

Synthesis and Structural Characterization of Mixed Ligand Complexes of Manganese (II) With Some Nitrogen and Sulphur Donors by Magnetic and Spectroscopic Methods

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Abstract: Mixed ligand complexes of Mn(II) ion with some heterocyclic nitrogen bases and 1-cyano-1-carboethoxyethylene-2,2-dithiolate ion (CED^{2-}) of the compositions, $Mn(N-N)_n(CED)$ and $Mn(N-N)(CED)L_2$ [$N-N = o\text{-phen}$, $n = 2$ or 3 , $CED^{2-} = 1\text{-cyano-1-carboethoxyethylene-2,2-dithiolate}$, $L = H_2O$, pyridine (py), α -picoline ($\alpha\text{-pic}$), β -picoline ($\beta\text{-pic}$) or γ -picoline ($\gamma\text{-pic}$)] 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-} , 1,10-phenanthroline 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 liver which converts nitrogenous waste products into urea in the ornithine 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 manganese-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 mixed ligand complexes of manganese(II) with 1-cyano-1-carboethoxyethylene-2,2-dithiolate and nitrogen donors such as 1,10-phenanthroline($o\text{-phen}$) 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

2.1. 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. $K_2CED \cdot 2H_2O$ was prepared by a known literature procedure [26].

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

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

IR: $\nu(C\equiv N)$ 2190 cm^{-1} ; $\nu(C=O)$ 1642 cm^{-1} , $\nu(C=CS_2)$ 1375, 1320 cm^{-1} , $\nu(C-S)$ 1032, 953 cm^{-1}

2.2. Analysis of the complexes

The complexes were analyzed for their metal contents gravimetrically following standard literature procedures [27]. Carbon, hydrogen and nitrogen were estimated microanalytically and sulphur gravimetrically as $BaSO_4$. Weight loss experiments were carried out in hot air oven in the temperature range 100-200 $^{\circ}C$ 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.

2.3. 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 $Cu(CH_3COO)_2 \cdot H_2O$ as calibrant and corrected for diamagnetism by the procedures described by Figgis and Lewis [28] and Earnshaw [29].

The electronic spectra of the complexes and ligands were recorded on Perkin-Elmer Lambda 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.* [30].

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 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.

2.4. Synthesis of Complexes

Mn(o-phen)(CED).2H₂O (1)

1,10-phenanthroline monohydrate (0.9912g, 5mM) was added to a 20mL aqueous solution containing $Mn(OAc)_2 \cdot 4H_2O$ (1.2254g, 5mM) with stirring which gave light yellow coloured solution. To this solution, 20mL aqueous solution of $K_2CED \cdot H_2O$ (1.4171g, 5mM) was added with stirring yielding buff coloured precipitate which turned to 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: 1.647g (52.94%).

Mn(o-phen)₂(CED) (2)

1,10-phenanthroline monohydrate (1.9823g, 10mM) was added to a 20mL aqueous solution containing $Mn(OAc)_2 \cdot 4H_2O$ (1.2254g, 5mM) with stirring which resulted light yellow coloured solution. To this resulting solution, 20mL aqueous solution of $K_2CED \cdot H_2O$ (1.4171g, 5mM) was added with stirring which yielded buff coloured precipitate and was further stirred for 15 minutes. The precipitate was suction filtered, washed with water, alcohol and ether and dried *in vacuo* over fused $CaCl_2$. After drying the colour of precipitate was found light brown. Yield: 1.828g (60.29%).

Mn(o-phen)₃(CED) (3)

1,10-phenanthroline monohydrate (2.9734g, 15mM) was added to a 25mL aqueous solution containing $Mn(OAc)_2 \cdot 4H_2O$ (1.2254g, 5mM) with stirring which gave light yellow coloured solution. To this resulting solution, 25mL aqueous solution of $K_2CED \cdot H_2O$ (1.4171g, 5mM) was added with stirring which yielded buff coloured precipitate after stirring for 15 minutes. The precipitate was suction filtered, washed with water, alcohol and ether and dried *in vacuo* over fused $CaCl_2$. After drying the colour of product was orange. Yield: 2.523g (64.46%).

Mn(o-phen)(CED)(py)₂ (4)

0.7g of $Mn(o-phen)(CED).2H_2O$ was dissolved in 20mL pyridine with stirring and finally filtered through ordinary filter paper. The filtrate was left for natural evaporation which yielded black sticky mass. This

was washed with ether several times until washing were colourless and dried in open air which resulted deep yellow coloured precipitate.

Yield: 0.6078g (68.56%).

Mn(o-phen)(CED)(α-pic)₂ (5)

0.8g of *Mn(o-phen)(CED).2H₂O* was dissolved in 20mL DMSO and 20ml of α-picoline was added to it with stirring which do not give any precipitate. The dark coloured solution was left for natural evaporation which resulted dark coloured mass. It was washed with ether several times till the washing liquid became colourless and yielded deep brown precipitate. Yield: 0.5056g (47.60%).

Mn(o-phen)(CED)(β-pic/γ-pic)₂ (6 / 7)

Mn(o-phen)(CED)(β-pic)₂ and *Mn(o-phen)(CED)(γ-pic)₂* were synthesized exactly in the same manner to *Mn(o-phen)(CED)(α-pic)₂* in which α-picoline was replaced by β-picoline and γ-picoline respectively. The resulting complexes were of brown colour.

Yield for *Mn(o-phen)(CED)(β-pic)₂*: 0.6040g (56.86%)

Yield for *Mn(o-phen)(CED)(γ-pic)₂*: 0.6085g (57.29%).

III. Results And Discussion

The analytical data indicate the formation of mixed ligand complexes of Mn(II) of the general formulae *Mn(N-N)_n(CED)* and *Mn(N-N)(CED)L₂* [N-N = *o-phen*, n = 2 or 3, CED²⁻ = 1-cyano-1-carboethoxyethylene-2,2-dithiolate, L = H₂O, pyridine (py), α-picoline (α-pic), β-picoline (β-pic) or γ-picoline (γ-pic)].

All the complexes decompose below 250⁰C 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 complexes *Mn(N-N)(CED).2H₂O* [N-N = *o-phen*] were 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 180⁰C. The complexes show loss of weight in the temperature range 150-180⁰C corresponding to two water molecules suggesting that they possess two water molecules in their coordination sphere [31].

3.1.Molar Conductance Study

The molar conductance values lie in the range 17.0 - 45.0 ohm⁻¹cm² mole⁻¹ for the complexes *Mn(N-N)₂(CED)* and *Mn(N-N)(CED)L₂* in DMF solution (10⁻³M) suggesting the non-electrolytic nature for the complexes while complexes *Mn(o-phen)₃(CED)* shows Λ_M value 65.0 ohm⁻¹cm² mole⁻¹ supporting 1:1 electrolytic nature [32].

3.2.Magnetic Susceptibility Study

All the manganese complexes except (1) have μ_{eff} values in the range 5.46-6.57 B.M. which are consistent with essentially spin only temperature independent magnetic moment of manganese(II) complexes adopting a high spin d⁵ electronic configuration [33-35]. However, the complex (1) has μ_{eff} values 5.36 B.M. which is lower than the d⁵ high-spin electronic configuration and but higher than the d⁴ 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 rule 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.

3.3.Electronic Spectral Study

The majority of Mn(II) complexes with d⁵ 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 [36].

The spin quartets arise from the configurations t_{2g}⁴e_g¹, t_{2g}³e_g² and t_{2g}²e_g³ with strong crystal field energies -10Dq, 0 and +10Dq respectively. The t_{2g}⁴e_g¹ and t_{2g}²e_g³ configurations each give rise to one ⁴T_{1g} and one ⁴T_{2g} whilst the t_{2g}³e_g² 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 [37].

Out of many possible transitions in octahedral Mn(II) complexes the three lowest energy bands may be assigned to ⁶A_{1g}→⁴T_{1g} (ν₁), ⁶A_{1g}→⁴T_{2g} (ν₂), ⁶A_{1g}→⁴E_g, ⁴A_{1g} (ν₃) 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 17,452-19,646 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 21,276-22,075 and 24,038-24,813 cm^{-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 29,239-29,325 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.

3.4. Infrared Spectral Study

The IR spectra of Mn(II) mixed ligand complexes have been interpreted in the light of earlier investigations [4,5,26,38-43] 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.

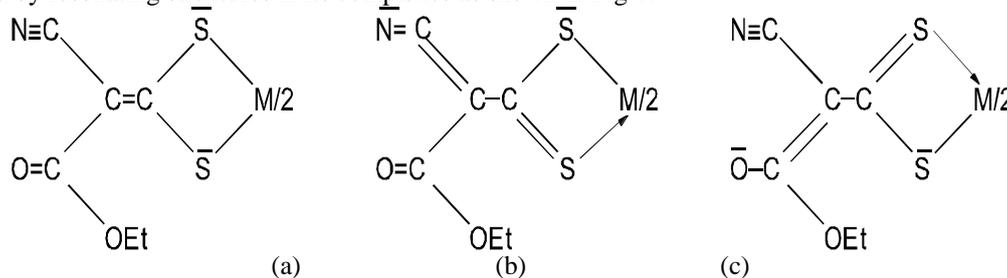


Fig.1. Resonance forms of CED complexes.

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 $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$, $=\text{CS}_2$, $\text{C}-\text{S}$ and $\text{M}-\text{S}$ from CED^{2-} ; aryl heterocyclic ring vibrations with metal heterocyclic nitrogen vibrations from *o*-phenanthroline (*o*-phen), pyridine (py), α -picoline (α -pic), β -picoline (β -pic) and γ -picoline (γ -pic).

The $\nu(\text{C}\equiv\text{N})$ band appearing at 2190 cm^{-1} in $\text{K}_2\text{CED}\cdot\text{H}_2\text{O}$ is observed in the range 2190-2199 cm^{-1} in its mixed ligand 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 $\nu(\text{C}=\text{O})$ bands in 1720-1750 and 1620-1630 cm^{-1} regions respectively. The $\nu(\text{C}=\text{O})$ stretching band of ester group in these complexes appears as a strong band in the region 1622-1633 cm^{-1} , which is more lowered than by usual α,β -unsaturation is indicative of delocalization of $\text{C}=\text{O}$ group with the adjacent $\text{C}=\text{C}$ bond. The existence of $\nu(\text{C}=\text{O})$ frequency in these mixed ligand complexes in the same region as observed for $\text{K}_2\text{CED}\cdot\text{H}_2\text{O}$ suggests that the carbonyl oxygen is not involved in bonding. The complexes exhibit three strong to very strong bands in the regions 1369-1385, 1025-1030 and 920-930 cm^{-1} assignable to $\nu_1[\nu(\text{C}=\text{C})]$, $\nu_4[\nu_{\text{as}}(=\text{CS}_2)]$ and $\nu_2[\nu_{\text{s}}(=\text{CS}_2)]$ vibrations of $>\text{C}=\text{CS}_2$ structural unit which were found in $\text{K}_2\text{CED}\cdot\text{H}_2\text{O}$ at 1320, 1020 and 930 cm^{-1} respectively [26]. In some complexes $\nu(\text{C}=\text{C})$ appears as splitted (doublet or triplet) indicating lowering of its symmetry. The positive shifts in $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{C})$ 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 842-865 cm^{-1} for $\nu(\text{C}-\text{S})$ in these mixed ligand 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 620-641 and 420-424 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 [44]. The Mn(II) complexes also show weak to medium intensity band in the region 1070-1095 cm^{-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 [45]. The $\nu(\text{C}-\text{H})$ (aromatic ring) arising from aromatic ligands in these complexes is observed as weak band(s) in the region 3056-3134 cm^{-1} . The $\nu(\text{C}-\text{H})$ (aliphatic) for complexes is observed as very weak intensity bands in the region 2925-2992 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 $\nu(\text{O}-\text{H})$, of co-ordinated water present in complex (1) appears as a broad band in the region 3500-3000 cm^{-1} while the H-O-H bending modes appear in the region 1630-1610 cm^{-1} which overlaps with $\nu(\text{C}=\text{O})$ of CED^{2-} . As the complex (1) shows weight loss corresponding to two water molecules in the temperature range 150-180 $^\circ\text{C}$ 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 405-430 and 295-325 cm^{-1} in the spectra of mixed ligand complexes are tentatively assigned to $\nu(\text{M-N})$ [40] and $\nu(\text{M-S})$ [44] modes respectively.

IV.Reactivity of the Complexes

When $\text{Mn}(o\text{-phen})(\text{CED}).2\text{H}_2\text{O}$ (1) was treated with heterocyclic nitrogen donors (py, α -pic, β -pic or γ -pic) under different experimental conditions then they yielded substitution product $\text{Mn}(\text{N-N})(\text{CED})\text{L}_2$ [$\text{N-N} = o\text{-phen}$; $\text{L} = \text{py}, \alpha\text{-pic}, \beta\text{-pic}$ or $\gamma\text{-pic}$] suggesting ligand exchange reaction in which water molecules were replaced by strong heterocyclic nitrogen donors.

IV. Conclusion

In the present study, it has been found that $\text{Mn}(\text{OAc})_2.4\text{H}_2\text{O}$ reacts with $\text{K}_2\text{CED.H}_2\text{O}$ in presence of $o\text{-phen}$ in different molar ratio yielding a variety of mixed ligand complexes of $\text{Mn}(\text{II})$ ion. The complex $\text{Mn}(o\text{-phen})(\text{CED}).2\text{H}_2\text{O}$ 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 $\text{Mn}(\text{II})$ ion in these mixed ligand complexes have been proposed. The proposed structures of the complexes are given in Fig.2.

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References

- [1] M. Bousseau, L. Valade, J. P. Legros, P. Cassoux, M. Garbaskas and L. V. Interante *J. Am. Chem. Soc.*, 108, 1908 (1986).
- [2] A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Chem. Lett.*, 387(1986).
- [3] J. A. McCleverty *Molecular Metals*, plenum, New York, 1979.
- [4] D. Coucouvanis *Progress in Inorganic Chemistry*, Vol. 11, edited by S. J. Lippard, (Interscience, New York, 1970, P 233 and references therein.
- [5] D. Coucouvanis *Progress in Inorganic Chemistry*, Vol. 26, edited by S. J. Lippard, (Interscience, New York, 1979, P-301 and references therein.
- [6] R.P. Burns, F.P. McCullough and C.A. McAuliffe *Advances in Inorganic chemistry and Radiochemistry* Vol.23, edited by H. J. Emeleus and A. G. Sharpe, (Academic Press, New York), 1980, P. 211
- [7] P.J. Nieuwenhuizen, A.W. Ehlers, J.G. Hassnoot, S.R. Janse, J. Reedijk and E.J. Baerends, *J. Am. Chem. Soc.*, 121, 163(1999)
- [8] P.J. Nieuwenhuizen, S. Timal, J.G. Hassnoot, A.L. Spek and J. Reedijk, *Chem.- Eur.J.*,3, 1846(1997).
- [9] P. O'Brien, J.R. Walsh, I.M. Watson, M. Motevalli and L. Henriksen, *J. Chem. Soc., Dalton Trans.*, 2491(1996)
- [10] L. Hart, P. O'Brien, S.R.P. Silva, J. R. Walsh and M.I. Watson, *J. Cryst. Growth*, 167, 133 (1996).
- [11] R.D. Pike, H. Cui, R. Kershaw, K. Dwight, A. Wold, T.N. Blanton, A.A. Wernberg and H.J. Gysling, *Thin solid films*, 224, 221(1993).
- [12] *Chem. Abstr.*, 102, P 195283Z (1985).
- [13] V.K. Mukhomorov, *Radiobiologiya*, 26(4), 560 (1986).
- [14] *Chem. Abstr.*, 106, P 67474 h(1987).
- [15] *Chem. Abstr.* 100, p115000 a (1984); 102, p31934m (1985); 104, p192920 k, p88608 d (1986).
- [16] N.K. Singh, P.P. Aggarwal and N. Singh, *Trans. Met. Chem.*, 15(4), 325(1990).
- [17] R.C. Aggarwal and R. Mitra, *Indian J. Chem.*, 33A, 55(1994).
- [18] N.K. Singh, P.P. Aggarwal and N. Singh *Synth. React. Inorg. Met.-Org. Chem.*, 21(4), 541(1991).
- [19] U. Abram, W. Dietzsch and R. Kirmse *Z. Chem.*, 22(8), 305 (1982).
- [20] J. Barber and B. Anderson *Nature*, 370, 31 (1994);
- [21] J.E. Penner-Holm *In Manganese Redox Enzymes*, V.L. Pecoraro, ed., Verlag Chemie, New York, (Chapter 2) 1991.
- [22] P.J. Riggs, R. Mei, C.F. Yocum and J.E. Penner-Holm, *J. Am. Chem. Soc.*, 114, 10650(1992).
- [23] R. Mansfield and J. Berber, *FEBS Lett.*, 140, 165 (1982).
- [24] M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald and C.G. Pierport, *J. Am. Chem. Soc.*, 106, 20416(1984).
- [25] V.V. Kilmor, S.I. Allokhverdies, V.A. Shuvalov and A.A. Krasnovshy, *FEBS Lett.*, 140, 307(1982)
- [26] K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, 22, 1107(1968)
- [27] A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longman, London), 3rd Edn., 1961.
- [28] B. N. Figgis and J. Lewis, *Modern Coordination Chemistry*, edited by J. Lewis and R. G. Wilkins (Interscience, New York), 1960, p. 403.
- [29] A. Earnshaw, *Introduction to Magnetochemistry*, (Academic press, London), 1968.
- [30] R.H. Lee, G. Grishwold and J. Kleinberg, *Inorg. Chem.*, 3, 1278(1964).
- [31] A.V. Nikolov, V.A. Logvineenko and L.T. Myachina, *Thermal Analysis*, Vol.2, Academic Press, New York, 1969.
- [32] W. J. Geary *Coord. Chem. Rev.*, 7, 81 (1971).
- [33] B.N. Figgis *Introduction to ligand Fields*, Wiley Eastern Limited, Chapter-10 (1976).
- [34] N.K. Singh and S.B. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 32(1), 25(2002).
- [35] S.M. Godfrey, C.A. McAuliffe, *Chem. Soc., Dalton Trans.*, 2229 (1993).

- [36] F.A. Cotton, G.Wilkinson, C.A. Murillo and M.Bochmann Advanced Inorganic Chemistry, 5th edn., John Wiley & Sons, New York, 1988, 702-750.
- [37] A.B.P. Lever Inorganic Electronic Spectroscopy, Elsevier, Publishing company,New York,1968, 318.
- [38] J.P. Fackler, Jr. and D. Coucouvanis, J. Am. Chem. Soc., 88, 3913(1966).
- [39] A. Davison, N. Edelstein, R. H. Holm , J. Am. Chem. Soc., 86, 2799(1964). And A. H. Maki
- [40] G. N. Schrauzer and V. P. Meyweg , J. Am. Chem. Soc., 87, 3585(1965).
- [41] D. M. Adams and J. B. Cornell, J.Chem. Soc. (A), 884(1967).
- [42] D. G. Turk and M. K. Yang, J. Chem. Soc. (A), 214(1971).
- [43] M.L.Caffery and D.Coucouvanis, J. Inorg. Nucl. Chem.,37,2081(1975).
- [44] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd Edn., Wiley - Interscience, New York, 1978.
- [45] R.A. Lal, M.L. Pal and S. Adhikari, Synth. React. Inorg. Met.-Org. Chem., 26, 997 (1996).

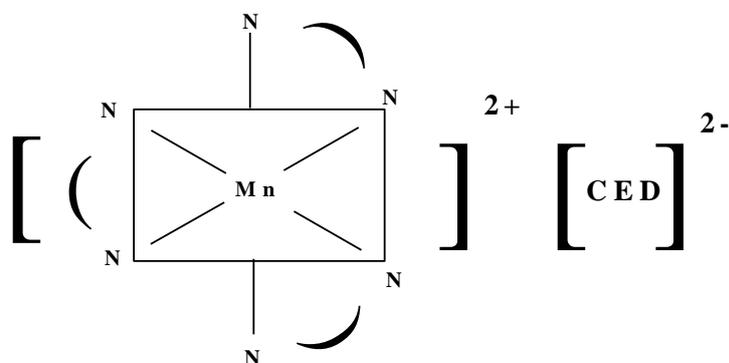


Fig.2(a): $Mn(N-N)_3(CED)$ [N-N = *o*-phen]

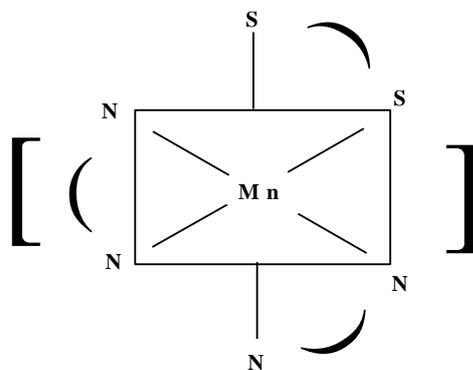


Fig.2(b): $Mn(N-N)_2(S-S)$ [N-N = *o*-phen; S-S = CED^{2-}]

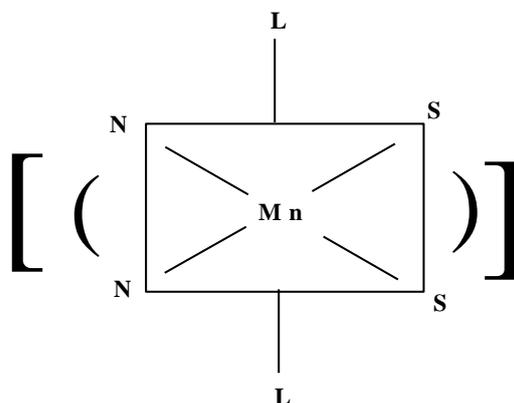


Fig.2(c): $Mn(N-N)(S-S)L_2$ [N-N = *o*-phen; S-S = CED^{2-} ;
[L = py, α -pic, β -pic or γ -pic]

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

Complex (Colour)	% yield (Dec. Temp. °C)	Found (Calcd.),%					Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) (DMF)	μ_{eff} (B.M.)
		Mn	S	C	H	N		
Mn(o-phen)(CED).2H ₂ O (1) (Brown)	75 (204)	12.27 (11.98)	13.63 (13.98)	46.95 (47.15)	3.56 (3.73)	8.81 (9.16)	32.00	5.36
Mn(o-phen) ₂ (CED) (2) (Brown)	60 (210)	9.10 (9.11)	10.24 (10.63)	59.53 (59.78)	3.26 (3.50)	11.32 (11.61)	45.00	5.46
Mn(o-phen) ₃ (CED) (3) (Orange)	60 (215)	7.57 (7.01)	8.64 (8.18)	64.10 (64.43)	3.52 (3.73)	12.10 (12.51)	65.00	5.99
Mn(o-phen)(CED)(py) ₂ (4) (Yellow)	65 (230)	9.82 (9.46)	10.83 (11.04)	57.53 (57.92)	3.73 (3.98)	11.85 (12.05)	33.00	5.55
Mn(o-phen)(CED)(α -pic) ₂ (5) (Brown)	55 (244)	9.41 (9.02)	10.20 (10.53)	58.93 (59.19)	4.21 (4.46)	11.23 (11.50)	36.00	6.57
Mn(o-phen)(CED)(β -pic) ₂ (6) (Brown)	70 (240)	9.38 (9.02)	10.60 (10.53)	58.73 (59.19)	4.13 (4.46)	11.12 (11.50)	22.00	6.33
Mn(o-phen)(CED)(γ -pic) ₂ (7) (Brown)	80 (252)	9.48 (9.02)	10.30 (10.53)	58.83 (59.19)	4.10 (4.46)	11.01 (11.50)	17.00	6.19

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)	${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ (ν_3), ${}^4E_g(G)$	${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ (ν_4)	${}^6A_{1g} \rightarrow {}^4E_g(D)$ (ν_5)
Mn(o-phen)(CED).2H ₂ O (1)	17452, 18867	-	-	-	-
Mn(o-phen) ₂ (CED) (2)	17667, 19047	-	24691	-	-
Mn(o-phen) ₃ (CED) (3)	18518, 19646	-	-	-	-
Mn(o-phen)(CED)(py) ₂ (4)	17667	22026	24813	-	-
Mn(o-phen)(CED)(α -pic) ₂ (5)	17667	21276	24213	-	-
Mn(o-phen)(CED)(β -pic) ₂ (6)	-	21691	24509	-	29239
Mn(o-phen)(CED)(γ -pic) ₂ (7)	-	22075	24038	-	29325

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

Complex	$\nu(\equiv N)$	$\nu(C=O)$	$\nu(C=C)$	$\nu_{\text{as}} = \text{CS}_2$	$\nu_{\text{s}} = \text{CS}_2$	$\nu(C-S)$	$\nu(M-N)$	$\nu(M-S)$	In Plane ring deformation	Out of Plane ring deformation	$\nu(C-H)$ Aromatic/ Aliphatic
K ₂ CED.H ₂ O	2190vs	1642s	1320vs 1375vs	1020s	930s	886s	-	-	-	-	2982w
Mn(o-phen)(CED).2H ₂ O (1)	2199s	1624s	1370vs	1027s	926s	845s 865m	430w	322w	639w	421w	3060w / 2980w
Mn(o-phen) ₂ (CED) (2)	2190s	1623s	1369vs	1029s	921m	845s 864m	428w	325w	639w	421w	3061w / 2973w
Mn(o-phen) ₃ (CED) (3)	2191vs	1622s	1369vs	1028s	920m	842s 863s	427w	320w	638w	421w	3057w / 2969w
Mn(o-phen)(CED)(py) ₂ (4)	2192s	1623s	1370s	1030vs	921w	846s 864m	428w	305w	639w	421w	3056w / 2979w
Mn(o-phen)(CED)(α -pic) ₂ (5)	2199s	1624s	1385s	1028s	930w	850s	410w	298w	641m	420w	3073w / 2980w
Mn(o-phen)(CED)(β -pic) ₂ (6)	2199s	1624s	1372s	1025s	928w	854s	405w	300w	620m	424w	3134w / 2979w
Mn(o-phen)(CED)(γ -pic) ₂ (7)	2195s	1633s	1371s	1030s	925w	846s	412w	295w	638s	421w	3071w / 2992w