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Mixed Ligand Complexes of Iron(II) and Manganese(II)

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Six compunds of the type [M(AA)(BB)(L)$_2$] where M = Mn or Fe, AA = diethyldithiocarbamate, BB = acetylacetonate, benzoylacetonate and L = 3-picoline were isolated by reacting the metal salts with sodium salt of diethyldithiocarbamic acid (Naet$_2$dtc), acetylacetone (acac)/benzoylacetone (bzac)/8-hydroxyquinoline (ox) and 3-picoline in stoichiometric ratio. The compounds were characterized on the basis of their analyses, molar conductance, magnetic susceptibility, infrared, electronic spectral data and molecular weight measurement.

INTRODUCTION

The study of mixed ligand complexes has evinced considerable interest among coordination chemists due to the biological importance in the living system[1, 2]. It has been observed that the quaternary complexes are more stable than the ternary ones and limited number of such complexes are known[3, 4]. The versatility of chelates diethyldithiocarbamate, acetylacetonate, benzoylacetonate, oxinate and ligand 3-picoline is well known[5–7]. In continuation to the previous work on study of mixed ligand complexes[8, 9] it is intended to study the behaviour of some transition metal ions in heterochelate environment.

EXPERIMENTAL

All the chemicals used were AnalaR grade. Analyses of iron and sulphur were carried out by standard methods[34]. Infrared spectra of the complexes were recorded as KBr discs on a Perkin-Elmer spectrophotometer model 337. Electronic spectra of the complexes in 10^{-3} M nitromethane solution were recorded on Unicam SP-500 spectrophotometer. Molar conductivity of the complexes in *ca.* 10^{-3} M nitromethane were measured using Systronic Direct Reading Conductivity Meter 303. Magnetic susceptibility was measured at room temperature (25 ± 1°C) by Gouy method using Hg[Co(NCS)$_4$] as calibrant. Molecular weight measurements were carried out by Rast's method using biphenyl as solvent.

Preparation of Complexes

An ethanolic solution (20 ml) of manganous chloride (0.01 mol) or a solution of ferrous sulphate (0.01 mol) in 1 : 1 water-ethanol mixture (20 ml) and acetylacetone/benzoylacetone/8-hydroxyquinoline (0.01 mol) in ethanol was refluxed for 1 h to ensure the coordination of the ligand with the metal ion in solution. A mixture containing equimolar proportion of sodium salt of diethyldithiocarbamate (0.01 mol) in ethanol (20 ml) and excess of 3-picoline (0.05 mol) was added to the clear solution obtained in the previous stage. The resultant mixture solution was stirred while the complexes were separated out as precipitate. The complexes were filtered, washed with ethanol, ether and dried *in vacuo*, yield 80%. The products were recrystallized from nitromethane and the purity of the complexes was checked by TLC.

RESULTS AND DISCUSSION

The elemental analyses, molar conductance and molecular weight data of the complexes are consistent with the formulation of the compounds $[M(AA)(BB)(L)_2]$, where M=Mn or Fe, AA=diethyldithiocarbamate, BB=acetylacetone/benzoylacetonate/oxinate and L = 3-picoline. All the compounds have melting point above 300°C, are soluble in nitromethane and sparingly soluble in most other organic solvents. The low values of molar conductance (Table 1) in *ca.* 10^{-3} M nitromethane medium indicate that the complexes are essentially non-electrolytes. The molecular weight measurement indicated that the compounds are monomeric in nature. In an octahedral field manganese(II) ion ($3d^5$) has a ground term $^6A_{1g}(t_{2g}^3e_g^2)$ for high-spin and $^2T_{2g}(t_{2g}^5e_g^0)$ for a low-spin state depending upon the strength of the crystal field. The high-spin manganese(II) complexes ($S = 5/2$) are expected to exhibit magnetic moment value of 5.92 B.M., which is temperature independent, whereas low-spin compounds show value in the range of 1.8–2.1 B.M. For the manganese complexes reported here, the μ_{eff} value was found within the range 5.90–6.01 B.M. as expected for high-spin manganese(II) complexes with $S = 5/2$. For a spin-free divalent iron d^6, $S = 2$ and the ground term is $^5E_g(t_{2g}^4e_g^2)$ in an octahedral environment. The magnetic moment is normally found in the range of 5.0–5.2 B.M. owing to the spin of four unpaired electrons and a small second order orbital contribution[10]. In the complexes of iron under investigation, the μ_{eff} value was found between 4.1–4.7 B.M. (Table 1). This value is slightly lower than expected for high-spin iron (II) complex[11, 12].

The infrared spectral bands of the complexes with their tentative assignments are given in Table 2. The ligand dithiocarbamate is known to behave as a bidentate or a monodentate one. The former exhibits ν_{as}C–S near 1000 cm^{-1} as a single band, whereas the latter shows a doublet in the same region[13]. Also, the νC=N of the former (above 1485 cm^{-1}) is higher than that of the latter (below 1485 cm^{-1})[14]. In the present case the νC–S band was obtained at 1000 cm^{-1} as a single band and νC=N band was found above 1485 cm^{-1}, in all complexes, indicating that diethyldithiocarbamate is coordinated to the metal ion as a uninegative bidentate ligand through both the sulphur atoms[15]. Infrared spectra of β-diketonate complexes have been studied extensively[7, 16–18]. The ligand acetylacetone and benzoylacetone can coordinate with variety of coordination modes[7]. In the four (acetylacetonato/benzoylacetonato) chelates of manganese(II)

TABLE 1
ANALYTICAL DATA OF MIXED LIGAND COMPLEXES OF IRON AND MANGANESE

S.No.	Complexes (Colour)	Melting Point (°C)	Mol. Wt. Found (Calcd.)	% Found (Calcd.)				μ_{eff} (B.M)	Λ_m (mhos)
				Mn/Fe	S	C	H		
1.	[Mn(et_2dtc)(acac)(3–pic)$_2$] (Ash colour)	>300	480.00 (488)	11.01 (11.25)	11.98 (12.99)	54.11 (54.11)	6.12 (6.35)	6.01	3.6
2.	[Mn(et_2dtc)(bzac)(3–pic)$_2$] (Cream colour)	>300	612 (612)	8.96 (8.97)	10.42 (10.45)	62.25 (62.75)	5.45 (5.71)	5.94	3.2
3.	[Mn(et_2dtc)(ox)(3–pic)$_2$] (Light yellow)	>300	513 (533)	10.26 (10.31)	11.35 (12.00)	58.02 (58.54)	5.61 (5.62)	5.90	9.3
4.	[Fe(et_2dtc)(acac)(3–pic)$_2$] (Reddish brown)	>300	450.00 (489)	10.91 (11.42)	12.12 (12.96)	53.84 (54.00)	5.98 (6.34)	4.31	9.6
5.	[Fe(et_2dtc)(bzac)(3–pic)$_2$] (Reddish brown)	>300	596.00 (613)	9.98 (9.11)	10.96 (10.44)	62.01 (62.65)	5.67 (5.71)	4.12	1.3
6.	[Fe(et_2dtc)(ox)(3–pic)$_2$] (Blackish brown)	>300	513.00 (534)	10.12 (10.46)	11.86 (11.99)	58.53 (58.44)	5.60 (5.61)	4.71	6.4

TABLE 2
INFRARED SPECTRAL DATA (cm^{-1})OF MIXED LIGAND COMPLEXES OF IRON AND MANGANESE

S.No.	Complexes	Dithiocarbamate		Acetylacetone/benzoylacetone		Oxine	3-Picoline	
		νC=N	ν_{as}C–S	νC=O	νC=C	νC–O	νC=C + νC=N	νC–H
1.	[Mn(et_2dtc)(acac)(3-pic)$_2$]	1520	1000	1610	1550	—	a	2900
2.	[Mn(et_2dtc)(bzac)(3-pic)$_2$]	1520	1000	1610	1540	—	b	2900
3.	[Mn(et_2dtc)(ox)(3-pic)$_2$]	1520	1000	—	—	1105	1605, 1525	2900
4.	[Fe(et_2dtc)(acac)(3-pic)$_2$]	1520	1000	1605	1550	—	a	2900
5.	[Fe(et_2dtc)(bzac)(3-pic)$_2$]	1525	1000	1605	1550	—	b	2900
6.	[Fe(et_2dtc)(ox)(3-pic)$_2$]	1520	1000	—	—	1105	1605, 1520	2900

a: overlap with bands of acac b: overlap with bands of bzac and iron(II), the νC=O band was found between 1602–1610 cm^{-1} and νC=C at 1540–1550 cm^{-1} (Table 2) indicating that the ligand was coordinated to the metal ion as a uninegative bidentate one through the oxygen atoms[19–22]. Similar observations were also reported by Graddon[23]. Charles *et al.*[24] have reported that in case of oxinate complexes of metals, the νC–O was obtained at 1120 cm^{-1} region, the position of the band slightly varying with the metal. In the present case, the νC=O band due to oxine was found at 1105 cm^{-1} (Table 2) indicating the coordination of the ligand through nitrogen and oxygen atoms as uninegative bidentate one. The νC=C + νC=N band due to 3-picoline was found to overlap with the bands of β-diketonate complexes. However, bands are found at *ca.* 1600 and 1520 cm^{-1} in the complexes $[Mn(et_2dtc)(ox)(3\text{-}pic)_2]$ and $[Fe(et_2dtc)(ox)(3\text{-}pic)_2]$. The C–H stretching vibration of pyridine ring at about 3000 cm^{-1} is shifted to lower frequency in the mixed ligand complexes indicating the coordination of the ligand[25, 26].

Electronic Spectra

The electronic spectral data of all high-spin manganese(II) compounds show essentially the same features. The electronic absorption maxima found at 16,900 cm^{-1}, 22,900 cm^{-1} and 27,400 cm^{-1} for all the manganese(II) complexes may be assigned as ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$, respectively. These bands are consistent with the octahedral nature of the compounds[27]. For a high-spin six-coordinated iron(II) complex, the octahedral ground state is ${}^5T_{2g}(t_{2g}^4e_g^2)$ and the only spin allowed excited state is ${}^5E_g(t_{2g}^3e_g^3)$. The excited state is subject to Jahn-Teller distortion resulting in splitting into ${}^5A_1 + {}^5B_1$ in D_{4h}. Thus, almost all 'octahedral' iron(II) complexes show a broad absorption which either is split into two or shows a definite shoulder due to the splitting of the ${}^5E_g$ state[28]. In the iron(II) complexes reported under present investigation, two bands are observed at 8,500 and 10,600 cm^{-1} due to ${}^5T_2 \rightarrow {}^5A_1$ and ${}^5T_2 \rightarrow {}^5B_1$ transitions respectively as expected for high-spin six-coordinated octahedral iron(II) complexes with tetragonal distortion. Kepert[29] also suggested that the regular octahedral stereochemistry would experience distortion due to presence of dissimilar chelating agents. Hence, it is concluded that the six compounds reported here are high-spin mixed ligand complexes of manganese(II) and iron(II) with distorted octahedral stereochemistry.

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