculated values of ligand field parameters found to be  $\text{Dq} = 1560 \text{ cm}^{-1}$ ,  $\text{B} = 485 \text{ cm}^{-1}$  and  $\beta = 0.51$ , respectively also support the octahedral geometry. The magnetic moment value of Mn(II) complex was found to be 5.70 B.M. corresponding to five unpaired electrons in an octahedral field.<sup>18</sup> The Fe(II) complex has a magnetic moment of 5.82 B.M., which is in the range required for octahedral complexes. Structural information is further supported from the  $d$ – $d$  spectral bands in Fe(II) complex. It shows bands at 10832 and 25250  $\text{cm}^{-1}$ , assignable to  ${}^5\text{T}_{2g} \rightarrow {}^6\text{E}_g$  and charge transfer transitions, respectively, suggesting an octahedral structure.<sup>19</sup> The Racah parameters  $\text{Dq} = 1083 \text{ cm}^{-1}$ ,  $\text{B} = 585 \text{ cm}^{-1}$ ,  $\beta = 0.53$  and  $\text{LFSE} = 52 \text{ kJmol}^{-1}$  are also in favour of the octahedral geometry of the Fe(II) complex.

The Co(II) complex shows the electronic spectral features of six-coordinated complex. The absorption bands observed at 8808 ( $\nu_1$ ), 17 000 ( $\nu_2$ ) and 19 590  $\text{cm}^{-1}$  ( $\nu_3$ ) attributed to  ${}^4T_{1g}(F) \rightarrow {}^6E_g(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^6A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^6E_g(F)$  transitions, respectively, are indicative of an octahedral geometry. The observed magnetic moment value of Co(II) complex is 3.75 B.M. attributed to octahedral symmetry.<sup>20</sup> The calculated values of crystal field parameters  $Dq = 881 \text{ cm}^{-1}$ ,  $B = 795 \text{ cm}^{-1}$ ,  $\beta = 0.82$ ,  $\nu_2/\nu_1 = 1.93$ . LFSE = 63.42  $\text{kJmol}^{-1}$  further support the octahedral structure for Co(II) complex.

The magnetic moment value of Ni(II) complex is 2.79 B.M. which support the octahedral nature of Ni(II) complex.<sup>21</sup> It exhibits three bands at 10695, 16500 and 25800  $\text{cm}^{-1}$  which may be assigned to the transitions  ${}^3A_{2g}(F) \rightarrow {}^3E_g(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3E_g(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3E_g(F)$ , respectively. The position and assignment of the bands indicated octahedral geometry around Ni(II) ion. The ligand field parameters  $Dq = 1070 \text{ cm}^{-1}$ ,  $B = 683 \text{ cm}^{-1}$ ,  $\beta = 0.66$ ,  $\beta\% = 33.68$ ,  $\nu_2/\nu_1 = 1.543$ , LFSE = 153.72  $\text{kJmol}^{-1}$  also support octahedral geometry.

The  $\beta$  value is less than unity suggesting considerable amount of covalent character in the metal-ligand bond. The B value is lower than the free ion value of Ni(II) ion (1030  $\text{cm}^{-1}$ ), thereby indicating the orbital overlap and delocalisation of *d*-orbitals. The general pattern from the spectral data and  $\nu_2/\nu_1$  ratio is in agreement with an octahedral symmetry.

The magnetic moment of Cu(II) complex is 1.68 B.M. In the electronic spectrum of Cu(II) complex two bands are observed at 17779 and 18824  $\text{cm}^{-1}$  due to  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions, respectively. The broad band at 25 256  $\text{cm}^{-1}$  was assigned to a charge transfer transition. These transitions are observed in normally expected region for square planar geometry.<sup>22,23</sup> The observed *Dq* and LFSE values of Cu(II) complex are 1778  $\text{cm}^{-1}$  and 244  $\text{kJmol}^{-1}$  respectively, favouring square planar geometry. The reflectance spectrum of VO(IV) complex exhibits bands at 10 669, 16 553 and 20 421  $\text{cm}^{-1}$  assignable to  ${}^2B_2 \rightarrow {}^2E$ ,  ${}^2B_2 \rightarrow {}^2E$  and  ${}^2B_2 \rightarrow {}^2E$  transitions, respectively characteristic of square pyramidal geometry.<sup>24</sup> The  $\mu^{\text{eff}}$  value of VO(IV) complex is 1.60 B.M. indicating square pyramidal geometry. The Zn(II) and Cd(II) complexes are diamagnetic as expected for  $d^{10}$  configuration and may have four coordinated tetrahedral geometry.<sup>25</sup>

The d.c. electrical conductivity of all the complexes was studied over a wide range of temperature. The general behaviour of electrical conductivity obeys the well known equation.

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

where  $\sigma_0$  is a constant,  $E_a$  is the activation energy of conduction process and *K* is the Boltzmann constant. The plots of  $\log \sigma$  vs  $1/T$  for all the complexes are found to be linear over a studied temperature range 308–498 K indicating the semiconducting behaviour of the complexes.<sup>26</sup> All the plots show higher slope in higher temperature region while lower energy of activation has been observed in lower temperature region. The lower temperature range is the region of extrinsic semiconductors where the conduction is due to the excitation of carrier from donor localized level to the conduction band. In the upper temperature range, the intrinsic region is reached where carriers are thermally activated from the valence band to the conduction band.<sup>27</sup> This behaviour can be attributed to interactions between the electrons of *d*-orbitals of metal and  $\pi$  orbitals of ligand in the upper temperature range.<sup>28</sup> This interaction will lead to localized action of  $\pi$ -electronic charge on the ligand which tends to increase the energy of activation. On the other hand it is known that increasing of complex stability results in decreasing the conductivity due to a decrease in  $\pi$ -electron mobility, which agrees with the observed results.<sup>29</sup> A higher value of electrical conductivity of ligand may be attributed to the presence of large number of  $\pi$  and lone pair of electrons in conjugation, the mobility of which increases at high temperature. At 473 K, the electrical conductivity of the complexes decreases in the order HMASMZ > VO(IV) > Cu(II) > Zn(II) > Cd(II) > Fe(II) > Mn(II) > Co(II) > Ni(II).

The thermal degradation of the prepared complexes was studied thermogravimetrically and thermal decomposition results revealed that all the complexes decompose gradually. The elimination of lattice and

coordinated water molecules takes place in the first step. In the present study Mn(II), Fe(II), Co(II) and Ni(II) complexes show weight loss in the 160–90°C temperature range equal to ~10.49%, 10%, 10.30% and 10.35%, respectively, which corresponds to two water molecules essentially present in the coordinated sphere of the complex. Then, a continuous mass loss is observed up to 560°C with the elimination of ligand moiety. Thereafter a continuous mass loss is observed in the 670–700°C range and the organic ligand was completely lost, forming corresponding metal oxide. In Cu(II) complex, the weight loss at about 130°C equal to 5.38% corresponds to lattice water molecules in this complex. A careful analysis of VO(IV), Zn(II) and Cd(II) complexes suggests that these complexes do not possess any water molecules. *i.e.* neither in nor out of the coordinated sphere. These complexes are stable up to 230°C and then exhibited a gradual mass loss up to 570°C which may be due to thermo-oxidative degradation and formation of volatile products from the complex melt and residue left as metal oxide.

Using the thermal degradation data, thermal activation energy<sup>30–32</sup> and various thermodynamic parameters for all the complexes have been evaluated and comparable values are given in Table 2. The similarity of the thermodynamic parameters indicate a common reaction mode.<sup>33</sup> The higher value of energy of activation suggests the higher stability. Higher values of activation energy and lower values of Z favour the reaction to proceed slower than the normal.<sup>34</sup> The order of the thermal stability of the compounds comes to be Zn > Mn > Co > Cd > Ni > Cu > Fe > VO on the basis of decomposition temperature. The order of the stability of the complexes on the basis of the values of activation energy, can set as Co > Ni > Cd > Cu > Mn > Fe > VO > Zn.

Table 2  
Thermal data of HMASMZ complexes

Compounds	Decomp. Temp (°C)	Activation Energy (kJmol <sup>-1</sup> )	-ΔS (JK <sup>-1</sup> mol <sup>-1</sup> )	ΔF (kJmol <sup>-1</sup> )	Z (S <sup>-1</sup> )	
HMASMZ	175	FC	14.04	300.72	110.04	0.25
		SW	23.93	208.47	89.18	0.14
		CR	16.73	246.48	93.88	0.05
Mn-L	280	FC	18.82	299.03	112.43	0.04
		SW	18.13	220.16	87.04	0.04
		CR	22.52	245.16	99.26	0.03
Fe-L	190	FC	18.81	289.27	108.71	0.01
		SW	18.50	214.25	85.56	0.04
		CR	20.05	248.32	97.15	0.06
Co-L	275	FC	22.97	305.11	118.42	0.03
		SW	21.05	209.538	88.82	0.03
		CR	19.94	241.03	96.63	0.03
Ni-L	230	FC	21.50	304.70	116.87	0.21
		SW	21.53	214.13	88.54	0.02
		CR	21.87	252.30	100.84	0.90
Cu-L	210	FC	19.14	295.80	111.73	0.02
		SW	19.14	295.80	111.73	0.02
		CR	18.57	252.35	97.49	0.02
Zn-L	300	FC	14.64	294.30	106.30	0.02
		SW	28.71	214.42	95.83	0.23
		CR	22.23	243.23	99.09	0.11
Cd-L	240	FC	20.42	305.52	116.05	0.16
		SW	21.05	219.88	89.88	0.08
		CR	20.27	254.08	99.80	0.02
Vo-L	185	FC	14.93	308.78	111.58	0.12
		SW	13.82	225.67	84.46	0.11
		CR	17.89	257.22	98.41	0.20

FC = Freeman–Carroll

SW = Sharp–Wentworth

CR = Coats–Redfern

## EXPERIMENTAL

All the chemicals and reagents were used as supplied, 2-hydroxy-5-methyl-acetophenone and *s*-methylthiocarbamate were prepared by known methods.<sup>35,36</sup>

### Synthesis of Schiff base (HMASMZ)

The Schiff base was prepared by the condensation of 2-hydroxy-5-methylacetophenone with *s*-methylthiocarbamate in ethanolic medium. The solid orange coloured product obtained was crystallised from ethanol and dried *in vacuo*. Purity of ligand was checked by tlc and m.p. It was also characterised by <sup>1</sup>H-NMR, IR and elemental analysis.

Yield 70%, m.p. 185°C.

### Synthesis of metal complexes

Equimolar amounts of methanolic solution of appropriate metal salt and ethanolic solution of HMASMZ were mixed and the solution thus obtained was refluxed over a water bath for about 4–5 h. The resulting coloured products obtained were filtered, washed with hot water, methanol and ethanol to remove unreacted reactants. The complexes were dried under reduced pressure over anhydrous CaCl<sub>2</sub> in a desiccator. Physico-chemical methods were used as described earlier.<sup>37</sup>

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