

## Synthesis and Characterization of Schiff Bases Complexes of Divalent Metals

R.P. SINGH\*<sup>†</sup> and D. GUPTA

Department of Chemistry, Sanjay Gandhi Postgraduate College, Sarurpur Khurd-250 344, India

E-mail: rpsingh.mzn@gmail.com

This paper reports the synthesis of Mn(II), Fe(II) and cochelates derived from 2,6-diacetyl pyridine dihydrazide and diacetyl with the general composition  $[M(C_{13}H_{15}N_5)X_2]$  where,  $M = Mn^{2+}, Fe^{2+}, Co^{2+}$  and  $X = Cl, Br, NO_3$  or  $NCS$ . All the chelates were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, electronic and IR spectral studies. On the basis of these studies, the divalent metal complexes have been assigned trigonal bipyramidal geometry with high spin.

**Key Words:** 2, 6-Diacetyl pyridine dihydrazide, Diacetyl, Magnetic susceptibility.

### INTRODUCTION

The most important feature of  $Mn^{2+}, Fe^{2+}, Co^{2+}$  metal ions is the exhibition of varied stereochemistries<sup>1-7</sup>. The recent interest has led to the synthesis and characterization of metal complexes of acid hydrazides and their hydrazones which have been a subject of intensive investigation, due to their biological activities and versatile chelating power to form various types of complexes confirming varied stereochemistries<sup>8-11</sup>. The present study is based upon the synthesis and characterization of complexes of divalent transition metal of manganese, iron and cobalt with the hydrazone derived from 2,6-diacetyl pyridine and dihydrazide<sup>12-15</sup>.

### EXPERIMENTAL

All the chemicals and reagents used were of analaR grade:

**Synthesis and isolation of chelates:** 0.05 Mol of 2,6-diacetyl pyridine dihydrazide and 0.05 mol of diacetyl was dissolved in 100 mL of ethanol by refluxing for 1 h. Divalent manganese, iron and cobalt salt (0.05 mol) dissolved in 100 mL of ethanol was added to ligand solution separately. 1-2 Drops of glacial acetic acid was added and the solution is refluxed for 4 to 6 h over a water bath. Different coloured solutions were concentrated to half to their volumes and kept in a vacuum desiccator for three days. The coloured crystals separated, were filtered off, washed with water and recrystallized with ethanol and dried under *in vacuo*  $P_4O_{10}$  yield 50 %.

<sup>†</sup>Present Address: Chemistry Department, D.A.V. College, Muzaffarnagar-251 001, India.

The nitrate complexes were prepared from metal nitrates. The bromo and thiocyanate salts were prepared by adding slowly potassium bromide and potassium thiocyanate solutions to ethanolic solutions of metal chlorides and stirring for 3 h. The potassium chloride was filtered off and the filtrate was used to synthesis of bromo and thiocyanate complexes of divalent metal ions. The complexes are soluble in hot alcohols, but are insoluble in water. Their thermal stability varies from 150 to 300 °C.

## RESULTS AND DISCUSSION

The analytical data (Table-1) show that the chelates have their molecular formula as  $[M(C_{13}H_{15}N_5)X_2]$  where,  $M = Mn^{2+}$ ,  $Fe^{2+}$  and  $Co^{2+}$  and  $X = Cl$ ,  $Br$ ,  $NO_3$  and  $NCS$ . The tests for anions are given only after decomposing the complexes showing their presence inside the coordination sphere. The conductance measurements indicate that these chelates are non-electrolytes.

TABLE-1  
ANALYTICAL DATA OF DIVALENT MANGANESE, IRON  
AND COBALT COMPLEXES

Complex	Colour	Elemental analysis (%): Found (calcd.)				
		C	H	N	M	X
$[Mn(C_{13}H_{15}N_5)Cl_2]$	Light Brown	42.20 (42.62)	4.00 (4.10)	19.20 (19.12)	14.60 (14.75)	19.50 (19.40)
$[Mn(C_{13}H_{15}N_5)Br_2]$	Brown	— (34.29)	— (3.30)	— (15.38)	11.88 (11.86)	35.20 (35.16)
$[Mn(C_{13}H_{15}N_5)(NO_3)_2]$	Brown	— (37.23)	— (3.58)	— (16.71)	12.80 (12.80)	— (29.59)
$[Mn(C_{13}H_{15}N_5)(NCS)_2]$	Brown	37.85 (37.96)	3.62 (3.65)	17.10 (17.03)	13.12 (13.14)	28.02 (28.22)
$[Fe(C_{13}H_{15}N_5)Cl_2]$	Yellowish red	— (42.39)	— (4.08)	— (19.02)	15.18 (15.22)	19.30 (19.29)
$[Fe(C_{13}H_{15}N_5)Br_2]$	Yellowish red	34.00 (34.14)	3.22 (3.28)	15.28 (15.32)	12.15 (12.25)	35.00 (35.01)
$[Fe(C_{13}H_{15}N_5)(NO_3)_2]$	Yellowish red	— (37.05)	— (3.56)	— (16.63)	13.25 (13.30)	— (29.45)
$[Fe(C_{13}H_{15}N_5)(NCS)_2]$	Yellowish brown	— (37.77)	— (3.63)	— (16.95)	13.52 (13.56)	— (28.09)
$[Co(C_{13}H_{15}N_5)Cl_2]$	Dark red	— (42.05)	— (4.04)	— (18.87)	15.85 (15.90)	19.20 (19.14)
$[Co(C_{13}H_{15}N_5)Br_2]$	Dark red	33.84 (33.91)	3.21 (3.26)	15.20 (15.22)	12.75 (12.83)	34.62 (34.78)
$[Co(C_{13}H_{15}N_5)(NO_3)_2]$	Reddish brown	— (36.79)	— (3.54)	— (16.51)	13.90 (13.92)	— (29.25)
$[Co(C_{13}H_{15}N_5)(NCS)_2]$	Reddish brown	37.40 (37.50)	3.58 (3.61)	16.85 (16.82)	14.00 (14.18)	27.81 (27.80)

X = Cl, Br or NCS

**Infrared spectra:** The spectral bands appearing in the free 2,6-diacetyl pyridine di hydrazide *ca.* 1610-1590, 1585-1570, 1490-1450 and 1440-1435  $cm^{-1}$  can be assigned to four (C=C) and (C=N) skeletal frequencies.

Two strong bond *ca.* 790 and 735  $\text{cm}^{-1}$  are assigned to  $\nu(\text{C-H})$  and  $\phi(\text{C-C})$  vibrations, respectively<sup>16</sup>. The four skeletal frequencies of pyridine exhibit downward shifts indicating the coordination of pyridine nitrogen to the metal atom. The band *ca.* 990  $\text{cm}^{-1}$  disappear and is replaced by a band<sup>17</sup> *ca.* 1015-1010  $\text{cm}^{-1}$ . The band assigned  $\phi(\text{C-C})$  splits into two components appearing at 720 and 740  $\text{cm}^{-1}$  while  $\nu(\text{C-H})$  appears *ca.* 780  $\text{cm}^{-1}$  as a single bond<sup>18</sup>. These changes show the involvement of pyridine nitrogen in coordination. Further more, two bands present in 2,6-diacetyl pyridine dihydrazide *ca.* 610 and *ca.* 410  $\text{cm}^{-1}$  undergo an upward shift of 15-20  $\text{cm}^{-1}$  in the spectra of metal chelates and appearing at 630-625  $\text{cm}^{-1}$ , 430-415  $\text{cm}^{-1}$  and 435-430  $\text{cm}^{-1}$ , respectively. All these changes are consistent with pyridine nitrogen coordination to the metal atom<sup>19,20</sup>.

The azomethine linkage (C=N) which occur in hydrazone has been assigned and cover a wide frequency range [1675-1600  $\text{cm}^{-1}$ ]<sup>21,22</sup>. These bands have been assigned with great accuracy and three diagnostic factors have been postulated for establishing the involvement of unsaturated nitrogen of the C=N group. These include change in lowering in the intensity of bands associated with it and appearance of a new band at lower frequency range<sup>23</sup>. Strong bands 1630-1580  $\text{cm}^{-1}$  region present in the spectra of all the complexes are associated with phenyl ring vibrations but conjugated system containing (C=C) and (C=N) linkage often exhibit one or more strong band on this region. A conventions method of stringent assignment of  $\nu(\text{C=N})$  vibrations can be made by comparing the spectra of hydrazide with those of hydrazones. On comparison it is found that the strong band *ca.* 1625 with *ca.* 1610  $\text{cm}^{-1}$  may be assigned to symmetric and assymmetric  $\nu(\text{C=N})$  frequencies, respectively<sup>22,24</sup>. Thus, the spectra of all the complexes exhibit a downward shift of 15 to 26  $\text{cm}^{-1}$   $\nu(\text{C=N})$  band and is consistant with the coordination of azomethine nitrogen to the metal atom.

Thus, it appears that the diacetyl molecule has reacted with  $-\text{NH}_2$  groups of dihydrazide molecules where on acetyl acetone reacts with available amino group and leads to ring closure<sup>25</sup>. This contention finds support by the presence of new bands in the spectra of complexes at 2920, 1350, 1265, 1190 and 690  $\text{cm}^{-1}$  characteristic of diacetyl moiety and are assigned to  $\nu(\text{CH}_3)$ ,  $\delta_{\text{sym.}}(\text{CH}_3)$ ,  $\nu(\text{C-CH}_3)$  and ring deformation, respectively<sup>26</sup>.

**Magnetic and electronic spectral studies manganese complex:** The magnetic moments for manganese(II) complexes at room temperature lie in 5.80-5.88 BM range reported to high spin manganese complexes.

The diffuse reflectance spectra of manganese complexes as well as in dimethyl formamide show bands at *ca.* 16500-17000, 19200-20000 and 21500-22000  $\text{cm}^{-1}$  reported to five coordinated geometry has been established by X-ray measurements. The weak intensity of spectral bands can be attributed to the spin forbidden transitions from the ground sextet to the first excited quarter levels. The constriction of molecular model reveal that trigonal bipyramidal geometry in more favourable, the ligand molecule occupying a trigonal plane and anion being present on the axial positions.

These assuming the effective symmetry to be  $D_{3h}$ , for manganese ion, the five  $d$ -orbitals split into three orbital singlets and a doublet denoted as  $b_1(dx^2 - y^2)$ ,  $a_1(d_z^2 - r^2)$ ,  $e(d_{xy}, d_{yz})$  and  $b_2(d_{zx})$  where,  $r$  is a formation constant and depends upon the distortion of the molecule.

**Iron complexes:** The magnetic moments of iron(II)-complexes lie in 5.20-5.30 BM range at room temperature. The values are lower than the predicted values of high spin (5.10-5.50 BM) for iron complexes due to the pyridine nitrogen coordination in these complexes.

The electronic spectra of iron(II) complexes show mainly bands at *ca.* 12000  $\text{cm}^{-1}$  and *ca.* 4000  $\text{cm}^{-1}$ . The bands observed *ca.* 12000  $\text{cm}^{-1}$  indicates that iron(II) complexes are five coordinated. Ciampolini *et al.*<sup>27</sup> have presented on the basis of simple crystal field calculations that two spin allowed bands are possible for trigonal complexes. Accordingly the band *ca.* 12000  $\text{cm}^{-1}$  can be assigned to  $S_A-S_{E(1)}$  and the possible assignment of the band *ca.* 4000  $\text{cm}^{-1}$  may be  $S_A-S_{E(2)}$  in trigonal bipyramidal field. The electronic spectra in coordinating dimethyl formamide or pyridine and in nujol mull are almost similar indicating penta coordination in solid state as well as in solution.

**Cobalt complexes:** The magnetic moments of cobalt complexes(II) lie in 4.20-4.50 BM range at room temperature, suggested for high spin five coordinate complexes.

The electronic spectra of cobalt(II) complexes exhibited various bands in the region *ca.* 6250-6350, 13150-13250, 19750-19850 and 28400-28600  $\text{cm}^{-1}$ . The spectral bands indicate to the high spin five coordinates. Thus assuming the effective symmetry to be  $D_{3h}$  for these complexes, the various bands may be assigned to *ca.* 6300  $\text{cm}^{-1}$ , ( $4_{A_2} \rightarrow 4_E$ ), 13200  $\text{cm}^{-1}$  ( $4_{A_2'} \rightarrow 4_E$ ), 19850  $\text{cm}^{-1}$   $4_{A_2'} \rightarrow 4_E$  (P), respectively. Thus keeping in view the construction of molecular models, steric requirements of the ligand and coordination interaction between pyridine nitrogen and metal ion, it can be concluded that ligand assumes a trigonal plane and anions are present on axial positions. Assuming the effective symmetry to be  $D_{3h}$ , the highest energy level  $d_{x^2-y^2}$  would be considerably raised and the total spread level of spectral bands in markedly decreased due to distortion, therefore for a given set of donor atoms, the bond length and the appearance of frequencies of  $d-d$  transitions for trigonal bipyramidal cobalt complexes should become smaller with greater distortion of the molecule. The spread of electronic spectra of cobalt complex in quite in agreement with high spin five coordinate trigonal bipyramidal geometry.

**Far infrared:** The far IR spectra of divalent metal chelates derived from the macrocycle derived from 2,6-diacetyl pyridine dihydrazide and diacetyl exhibit various bands in this region which are assignable to various metal ligand vibrations.

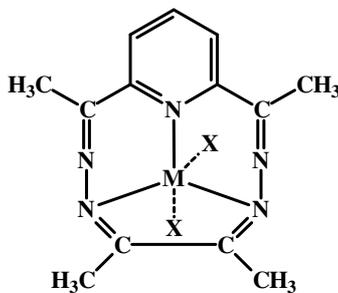
In pyridine based complexes, these vibrations may be termed as metal pyridine vibrations. The  $\nu(M-N)$  stretching frequencies of pyridine complexes with divalent metal ions have been found to occur *ca.* 280-250  $\text{cm}^{-1}$ . However, deviations have also been observed. Some new bands found in the region *ca.* 290-250  $\text{cm}^{-1}$  in the spectra of divalent metal complexes and these are, manganese (254-250  $\text{cm}^{-1}$ ), iron

(265  $\text{cm}^{-1}$ ), cobalt (270-260  $\text{cm}^{-1}$ ) and may be assigned to  $\nu(\text{Mn-py})$ ,  $\nu(\text{Fe-py})$ ,  $\nu(\text{Co-py})$  vibrations, respectively. These bands are well with in the range reported for five coordinate complexes of respective metal ions. The intensity of these bands is however weak, probably due to weak coordinate of pyridine nitrogen to the metal atom.

The bands appearing in the spectra of all the manganese, iron and cobalt *ca.* 490-480, 475-460 and 480-475  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{Mn-N})$ ,  $\nu(\text{Fe-N})$  and  $\nu(\text{Co-N})$  of metal azomethine nitrogen vibrations, respectively and their frequencies further substantive five coordinate stereochemistry of complexes of the respective metal ions. Other bands in the far infrared spectra in the region *ca.* 420-385  $\text{cm}^{-1}$  may have been originated from  $\nu(\text{M-N})$  of the coordinated  $-\text{CNS}$  group. The bands in the ranges *ca.* 387-380  $\text{cm}^{-1}$  (manganese), 385  $\text{cm}^{-1}$  (iron) and 395  $\text{cm}^{-1}$  (cobalt) may be assigned to  $\nu(\text{Mn-N})$ ,  $\nu(\text{Fe-N})$ ,  $\nu(\text{Co-N})$  vibration modes, respectively of metal thiocyanate complexes.

The chloro and bromo complexes show intensity bands *ca.* 265-260  $\text{cm}^{-1}$  and *ca.* 215-210  $\text{cm}^{-1}$  and may be assigned  $\nu(\text{M-Cl})$  and  $\nu(\text{M-Br})$  vibrations, respectively. The metal halogen frequencies suggest that the present complexes are in five coordinates. The ratio  $\nu(\text{M-Cl})/\nu(\text{M-Br})$  in the present complexes comes out to be 0.87-0.81 and is consistent with five coordinate complexes. The nitrate complexes of cobalt exhibit spectral bands *ca.* 235-220  $\text{cm}^{-1}$  and may be assigned to  $\nu(\text{M-O-NO}_2)$  vibrational modes, reported to five coordination geometry.

Thus, based on various physicochemical studies, proposed structure of complex is shown as:



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*Contact:*

The Secretariat-SP3, C/o Professor Andrew Mills, University of Strathclyde,  
Department of Pure and Applied Chemistry, Thomas Graham Building,  
295 Cathedral Street, Glasgow, G1 1XL, United Kingdom  
Tel: +44 141 548 4760; Fax: +44 141 548 4822  
E-mail: [enquiries@sp3conference.com](mailto:enquiries@sp3conference.com)  
Website: <http://www.sp3conference.com/>