

Physico-Chemical Studies on Some Manganese (II), Iron (II) and Iron (III) ISO Nicotinoyl Dithiocarbazates

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Abstract— Some new manganese(II), iron(II) and (III) dithiocarbazates, $M(\text{IN-Dtcz})_n$, $[\text{M}(\text{IN-DtczH})_2]X_n$ and $[\text{M}(\text{IN-DtczH-Sal})_2]X_n$ have been prepared and investigated. For $\text{M}(\text{IN-Dtcz})_2$ ($M = \text{Mn, Fe}$) IN-Dtcz behaves as tridentate ONS donor and in $\text{Fe}(\text{IN-Dtcz})_3$ as NS donor with six coordination. For $[\text{M}(\text{IN-DtczH})_2]X_2$ and $[\text{M}(\text{IN-DtczH-Sal})_2]X_2$; ($M = \text{Mn}$; $X = \text{Cl}$ and $M = \text{Fe}$; $X = \text{SO}_4$), ligands act as NS donors with four coordination number. The μ_{eff} values of iron(II) isonicotinoyldithiocarbazates and their temperature dependence has been attributed to spin crossover, ($^1A_{1g}$) \rightleftharpoons ($^5T_{2g}$). Complexes $\text{Fe}(\text{IN-Dtcz})_3$, $[\text{Fe}(\text{IN-DtczH})_3]\text{Cl}_3$ and $[\text{Fe}(\text{IN-DtczH-Sal})_3]\text{Cl}_3$ have NS bonded ligands and exhibited spin crossover, $S = 5/2 \rightleftharpoons S = 1/2$. $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ and $[\text{Fe}(\text{IN-DtczH-Sal})_3]\text{Cl}_3$ were evaluated for their antimicrobial activities

Index Terms— IN-DtczH, coordination, temperature dependence, spin crossover, antimicrobial

I. INTRODUCTION

The number and diversity of sulphur-nitrogen chelating agents used to prepare new coordination and organometallic compounds have increased rapidly during the past few years. Dithiocarbazate and its substituted derivatives have also been synthesized and investigated widely over the past few decades. The dithiocarbazates are an interesting class of thio ligands and these as well as their complex derivatives have been found to be active against viruses, bacteria, fungi and cancer systems. Their stereochemistry is also quite interesting as only the \square -nitrogen coordinates to the metal atom, while the \square -nitrogen atom remains uncoordinated. Interest remains high in these compounds and the Schiff bases derived from them through condensation with various aldehydes and ketones because of the intriguing observation that they sometimes show different biological properties, although they may differ only slightly in their molecular structures. However, we have observed that manganese and iron dithiocarbazate complexes have been relatively less studied in comparison to other metal ions. As part of our on-going study on transition metal dithiocarbazates, we report here the synthesis and studies on manganese(II), iron(II) and iron(III) complexes of dithiocarbazate ligands derived from isoniazid – an antitubercular drug compound.

II. RESULTS AND DISCUSSION

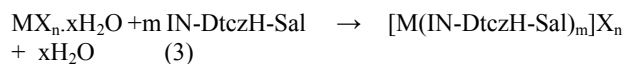
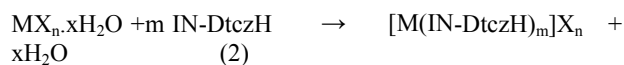
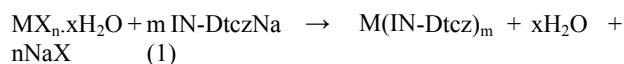
Preparation Of Complexes

$[\text{M}(\text{IN-DtczH})_n]X_n$ [$M = \text{Mn(II)}$ for $X = \text{Cl}$ and $n = 2$; $M = \text{Fe(III)}$ for $X = \text{Cl}$ and $n = 3$]: To the methanolic solution (50 ml) of the isonicotinoyldithiocarbazic acid (2.0 g; 9.38 mmol) prepared *in situ*, was added with stirring a solution of metal salt, $\text{MX}_n \cdot x\text{H}_2\text{O}$ (0.93 g, 4.69 mmol for $M = \text{Mn(II)}$, $X = \text{Cl}$, $n = 2$, $x = 4$; 0.51 g, 3.12 mmol for $M = \text{Fe(III)}$, $X = \text{Cl}$, $n = 3$, $x = 0$) in ethanol (30 ml) in small portions (~20 mg) after successive intervals of about 10-15 minutes, in a total period of about 5 hours. The reaction was carried out at 30-35 °C. Though the solid coloured product separates out immediately or during the course of the reaction, yet the reaction mixture was stirred for another 2 hours to ensure the completion of the reaction. The solid product obtained (light yellow when $M = \text{Mn(II)}$; light brown when $M = \text{Fe(III)}$) was filtered, washed with methanol, ethanol and finally with diethyl ether and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator.

$\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$: To a degassed methanolic solution (50 ml) of isonicotinoyldithiocarbazic acid (2.0 g; 9.38 mmol), prepared *in situ*, was added degassed methanolic solution (30 ml) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.30 g, 4.69 mmol) instantly. The reaction mixture, kept under nitrogen atmosphere, was further stirred for about half an hour. The solid coloured product separated out was filtered under vacuum, washed with degassed solvents, methanol and diethyl ether. Final drying of the sample was done by keeping it overnight in a vacuum desiccator.

$\text{M}(\text{IN-Dtcz})_n$ [$M = \text{Mn(II)}$, Fe(II) for $n = 2$ and $M = \text{Fe(III)}$ for $n = 3$]: Solution of the metal salt, $\text{MX}_n \cdot x\text{H}_2\text{O}$ (0.84 g, 4.25 mmol for $M = \text{Mn(II)}$, $X = \text{Cl}$, $n = 2$, $x = 4$; 1.18 g, 4.25 mmol for $M = \text{Fe(II)}$, $X = \text{SO}_4$, $n = 1$, $x = 7$; 0.46 g, 2.83 mmol for $M = \text{Fe(III)}$, $X = \text{Cl}$, $n = 3$, $x = 0$) in ethanol (30 ml) (when $M = \text{Mn(II)}$, Fe(III)) or in methanol (35 ml) (when $M = \text{Fe(II)}$) was added in small portions after successive intervals of 10-15 minutes in a total period of about 4 hours to a continuously stirred methanolic solution (60 ml) of sodium isonicotinoyldithiocarbazate (2.0 g; 8.50 mmol) prepared *in situ*. The reaction was carried out at 30-35 °C. The contents of the reaction mixture were further stirred for another 1 hour. The solid product obtained (orange-yellow when $M = \text{Mn(II)}$; dirty green when $M = \text{Fe(II)}$, Fe(III)), was filtered, washed with methanol and ethanol and finally with diethyl ether and then dried in air. The synthesis of the iron(II) by the same procedure complex was also carried out under nitrogen atmosphere. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator.

[M(IN-DtczH-Sal)_m]_nX_n [M = Mn(II) for X = Cl, m = n = 2; M = Fe(II) for X = SO₄, m = 2, n = 1 and M = Fe(III) for X = Cl, m = n = 3]: To the continuously stirred ethanolic (50 ml) [when M = Mn(II), Fe(II), Fe(III)] solution of IN-DtczH-Sal Schiff base (2.0 g, 6.30 mmol) was added the ethanolic solution (30 ml) of metal salt MX_n.xH₂O (0.62 g, 3.15 mmol for M = Mn(II), X = Cl and n = 2, x = 4; 0.34 g, 2.10 mmol for M = Fe(III), X = Cl and n = 3, x = 0) or methanolic solution (35 ml) of FeSO₄.7H₂O (0.88 g, 3.15 mmol) in small portions after successive intervals of about 10-15 minutes in a total period of about 3 hours. The reaction was carried out at 40-45 °C. The contents of the reaction mixture were further stirred for another 2 hours. The solid product obtained (light yellow when M = Mn(II); blackish-brown when M = Fe(II); reddish brown when M = Fe(III)) was filtered through Whatman filter paper no. 541, washed with methanol, ethanol and diethyl ether and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator. The complexes of the present investigation, viz. M(IN-Dtcz)_n (M = Mn(II), Fe(II) when n = 2; M = Fe(III) when n = 3), [M(IN-DtczH)₂]_nX_n and [M(IN-DtczH-Sal)₂]_nX_n (M = Mn(II) for X = Cl, n = 2; M = Fe(II) for X = SO₄, n = 1; M = Fe(III) for X = Cl, n = 3) have been obtained according to the following reactions (1), (2) and (3).



M = Mn(II) when X = Cl; m = n = 2 and x = 4
 M = Fe(II) when X = SO₄; m = 2, n = 1 and x = 7
 M = Fe(III) when X = Cl; m = n = 3 and x = 0

Since iron(II) is readily susceptible to air oxidation, the synthesis of iron(II) isonicotinoyldithiocarbazic acid complex was carried out under nitrogen atmosphere by instant mixing of the degassed methanolic solutions of the stoichiometric amounts of the reactants. Separation of the solid product of normal manganese(II) complex occurs only near the completion of the reaction. The synthesis of normal iron(II) isonicotinoyldithiocarbazate also followed the same general path but contrary to that of its Zwitterionic complex no unusual conditions were required. The coloured solids obtained are stable in air though it is advisable to store them in a desiccator over anhydrous CaCl₂. The complexes are insoluble in most of the common solvents, viz. cold/hot water, methanol, ethanol, acetone, chloroform, dichloromethane and carbon tetrachloride but have some solubility in dimethylsulfoxide. All the complexes decompose between 174-360 °C; some are even stable above that while one of the complexes melts at 240 °C (Table 1).

III. IR STUDIES

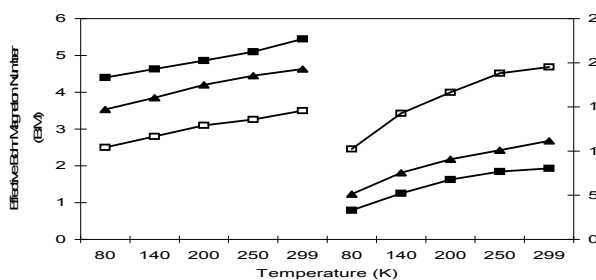
The ν(C=O) (Amide I band) stretching mode¹ in the infrared spectra of isoniazid IN-DtczH, IN-DtczNa and IN-DtczH-Sal

has been observed at lower wave numbers (1653-1652 cm⁻¹) (free INH shows this band at 1665 cm⁻¹). This band remains unshifted (1656-1654 cm⁻¹) for all the complexes, indicating non coordination of the carbonyl group (amide group) to the metal ion except in the M(IN-Dtcz)₂ (M = Mn(II), Fe(II)) where it exhibits a down field shift of ~40 cm⁻¹, indicating ONS binding of the ligand in these complexes. The azomethine ν(N-N) stretching vibration for isoniazid, IN-DtczH and IN-DtczNa is observed at 1065, 1055 and 1053 cm⁻¹ respectively^{2,3}. A shift of ~12 cm⁻¹, for this band towards higher energy in going from free IN-DtczH acid ligand to its metal complexes and IN-DtczH-Sal ligand suggest the bonding of the azomethine nitrogen atom to the metal ion and to salicylaldehyde^{4,5}. The azomethine ν(N-N) vibrational modes have been observed at 1064 and 1069-1059 cm⁻¹ for free IN-DtczH-Sal Schiff base and its metal complexes respectively. No change in its band frequency implies neutralization of the overall electronic effects of the whole

ligand. The ν(C-N) of $\begin{matrix} \text{O} \\ || \\ -\text{C}-\text{NH} \end{matrix}$ (Amide III band) appears at 1420 cm⁻¹ in isoniazid, while in IN-DtczH ligand it lies at a slightly lower frequency, 1410 cm⁻¹. Amide III band appears at 1408 cm⁻¹ in free IN-DtczH-Sal Schiff base (free IN-DtczH shows its absorption at 1410 cm⁻¹; no change in electronic effects). This band has been observed in the 1445-1443 cm⁻¹ range, with a blue shift of ~32-35 cm⁻¹ in case of all its transition metal complexes. Strong absorption near 1030-1000 cm⁻¹ is either split into two bands or has well defined shoulders which further supports the postulate of unidentate sulphur coordination associated with the NS bonded structure^{6,7}. Observation of additional bands in the 480-310 cm⁻¹ region, in the complexes, as compared to free IN-DtczH, IN-DtczNa and IN-DtczH-Sal ligands reveals the formation M-S, M-N and M-O bonds^{4,5,8}. The Fe(IN-DtczH)₂SO₄ and Fe(IN-DtczH-Sal)₂SO₄ complexes under study having sulphate as the counter anion exhibit bands around 985-990 (ν₁); 463-472 (ν₂); 1033-1059 and 1153-1160 (ν₃); and 642-648 and 615-618 (ν₄) cm⁻¹ (Table 2), thus indicating bridging bidentate mode of coordination of the sulphate group, with symmetry lowered to C_{2v}. The mode of sulphate binding leads to a polymeric type of structure for the complexes.

IV. MOLAR CONDUCTANCE STUDIES

The M(IN-Dtcz)_n (M = Mn(II), Fe(II), Fe(III)), Fe(IN-DtczH)₂SO₄ and Fe(IN-DtczH-Sal)₂SO₄ complexes exhibit non electrolytic nature. The molar conductance values of DMSO solutions of the Zwitterionic complexes, viz. [Mn(IN-DtczH)₂]₂Cl₂ and [Mn(IN-DtczH-Sal)₂]₂Cl₂ lie in the range 170-179 ohm⁻¹cm²mole⁻¹ corresponding to 1:2 electrolytic behaviour⁸ (Table 2). While the [Fe(IN-DtczH)₃]₃Cl₃ and [Fe(IN-DtczH-Sal)₃]₃Cl₃ exhibit molar conductance values in the range 252-260 ohm⁻¹cm²mole⁻¹ corresponding to 1:3 electrolytic behavior (Table 2).



Fig(1): Variation of Effective Bohr Magnetons and μ_{eff} of $\text{Fe}(\text{IN-Dtcz})_2$ (—▲—) $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ (—□—) and $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$ (—■—) with Temperature.

V. MAGNETIC SUSCEPTIBILITY STUDIES

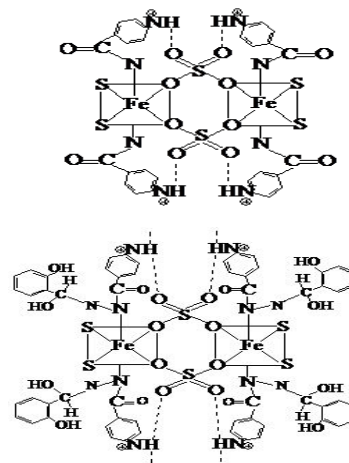
The room temperature magnetic moment values for the three manganese(II) dithiocarbamate complexes under present discussion with chromophores $[\text{MnO}_2\text{N}_2\text{S}_2]$ for $\text{Mn}(\text{IN-Dtcz})_2$ and $[\text{MnN}_2\text{S}_2]$ for $[\text{Mn}(\text{IN-DtczH})_2]\text{Cl}_2$ and $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ (based on IR spectra) lie in the range 5.94 - 6.01 B.M. and are indicative of five unpaired electrons in a manganese(II), d^5 case. All the three manganese complexes under study have been further subjected to variable temperature magnetic susceptibility measurements and the moments have not been found to vary with temperature. The observed μ_{eff} values for the three complexes under study as well as their non dependence on temperature reveal that the manganese in all the three complexes is in +2 oxidation state irrespective of octahedral or tetrahedral stereochemistry.

The three iron(II) isonicotinoyldithiocarbazates, viz. $\text{Fe}(\text{IN-Dtcz})_2$, $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ and $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$ having ONS binding modes with chromophore $[\text{FeO}_2\text{N}_2\text{S}_2]$ have room temperature μ_{eff} values in the range 3.50-5.45 B.M.. These values neither correspond to spin free nor to spin paired octahedral iron(II) complexes. On decrease of temperature the μ_{eff} values decrease to 2.50-4.40 at 80 K (Fig1). The observed anomalous room temperature magnetic moment values of the three iron(II) isonicotinoyldithiocarbazates under study and their concomitant temperature dependence may be attributed to the following factors: (i) occurrence of a spin crossover phenomenon involving low-spin ($^1A_{1g}$) and high-spin ($^5T_{2g}$) states, and (ii) antiferromagnetic interactions. This behaviour for iron(II) complexes is unusual in the sense that no iron(II) dithiocarbamate, a d^6 system, has been reported earlier to exhibit the above mentioned phenomena. It may be noted, however, that spin crossover system has been noticed in many complexes of iron(II), a d^6 system, e.g. $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ ⁹ and mixed nitrogen and oxygen containing system, e.g. hemoprotein.¹⁰ and also in oxide systems of cobalt(III), another d^6 system⁹. Though there is no direct literature support for such type of the anomalous magnetic behaviour in iron(II) dithiocarbamate complexes, yet most plausibly the interplay of steric and electronic effects of the ligands under study with oxygen (IN-Dtcz donor or due to sulphate bridging), nitrogen and sulphur donor atoms may place the iron(II) at the $^5T_{2g} \rightleftharpoons ^1A_{1g}$ spin crossover situation. The high-spin content (x) in the complexes, viz. $\text{Fe}(\text{IN-Dtcz})_2$, $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ and $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$

was calculated by fitting the experimental effective Bohr magneton numbers μ_{exp} , to the equation

$$\mu_{\text{exp}}^2 = x\mu_{\text{HS}}^2 + (1-x)\mu_{\text{LS}}^2$$

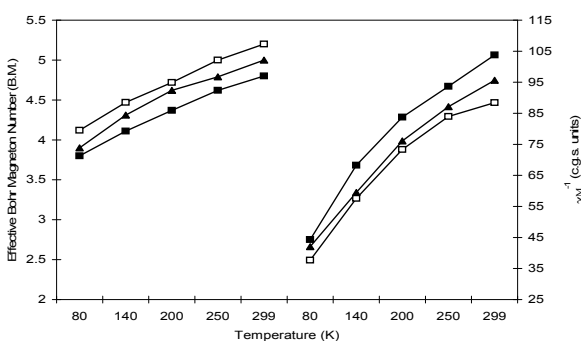
where μ_{HS} (5.5 B.M.) and μ_{LS} (0.0 B.M.) are the effective Bohr magneton numbers for the pure high-spin and pure low-spin states of an octahedral iron(II) complex. At room temperature the percentage of high spin isomer in the complexes was thus found to be 70.86, 40.49 and 98.19% respectively. Variable temperature magnetic susceptibility measurements indicate that as the temperature is lowered the population of the low-spin state increases and that of the high-spin state decreases. Secondly, antiferromagnetic interactions in the high spin octahedral state of the complexes $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ and $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$ (ignoring $\text{Fe}(\text{IN-Dtcz})_2$, in which possibility of polymeric chained compound cannot be explored) being the only cause of the observed magnetic behaviour can be ruled out because the reduction of magnetic moment is quite large which is not expected in these type of complexes¹¹ and such strong type of antiferromagnetic interactions have not earlier been reported in iron(II) dithiocarbazates with $[\text{FeO}_2\text{N}_2\text{S}_2]$ chromophore. However, the inference drawn from the infrared spectral discussion for the bridging bidentate mode of sulphate anion linking the two octahedral in the $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ and $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$ complexes (Fig 2) further supports the possibility of the presence of such type of interactions. Though it is difficult to say anything with certainty about the phenomenon which causes the abnormal magnetic behaviour observed in the complexes without X-ray structural studies at hand but, keeping in view the above discussion, it may be argued that both high spin-low spin equilibrium and weak antiferromagnetic interactions are operating simultaneously.



Fig(2): Proposed Structures for (a) $\text{Fe}(\text{IN-DtczH})_2\text{SO}_4$ and (b) $\text{Fe}(\text{IN-DtczH-Sal})_2\text{SO}_4$ Complexes

The room temperature magnetic moment values for the three iron(III) isonicotinoyldithiocarbazates, viz. $\text{Fe}(\text{IN-Dtcz})_3$, $[\text{Fe}(\text{IN-DtczH})_3]\text{Cl}_3$ and $[\text{Fe}(\text{IN-DtczH-Sal})_3]\text{Cl}_3$ under present study, having NS binding modes with $[\text{FeN}_3\text{S}_3]$ chromophores, lie in the range 4.8-5.2 B.M. These values are anomalous in the sense that they neither correspond to the octahedral high spin, $S = 5/2$ iron(III) center ($\mu_{\text{eff}} = 5.92$ B.M.) nor to the octahedral low-spin $S = 1/2$ iron(III) ($\mu_{\text{eff}} = 2.0$ B.M.) complexes. The variable temperature (299-80K) magnetic susceptibility data indicate that the magnetic moment values decrease as the temperature is lowered. The

temperature dependent magnetic behaviour for the three complexes under study is shown in Fig 3. The room temperature effective magnetic moments are consistent with the presence of a $S = 5/2 \rightleftharpoons S = 1/2$ spin crossover phenomenon and in no case a value corresponding to the spin only value for a high spin $S = 5/2$ state is obtained. The moment drops to a value between 3.80 - 4.12 B.M. at 80 K. The observed magnetic moments (4.8 - 5.2 B.M.) and their temperature dependent behaviour in the complexes under study have been attributed to the coexistence of spin-free and spin-paired isomers. Using the equation (4), and with $\mu_{HS} = 5.92$ and $\mu_{LS} = 2.0$ for high-spin and low-spin octahedral iron(III) complexes at room temperature, the percentage of high-spin isomer in the complexes $\text{Fe}(\text{IN-Dtcz})_3$, $[\text{Fe}(\text{IN-DtczH})_3]\text{Cl}_3$ and $[\text{Fe}(\text{IN-DtczH-Sal})_3]\text{Cl}_3$ is found to be 61.33, 67.64 and 74.21% respectively.



VI. ELECTRONIC SPECTRAL STUDIES

In the 10^{-4} DMSO solution electronic absorption spectrum of the complex $\text{Mn}(\text{IN-Dtcz})_2$ a well-defined weak band occurring at $17,545 \text{ cm}^{-1}$ ($\epsilon = 0.1 \text{ l mol}^{-1} \text{ cm}^{-1}$) is assigned to the ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$ transition. A sharp middle band at $24,500 \text{ cm}^{-1}$ ($\epsilon = 2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and the third very strong transition at $27,175 \text{ cm}^{-1}$ ($\epsilon = 2.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) are assigned to the ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$ and ${}^4E_g(G), {}^4A_{1g}(G) \leftarrow {}^6A_{1g}$ transitions respectively. The very high molar absorptivity value of the middle band indicates tailing of the ligand uv absorptions into the spin allowed charge transfer transition. The third band at $27,175 \text{ cm}^{-1}$ shows a sign of structure, thus indicating that this band has been appropriately assigned to the transitions to the terms which are almost degenerate: ${}^4E_g(G)$ and ${}^4A_{1g}(G)$. The 10^{-4} DMSO solution electronic spectra for the complexes $[\text{Mn}(\text{IN-DtczH})_2]\text{Cl}_2$ and $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ exhibit three absorptions in the energy regions $13,510\text{-}13,515 \text{ cm}^{-1}$ ($\epsilon = 10 \text{ l mol}^{-1} \text{ cm}^{-1}$), $17,700\text{-}17,800 \text{ cm}^{-1}$ ($\epsilon = 10 \text{ l mol}^{-1} \text{ cm}^{-1}$) and $26,315\text{-}29,155 \text{ cm}^{-1}$ ($\epsilon = 2.5 \times 10^2 - 3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). The range of molar absorptivity values lying between $10^1\text{-}10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the three bands reveal tetrahedral geometry around manganese(II)¹² and hence the absorption energies are being assigned to the transitions ${}^4T_1(G) \leftarrow {}^6A_1, {}^4T_2(G) \leftarrow {}^6A_1$ and ${}^4E(G), {}^4A_1(G) \leftarrow {}^6A_1$, respectively, of the tetrahedral stereochemistry. The molar absorptivity value of $8 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the highest energy transition of $[\text{Mn}(\text{IN-DtczH})_2]\text{Cl}_2$ complex can be attributed to the spin allowed, Laporte forbidden, with $d-p$ mixing nature of the transition in tetrahedral stereochemistry. While the very high molar absorptivity value of $3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the highest

energy transition of $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ complex can be attributed, in addition to all these factors, also to the tailing of ligand uv absorption into spin allowed charge transfer transitions. The higher molar absorptivity for the highest energy transition at the same concentration for $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ complex may arise because of the highly conjugated framework of the IN-DtczH-Sal ligand.

All the iron(II) isonicotinoyldithiocarbazates under present discussion exhibit a doublet of medium intensity falling in the region $18,870\text{-}19,850$ and $20,830\text{-}21,850 \text{ cm}^{-1}$, another band of high intensity around $25,000\text{-}26,880 \text{ cm}^{-1}$ and another doublet of medium intensity in the region $11,560\text{-}13,700$ and $13,600\text{-}14,705 \text{ cm}^{-1}$ in their DMSO solution electronic absorption spectra. The two high energy bands have been assigned to the spin-allowed ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ electronic transitions of octahedral low-spin iron(II) complexes respectively (in low spin trans- $\text{Fe}^{\text{II}}\text{L}_4\text{Z}_2$ species, the splitting of the ${}^1T_{1g}$ state is commonly observed, however, the splitting of the ${}^1T_{2g}$ state is rarely resolved). The third band of medium intensity may be assigned to the spin-forbidden ${}^3T_{2g}, {}^3T_{1g} \leftarrow {}^1A_{1g}$ transitions. As already discussed, the magnetic susceptibility studies reveal that these complexes observe spin-crossover equilibrium between ${}^5T_{2g}$ and ${}^1A_{1g}$ spin states. Keeping this in view, the lowest energy band of medium intensity may also consist of an absorption due to ${}^5E_g \leftarrow {}^5T_{2g}$ transition. The splitting of this band into two components around $13,600\text{-}14,705$ and $11,560\text{-}13,700 \text{ cm}^{-1}$ in the spectra of six coordinate and high spin octahedral iron(II) complexes has generally been discussed in terms of tetragonal distortion.

In the DMSO solution electronic absorption spectra, the three iron(III) isonicotinoyldithiocarbazates exhibit three well defined absorptions. The lowest energy band of medium intensity at $14,470 \text{ cm}^{-1}$ has unsymmetrical shape for the complex $\text{Fe}(\text{IN-Dtcz})_3$ and appears as a doublet around $13,600\text{-}13,700$ and $14,300\text{-}14,600 \text{ cm}^{-1}$ in the Zwitterionic complexes. The position and shape of this band has been attributed to the transitions ${}^4T_{1g} \leftarrow {}^6A_{1g}$ and ${}^4T_{1g} \leftarrow {}^2T_{2g}$. The second band also of medium intensity around $20,830\text{-}21,980 \text{ cm}^{-1}$ has been attributed to the transitions ${}^2A_{1g}, {}^2T_{1g} \leftarrow {}^2T_{2g}$. While the third intense band around $24,390\text{-}26,525 \text{ cm}^{-1}$ arises due to the internal transitions in the ligand, and to metal-ligand and ligand-metal charge transfer transitions. Observation of two separate peaks characteristic of low-spin and high-spin states in the solution electronic spectra of iron(II) and iron(III) complexes, and separate metal-ligand stretching frequencies ascribable to low- and high-spin isomers in the IR spectra in conjunction with the anomalous magnetic behaviour support the occurrence of the spin free \rightleftharpoons spin paired equilibrium in these complexes.

VII. IN VITRO ANTIMICROBIAL STUDIES

The $[\text{M}(\text{IN-DtczH-Sal})_n]\text{Cl}_n$ ($\text{M} = \text{Mn}(\text{II})$ for $n = 2$; $\text{M} = \text{Fe}(\text{III})$ for $n = 3$) complexes have been screened to assess their antimicrobial activity against the pathogenic fungus *Candida albicans*, the pathogenic gram-negative *Escherichia coli*, *Pseudomonas aeruginosa* and gram-positive *Staphylococcus aureus*, *Enterococcus faecalis* using the agar dilution method. The $[\text{Mn}(\text{IN-DtczH-Sal})_2]\text{Cl}_2$ complex was particularly active against *E. coli* and *C. albicans* with MIC values of 125 and 500 $\mu\text{g/ml}$ respectively (Table 3). While the

[Fe(IN-DtczH-Sal)₃]Cl₃ complex showed MIC value of 250 µg/ml against *C. albicans*. Both the manganese(II) and iron(III) complexes exhibited moderate activity against *P. aeruginosa*, *S. aureus* and *Enterococcus faecalis* with MIC values of 1000 µg/ml.

VIII. MATERIALS AND METHODS

All the chemicals used were of analytical grade and used as such. The ligands isonicotinoyldithiocarbamic acid (IN-DtczH), sodium salt of isonicotinoyldithiocarbamic acid (IN-DtczNa) and salicylaldehyde Schiff base of IN-DtczH (IN-DtczH-Sal) were prepared by the method as reported earlier.

ELEMENTAL ANALYSES, PHYSICAL MEASUREMENTS AND *IN VITRO* ANTIMICROBIAL STUDIES:

Manganese in the complexes was determined volumetrically by EDTA titration using Eriochrome Black T (EBT) as an indicator. Iron in the complexes was determined volumetrically by mercurous nitrate using ammonium thiocyanate as an indicator. Chloride content in the complexes were determined volumetrically by mercurimetric method. Sulphur in the complexes was determined gravimetrically as BaSO₄ (Table1). Carbon, hydrogen and nitrogen analysis, molar conductance measurements (10⁻⁴ M DMSO solutions) and IR and solution electronic spectral (DMSO), magnetic susceptibility measurements and molar conductance measurements were made by the methods described earlier⁶. *In vitro* antimicrobial studies were also performed by the agar dilution method as reported earlier.

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