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Manganese (II) Complexation with 1, 1-dithiolate and Nitrogen donors – Synthesis, Magnetic Properties and Spectroscopic Studies

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Abstract: *Complexes of Mn(II) ion with some heterocyclic nitrogen bases and 1-cyano-1-carboethoxyethylene-2,2-dithiolate ion (*CED^{2-}*) of the compositions, *$Mn(N\text{-}N)_n(CED)$* and *$Mn(N\text{-}N)(CED)L_2$* [N-N = 2,2*^{I}*-bipyridine (bipy), n =2 or 3, *CED^{2-}* = 1-cyano-1-carboethoxyethylene-2,2-dithiolate, L = *H_2O*, pyridine (py), α-picoline (α-pic), β-picoline (β-pic) or γ-picoline (γ-pic)] have been isolated and characterized on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral studies. The molar conductance data reveal non-electrolytic nature of the complexes in DMF. Magnetic moment values suggest high spin complexes. The electronic spectral data suggest octahedral stereochemistry around Mn(II) ion in these complexes. Infrared spectral studies suggest bidentate chelating behaviour of *CED^{2-}* , 2,2*^{I}*-bipyridine (bipy) while other ligands show unidentate behaviour in their complexes.*

Keywords: *Manganese(II), 1-cyano-1-carboethoxyethylene-2,2-dithiolate, Nitrogen donors, Mixed ligand complexes.*

I. Introduction

The coordination chemistry of transition as well as non-transition metal dithiolates has been area of interest for several decades [1-3].This interest has manifested itself in the general area of novel complex synthesis and in the field of "biological inorganic chemistry". The complexes of these ligand systems have been used with success as fungicides, herbicides, pesticides, phytocides, bacteriocides, vulcanization accelerators, insulators, semiconductors and UV stabilizers for polyethylene and nylon and more recently in the deposition of ZnS or CdS thin films by metal organic chemical vapour deposition [4-11]. The compounds are also used as optical recording materials [12] along with other components. The radio-protective activities of a number of S-containing compounds were also analyzed in terms of the radio-protective information contained in their individual chemistry constituents [13].

Anti-tumor activity of gallium complexes of dithiolate ligands have been examined [14] and found active anti-tumor agents at 1-50mg/kg in vitro in mice. The use of 1,1-dithio ligand complexes in processes of industrial and biological importance has stimulated much research which has resulted in a great number of patents [6,12,14,15].

Among 1,1-dithio ligands 1-cyano-1-carboethoxyethylene-2,2-dithiolate ion (CED^{2-}) shows exciting coordination properties by virtue of their chelating and bridging behaviours which has been found in their binary, ternary and heterobimetallic complexes [6,16-19].

Manganese is one of the important transition metal having various oxidation states and Mn(II) is being the most stable state. Manganese is important in both animal and plant enzymes [20]. In mammals, enzyme arginase is produced in the lever which converts nitrogenous waste products into urea in the arnithine arginine-citrulline cycle. It is essential in a group of enzymes called phosphotransferases. Manganese is also known to play several important roles in biological processes in the metabolism of dioxygen and its reduced forms such as dismutation of superoxide to hydrogen peroxide to dioxygen and water by the manganese catalase [21] and the four electron oxidation of two water molecules to form dioxygen by photosynthetic oxygen evolving complex (OEC) [22,23]. In the photosynthetic process, four manganese ions are essential for catalysis with the possibility that some or all of the manganese ions may interact during turnover [24]. While EXAFS data indicates that only N or O donor atoms are bound to manganese, there is no evidence for a mangano-porphyrin centre in the OEC [25].

It is evident from the literature survey that there is no report on mixed ligand complexes of manganese(II) with 1-cyano-1-carboethoxyethylene-2,2-dithiolate and nitrogen donors. Thus, in the light of importance of 1,1-dithioligands and manganese metal ion and absence of any report on mixed ligand complexes arising from these moieties with nitrogen donors in literature, it was thought of interest to undertake the synthesis and structural characterization of complexes of manganese(II) with 1-cyano-1-carboethoxyethylene-2,2-dithiolate and nitrogen donors such as 2,2^{I}-bipyridine (bipy) and their reaction products towards heterocyclic nitrogen donors [pyridine(py), α-picoline (α-pic), β-picoline (β-pic) or γ-picoline (γ-pic)]. The results of these investigations are described in this paper.

II. Experimental

Materials

All the chemicals used in this study were obtained from E. Merck of GR grade or equivalent quality. α-, β- and γ-picolines were obtained from Aldrich chemical company. $K_2CED.2H_2O$ was prepared by a known literature procedure [33].

Found: C, 25.02 ; H, 3.04 ; N, 5.14 ; S, 22.12.

Calcd. For: $K_2S_2C_6NO_2H_5$. H_2O: C, 25.42 ; H, 2.48 ; N, 4.94 ; S, 22.60.

IR: ν(C≡N) 2190cm^{-1}; ν (C=O) 1642cm^{-1}, ν (C=CS$_2$) 1375, 1320 cm^{-1}, ν (C-S) 1032, 953 cm^{-1}

Analysis of the complexes

The complexes were analyzed for their metal contents gravimetrically following standard literature procedures [42]. Carbon, hydrogen and nitrogen were estimated micro analytically and sulphur gravimetrically as $BaSO_4$. Weight loss experiments were carried out in hot air oven in the temperature range 100-200^{0}C for estimation of volatile moiety associated with the complexes such as water molecules etc. The analytical data of the mixed ligand complexes are presented in Table 1.

Physical Measurements

Molar conductance of the complexes at 10^{-3}M dilution in DMF solutions were determined using Systronics direct reading Conductometer-304 with a dip-type cell with platinized electrodes.

Magnetic susceptibility measurements were carried out at room temperature on Sherwood Scientific, Magnetic Susceptibility Balance (Auto) using $Cu(CH_3COO)_2.H_2O$ as calibrant and corrected for diamagnetism by the procedures described by Figgis and Lewis [43] and Earnshaw [44].

The electronic spectra of the complexes and ligands were recorded on Perkin-Elmer Lamda 25 UV-VIS Spectrophotometer or Shimadzu UV spectrophotometer model UV 1800. The spectra in nujol mull were recorded using the technique described by Lee *et.al* . [45].

Infrared spectra were recorded in KBr (4000 - 400 cm^{-1}), in nujol (4000 - 200 cm^{-1}) on Perkin Elmer spectrum 100 FT-IR spectrophotometer. The IR spectra is in the lower region (600-50 cm^{-1}) have been obtained from SAIF, I.I.T. Bombay.

The molar conductance and magnetic moments (μ_{eff}) of the complexes are included in Table 1. The position of the absorption bands in the electronic and IR spectra and assignments thereof are given in Table 2 and 3 respectively.

Synthesis of Complexes

Mn(bipy)(CED).2H$_2$O (1)

2,2^I-Bipyridine (0.7809g, 5mM) was added to a 30mL aqueous solution containing $Mn(OAc)_2.4H_2O$ (1.2254g, 5mM) with stirring resulting yellow coloured solution. To this solution, 25mL aqueous solution of $K_2CED.H_2O$ (1.4171g, 5mM) was added which gave buff coloured precipitate immediately which changed to dark brown after stirring for 15 minutes. The precipitate was suction filtered, washed with water, alcohol and ether and dried *in vacuo* over fused $CaCl_2$.

Yield: 1.2748g (64.1%).

Mn(bipy)$_2$(CED) (2)

2,2^I-Bipyridine (0.7809g, 5mM) was added to a 20mL aqueous solution containing $Mn(OAc)_2.4H_2O$ (0.6127g, 2.5mM) with stirring which gave yellow coloured solution. To this resulting solution, 20mL aqueous solution of $K_2CED.H_2O$ (0.7085g, 2.5mM) was added with stirring which yielded buff coloured precipitate immediately turning to deep brown colour after stirring the mixture for 10 minutes. The resulting precipitate was suction filtered, washed with water, alcohol and ether and dried *in vacuo* over fused $CaCl_2$.

Yield: 0.7975g (57.5%).

Mn(bipy)$_3$(CED) (3)

2,2^I-Bipyridine (2.3428g, 15mM) was added to a 25mL aqueous solution containing $Mn(OAc)_2.4H_2O$ (1.2254g, 5mM) with stirring which yielded yellow coloured solution. To this resulting solution, 25mL aqueous solution of $K_2CED.H_2O$ (1.4171g, 5mM) was added with stirring resulting buff coloured precipitate immediately which changed to brown colour after stirring the mixture for 15 minutes. The precipitate was suction filtered, washed with water, alcohol and ether and dried *in vacuo* over fused $CaCl_2$.

Yield: 1.6573g (46.6%).

Mn(bipy)(CED)(py)$_2$ (4)

Mn(bipy)(CED).2H_2O (0.7g) was dissolved in 20mL of pyridine with stirring which yielded dark coloured solution and no precipitate was obtained immediately. The solution was allowed to evaporate naturally giving dark coloured residue. It was washed with ether several times till the filtrate was found colourless. The yellow coloured precipitate was dried in open air. Yield: 0.6034g (61.7%).

Mn(bipy)(CED)(α-pic)$_2$ (5)

Mn(bipy)(CED).2H_2O (0.8g) was dissolved in 15ml of DMSO and to this solution 20mL of α-picoline was added with stirring. No precipitate was obtained immediately. The solution was allowed to evaporate naturally which resulted brown coloured precipitate. The precipitate was filtered, washed with ether several times and dried in open air.
Yield: 0.2568g (23.8%).

Mn(bipy)(CED)(β-pic)$_2$ (6)

The complex Mn(bipy)(CED)(β-pic)$_2$ was synthesized exactly in the same manner as the complex Mn(bipy)(CED)(α-pic)$_2$ by using β-picoline in place of α-picoline.
Yield: 0.6891g (64.00%).

Mn(bipy)(CED)(γ-pic)$_2$ (7)

The complex Mn(bipy)(CED)(γ-pic)$_2$ was prepared by the same method as the complex Mn(bipy)(CED)(py)$_2$, by treating Mn(bipy)(CED).2H_2O with γ-picoline in place of pyridine.
Yield: 0.7025g (74.5%).

III. Results and Discussion

The analytical data indicate the formation of complexes of Mn(II) of the general formulae Mn(N-N)$_n$(CED) and Mn(N-N)(CED)L$_2$ [N-N = bipy, n =2 or 3, CED^{2-} = 1-cyano-1-carboethoxyethylene-2,2-dithiolate, L = H_2O, pyridine (py), α-picoline (α-pic), β-picoline (β-pic) or γ-picoline (γ-pic)].

All the complexes decompose below 250^{0}C and their decomposition temperatures are mentioned in Table 1. The complexes are insoluble in water and common organic solvents but are slightly soluble in coordinating solvents such as DMF and DMSO.

The weight loss experiments for the complexe Mn(N-N)(CED).2H_2O [N-N = bipy] was carried out by heating a small amount of sample in a glass tube for 4hrs in an electric oven maintained at 100, 120, 150 and 180^{0}C. The complex shows loss of weight in the temperature range 150-180^{0}C corresponding to two water molecules suggesting that it possess two water molecules in their coordination sphere [26].

Molar Conductance Studies:

The molar conductance values lie in the range 21.0 - 54.0 ohm^{-1}cm^2 mole^{-1} for the complexes Mn(N-N)$_2$(CED) and Mn(N-N)(CED)L$_2$ in DMF solution (10^{-3}M) suggesting the non-electrolytic nature for the complexes while complexes Mn(bipy)$_3$(CED) shows Λ_M value 62.0 ohm^{-1}cm^2 mole^{-1} supporting 1:1 electrolytic nature [27].

Magnetic Susceptibility Studies:

All the manganese complexes except (1) have μ_{eff} values in the range 5.09-6.90 B.M. which are consistent with essentially spin only temperature independent magnetic moment of manganese(II) complexes adopting a high spin d^5 electronic configuration [28-30]. However, the complex (1) has μ_{eff} values 4.65 B.M. which is lower than the d^5 high-spin electronic configuration and but higher than the d^4 high-spin electronic configuration suggest that the lowering of magnetic moment may be due to anti-ferromagnetism (caused by the possibility of Mn--------Mn bond or Mn-ligand exchange). This also rules out the possibility of oxidation of Mn(II) to Mn(III). Thus the μ_{eff} values in these complexes correspond to the presence of Mn(II) in them.

Electronic Spectral Studies:

The majority of Mn(II) complexes with d^5 configurations are high spin. In octahedral fields this configuration gives spin-forbidden as well as Laporte(Parity) forbidden transitions, thus accounting for extremely pale colour of such compounds. In tetrahedral environments, the transitions are still spin-forbidden but no longer parity forbidden; these transitions are therefore ~100 times stronger and compounds have a noticeable pale yellow-green colour.

At sufficiently high values of Δ_o , a t_{2g}^5 configuration gives rise to a doublet ground state; for Mn(II) the pairing energy is high and only a few of the strongest ligands sets. In the square environment generally provided by phthalocyanine, Mn(II) has a $^4A_{1g}$ ground state [31].

The spin quartets arise from the configurations $t_{2g}^4e_g^1$, $t_{2g}^3e_g^2$ and $t_{2g}^2e_g^3$ with strong crystal field energies -10Dq, 0 and +10Dq respectively. The $t_{2g}^4e_g^1$ and $t_{2g}^2e_g^3$ configurations each give rise to one $^4T_{1g}$ and one $^4T_{2g}$ whilst the $t_{2g}^3e_g^2$ configuration yields $^4A_{1g}$, $^4A_{2g}$, $^4T_{1g}$ and two ^4E_g levels. It follows that the $^4A_{1g}$, $^4A_{2g}$ and ^4E_g levels have energies independent of the crystal field. In weak field limit, $^4A_{1g}$ and one ^4E_g derived from ^4G; $^4A_{2g}$ from ^4F and the remaining ^4E_g from ^4D are found [32].

Out of many possible transitions in octahedral Mn(II) complexes the three lowest energy bands may be assigned to $^6A_{1g}\rightarrow{}^4T_{1g}$ (ν_1), $^6A_{1g}\rightarrow{}^4T_{2g}$ (ν_2), $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (ν_3) with very low molar extinction coefficients. These bands fit in the Tanabe-Sugano diagram. In almost all the mixed ligand complexes of Mn(II) the lowest energy band is observed in the range 15,503-19,767 cm^{-1} assignable to $^6A_{1g}\rightarrow{}^4T_{1g}$ (ν_1). In some cases it is found as a doublet humps. The 2nd and 3rd bands have been found in some of the mixed ligand complexes in the regions 21,186-21,231 and 25,000cm^{-1} assignable to $^6A_{1g}\rightarrow{}^4T_{2g}$ (ν_2) and $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (ν_3) respectively. The other higher energy band $^6A_{1g}\rightarrow{}^4E_g$ (ν_5) have been observed in some of the complexes in the range 29,411-30,864 cm^{-1} respectively.

Thus based on the electronic spectral data, it has been proposed that these mixed ligand complexes have octahedral geometry around Mn(II) ion.

***Infrared Spectral Studies*:**

The IR spectra of Mn(II) mixed ligand complexes have been interpreted in the light of earlier investigations [4,5, 33-39] on transition and non-transition metal 1,1-dithiolates. The CED^{2-} ligand may be described by resonating structures in its complexes as shown in Fig.1.

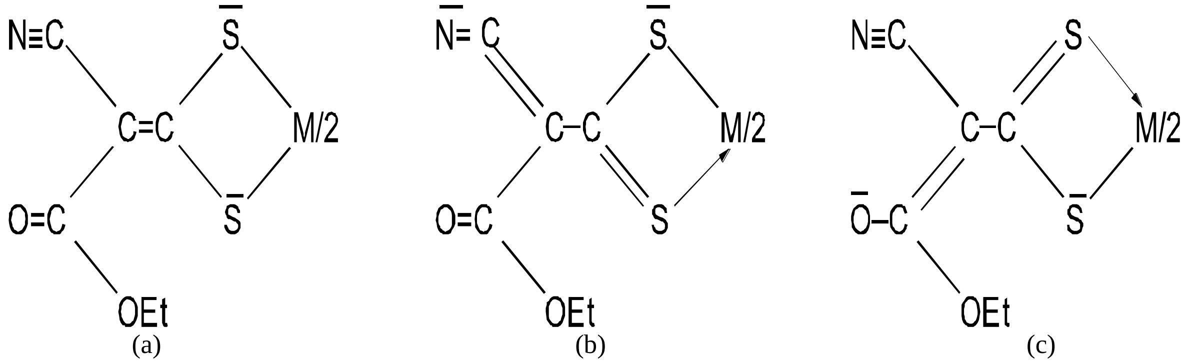
(a) (b) (c)

Fig.1. Resonance forms of CED complexes.

Each of the moieties in the mixed ligand complexes undergoes particular vibrations and contributes certain peaks in their IR spectra. The electron delocalization in the chelated CED^{2-} ring leads to the coupling of vibrational modes so that few bands in IR spectra represent pure vibrations. The IR spectra of the mixed ligand complexes display characteristic stretching frequencies associated with C≡N, C=C, $=CS_2$, C-S and M-S from CED^{2-}; aryl heterocyclic ring vibrations with metal heterocyclic nitrogen vibrations from 2,2^I-bipyridine (bipy), pyridine (py), α-picoline (α-pic), β-picoline (β-pic) and γ-picoline (γ-pic).

The ν(C≡N) band appearing at 2190cm^{-1} in $K_2CED.H_2O$ is observed in the range 2187-2202 cm^{-1} in its complexes suggesting non-involvement of nitrile group of the ligand in bonding. Compounds containing an un-conjugated and a conjugated (with acetyl or benzoyl group) ester group show ν(C=O) bands in 1720-1750 and 1620-1630 cm^{-1} regions respectively. The ν(C=O) stretching band of ester group in these complexes appears as a strong band in the region 1596-1636 cm^{-1}, which is more lowered than by usual α,β-unsaturation is indicative of delocalization of C=O group with the adjacent C=C bond. The existence of ν(C=O) frequency in these complexes in the same region as observed for $K_2CED.H_2O$ suggests that the carbonyl oxygen is not involved in bonding. The complexes exhibit three strong to very strong bands in the regions 1320-1375,1013-1027 and 894-935cm^{-1} assignable to $\nu_1[\nu(C=C)]$, $\nu_4[\nu_{as}(=CS_2)]$ and $\nu_2[\nu_s(=CS_2)]$ vibrations of $>C=CS_2$ structural unit which were found in $K_2CED.H_2O$ at 1320, 1020 and 930 cm^{-1} respectively [33]. In some complexes ν(C=C) appears as splitted (doublet or triplet) indicating lowering of its symmetry. The positive shifts in ν(C≡N) and ν(C=C) bands suggest that resonance form (a) (Fig.1) is more dominant in the 1-cyano-1-carboethoxyethylene-2,2-dithiolate complexes. The occurrence of a weak to strong band in the region 819-907 cm^{-1} for ν(C-S) in these complexes indicates symmetrical bonding of both the sulphur atoms of the ligand to the metal ion.

Mixed ligand complexes containing heterocyclic nitrogen donors show in-plane and out-of-plane ring deformation bands in the ranges 647-652 and 411- 422 cm^{-1} respectively indicating coordination of heterocyclic nitrogen donors through nitrogen atom as these bands have found positive shifts with respect to its corresponding bands in its free form [40]. The Mn(II) complexes also show weak to medium intensity band in the region 1070-1095cm^{-1}. This band is assigned to ring breathing mode of heterocyclic nitrogen donors in the complexes. The presence of this band in the complexes indicates that the co-ordination of heterocyclic nitrogen donors to the metal centre [41]. The ν(C-H) (aromatic ring) arising from aromatic ligands in these complexes is observed as weak band(s) in the region 3070-3113 cm^{-1}. The ν(C-H) (aliphatic) for complexes is observed as very weak intensity bands in the region 2925-2987 cm^{-1} suggesting presence of CED^{2-} and / or α-pic, β-pic, γ-pic in the mixed ligand complexes.

The antisymmetric and symmetric stretching modes ν(O–H), of co-ordinated water present in complex (1) appears as a broad band in the region 3500-3000cm^{-1} while the H-O-H bending modes appear in the region 1630-1610cm^{-1} which overlaps with ν(C=O) of CED^{2-}. As the complex (1) shows weight loss corresponding to two water molecules in the temperature range 150-180^{0}C and hence these water molecules are considered to be present in first co-ordination sphere around metal centre [31].

The non-ligand bands observed in the region 330-427 and 270-296 cm^{-1} in the spectra of complexes are tentatively assigned to ν(M-N) [36] and ν(M-S) [40] modes respectively.

IV. Reactivity of the Complexes

When Mn(bipy)(CED).2H_2O (1) was treated with heterocyclic nitrogen donors (py, α-pic, β-pic or γ-pic) under different experimental conditions then they yielded substitution product Mn(N-N)(CED)L_2 [N-N = bipy; L = py, α-pic, β-pic or γ-pic] suggesting ligand exchange reaction in which water molecules were replaced by strong heterocyclic nitrogen donors.

V. Conclusion

In the present study, it has been found that $Mn(OAc)_2.4H_2O$ reacts with $K_2CED.H_2O$ in presence of bipy in different molar ratio yielding a variety of complexes of Mn(II) ion. The complex, Mn(bipy)(CED).2H_2O, reacts with heterocyclic nitrogen donors (py, α-pic, β-pic or γ-pic) and yields the substitution products.

Based on physico-chemical and spectroscopic studies presented above, octahedral stereochemistry around Mn(II) ion in these mixed ligand complexes have been proposed. The proposed structures of the complexes are given in Fig.2.

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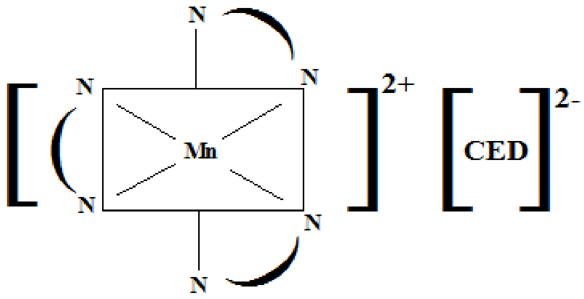

Fig.2(a): Mn(N-N)$_3$(CED) [N-N = bipy]

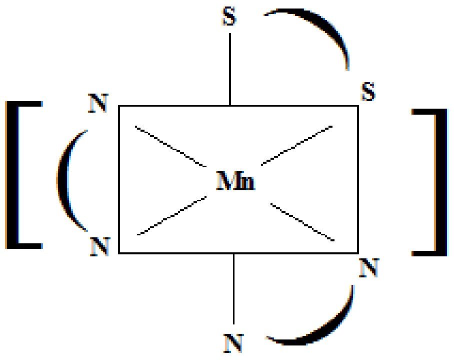

Fig.2(b): Mn(N-N)$_2$(S-S) [N-N = bipy; S-S = CED^{2-}]

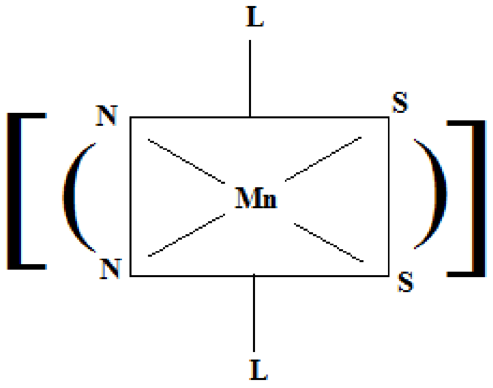

Fig.2(c): Mn(N-N)(S-S)L$_2$ [N-N = bipy; S-S = CED^{2-} ;
[L = py, α-pic, β-pic or γ-pic]

Table: 1. Analytical data, molar conductance and magnetic moments for the mixed ligand complexes of Mn(II) ion.

Complex (colour)	% yield (Dec. Temp. ^0C)	Found (Calcd.),%					Λ_M ($\Omega^{-1}cm^2 mol^{-1}$) (DMF)	μ_{eff} (B.M.)
		Mn	S	C	H	N		
Mn(bipy)(CED).2H_2O (1) (Brown)	75 (210)	12.66 (12.64)	15.04 (14.75)	44.01 (44.23)	4.01 (3.94)	9.23 (9.66)	38.00	4.65
Mn(bipy)$_2$(CED) (2) (Brown)	60 (220)	10.17 (9.90)	11.12 (11.56)	55.97 (56.30)	3.56 (3.81)	12.12 (12.62)	43.00	5.09
Mn(bipy)$_3$(CED) (3) (Orange)	60 (215)	7.92 (7.72)	8.82 (9.02)	60.63 (60.83)	3.98 (4.10)	13.54 (13.78)	62.00	5.89
Mn(bipy)(CED)(py)$_2$ (4) (Yellow)	65 (230)	9.69 (9.87)	11.83 (11.51)	55.89 (56.10)	3.95 (4.16)	11.23 (12.57)	37.00	5.43
Mn(bipy)(CED)(α-pic)$_2$ (5) (Brown)	55 (232)	9.41 (9.39)	10.10 (10.96)	57.12 (57.52)	4.30 (4.65)	11.58 (11.97)	21.00	6.78
Mn(bipy)(CED)(β-pic)$_2$ (6) (Brown)	70 (220)	9.48 (9.39)	11.09 (10.96)	57.23 (57.52)	4.20 (4.65)	11.61 (11.97)	47.00	6.66
Mn(bipy)(CED)(γ-pic)$_2$ (7) (Brown)	80 (240)	9.55 (9.39)	11.13 (10.96)	57.32 (57.52)	4.21 (4.65)	11.23 (11.97)	54.00	6.90

Table: 2 Electronic spectral data of Mn(II) mixed ligand complexes in cm^{-1}

Complex	$^6A_{1g}\rightarrow{}^4T_{1g}(G)$ (ν_1)	$^6A_{1g}\rightarrow{}^4T_{2g}(G)$ (ν_2)	$^6A_{1g}\rightarrow{}^4A_{1g}(G)(\nu_3)$, $^4E_g(G)$	$^6A_{1g}\rightarrow{}^4T_{2g}(D)$ (ν_4)	$^6A_{1g}\rightarrow{}^4E_g(D)$ (ν_5)
Mn(bipy)(CED).2H_2O (1)	18083,19342	-	25000	27777	-
Mn(bipy)$_2$(CED) (2)	17921, 19767	-	-	-	-
Mn(bipy)$_3$(CED) (3)	18903	-	-	-	-
Mn(bipy)(CED)(py)$_2$ (4)	15503	21231	-	-	29411
Mn(bipy)(CED)(α-pic) (5)	17513, 18832	-	-	-	-
Mn(bipy)(CED)(β-pic)$_2$ (6)	19011	21186	-	27397	30864
Mn(bipy)(CED)(γ-pic)$_2$ (7)	18416	-	-	27397	-

Table: 3 Characteristic i.r bands (cm^{-1}) for the mixed ligand complexes of Mn(II) ion

Complex	ν(C≡N)	ν(C=O)	ν(C=C)	ν_{as} =CS_2	ν_s =CS_2	ν(C-S)	ν(M-N)	ν(M-S)	In Plane ring deformation	Out of Plane ring deformation	ν(C-H) Aromatic/ Aliphatic
K_2CED.H_2O	2190vs	1642s	1320vs 1375vs	1020s	930s	886s	-	-	-	-	2982w
Mn(bipy)(CED).2H_2O (1)	2199s	1596s	1371s	1017vs	925w	805w	427w	285w	651w	422w	3072w / 2926w
Mn(bipy)$_2$(CED) (2)	2199s	1596vs	1371vs	1027vs	926m	841w 864w	380w	270w	651w	411w	3076w / 2980w
Mn(bipy)$_3$(CED) (3)	2187s	1596s	1369s	1016vs	926w	840w	360w	288w	651w	411w	3075w / 2925w
Mn(bipy)(CED)(py)$_2$ (4)	2192s	1596vs	1371s	1019vs	914w	841w	340w	275w	647w	413w	3113w / 2983w
Mn(bipy)(CED)(α-pic)$_2$ (5)	2199s	1596s	1371m	1021vs	894w	819w	330w	277w	652w	414w	3097w / 2926w
Mn(bipy)(CED)(β-pic)$_2$ (6)	2190s	1596s	1372m	1013vs	934w	907w	335w	287w	647m	413w	3101w / 2987w
Mn(bipy)(CED)(γ-pic)$_2$ (7)	2202s	1636s	1371m	1017vs	935w	907w	340w	296w	648w	413w	3070w / 2987w