Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(9):236-243

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and Characterization of Manganese (IV) Complexes of Polyfunctional Dihydrazones Containing Amide, Azomethine and Phenol Functions

Syamal Adhikari[1*], Ram A Lal[2], Alak Debnath[1] and Dipankar Dey[1]

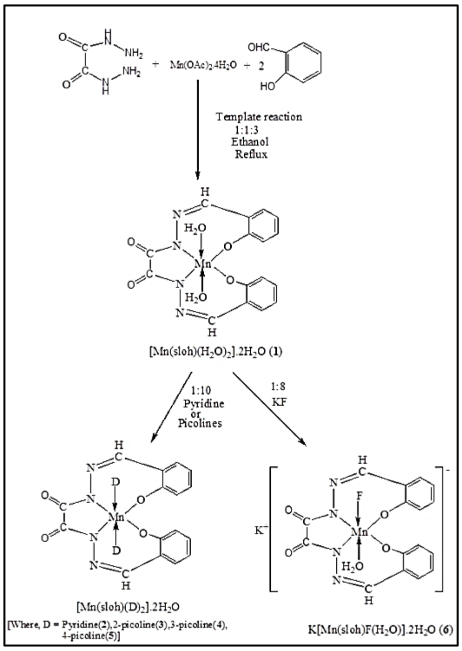
[1]Department of Chemistry, Bir Bikram Memorial College, Tripura University, Agartala, Tripura, India
[2]Department of Chemistry, North-Eastern Hill University, Shillong, Meghalaya, India

---

ABSTRACT

The mononuclear manganese(IV) complexes of the composition [Mn(sloh)(D)2].$2H_2O$(H4sloh= disalicylaldehyde oxaloyldihydrazone) (D= H_2O(1), py(2), 2-pic(3),3-pic(4), 4-pic(5)) and K[Mn(sloh)F(H_2O)]. $2H_2O$ have been synthesized in ethanol from manganese(II) acetate, oxaloyldihydrazine and salicylaldehyde directly by the template method and characterized by various physico-chemical and spectroscopic techniques. The stoichiometry of the complexes has been established based on elemental analyses, thermoanalytical, molecular weight and molar conductance data. The structural assessment of the complexes has been carried out on the basis of magnetic moment, electronic, IR and ESR spectral data. All of the complexes except complex 6 are nonelectrolytes. The µeff values suggest that in all of the complexes manganese is present in +4 oxidation state. The electronic spectra of the complexes are dominated by strong charge transfer bands. In all of the complexes, the dihydrazone coordinates to the manganese centre as a tetrabasic tetradentate ligand in keto form in the anti-cis-configuration.The complexes are suggested to have six-coordinate octahedral stereochemistry around the manganese centre.

GRAPHICAL ABSTRACT



Graphical abstract [Mn(sloh)(D)2] $2H_2O$, K[Mn(sloh)F(H_2O)] $2H_2O$

Keywords: Manganese (IV) complexes; Disalicylaldehydeoxaloyldihydrazone; Template method; Magnetic moment; Spectral studies

INTRODUCTION

Manganese plays an important role in our natural ecosystem. It is an essential cofactor of green plant photosynthesis in photosystem II for the oxidation of water to dioxygen [1]. In the PS II, the tetramanganese complex (the oxygen evolving complex, OEC) serves as an electron donor [2]. Another important role of manganese is as the active catalytic centre in mitochondrial and several bacterial superoxide dismutases [3]. It also occurs in some enzymes. Some multinuclear enzymes like arginase also require manganese to show their biological activity [4]. The coordination chemistry of manganese is dominated by stable manganese (II) and manganese (III). The chemistry of the manganese in higher oxidation states has not been as extensively investigated [5]. A few manganese (IV) complexes have been obtained with organic ligands [6] and some oxo-bridged dimanganese(IV) and dimanganese (III,IV) complexes [7] are known. Dihydrazones derived from the condensation of o-hydroxy aromatic aldehydes and ketones with acylhydrazines, aroylhydrazines and pyridoyl hydrazines are a class of potential polyfunctional ligands which contain amide, azomethine and phenol functions in their molecular skeleton [8-12]. These ligands can react with metal ions either in keto form or enol form to yield mononuclear and polynuclear complexes having discrete molecularity [8-12]. These complexes are of interest in studies related to homogeneous catalysis, activation of small molecules, multielectron transfer processes and redox catalysis [13]. It has been shown that oxaloyldihydrazine based ligands stabilise metals in higher oxidation states [14]. Disalicylaldehyde oxaloyldihydrazone is an example of these type of ligands. A survey of literature reveals that although some work on monometallic and heterobimetallic manganese (IV) and ruthenium (III) complexes of bis(2-hydroxy-1-naphthaldehyde)oxaloyl dihydrazone and crystal structure of binuclear manganese(IV)-salicylic acid complex have been reported [15-18], complexes of performed dihydrazone containing manganese in higher oxidation states have not been studied at all. In view of the above importance and the lack of work on complexes of performed dihydrazone with metals in higher oxidation states, It was of interest to synthesize and characterize manganese (IV) complexes of polyfunctional disalicylaldehyde oxaloydihydrazone (Figure 1). Hence the paper reports the result of such an investigation.

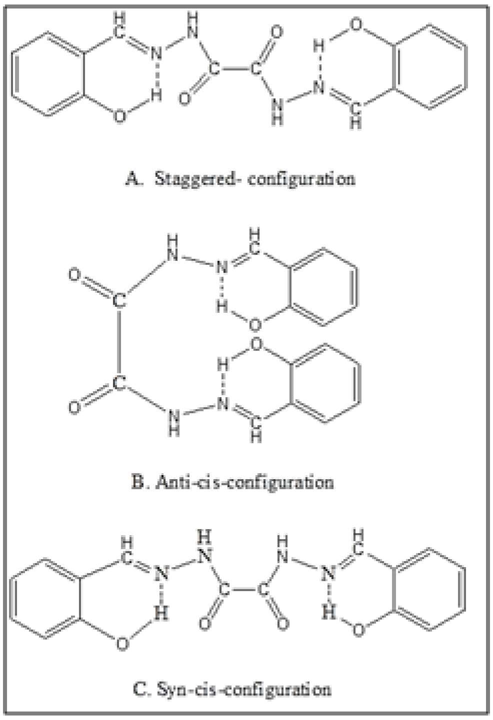


Figure 1: Disalicylaldehyde oxaloydihydrazone(H_4sloh)

EXPERIMENTAL SECTION

Materials and Methods

Manganese (II) acetate tetrahydrate, diethyloxalate, hydrazine hydrate, salicylaldehyde, pyridine, picolines, potassium fluoride were E-Merck grade reagents and used without purification. Oxaloyldihydrazine (ODH) was prepared by reacting diethyloxalate (10.30 g, 7.33 mmol) in ethanol (30 mL) with hydrazine hydrate (7.70 g, 15.4 mmol). The product was recrystallized from hot water. Manganese and potassium were determined by a standard literature method [19]. Carbon, hydrogen and nitrogen were determined by microanalysis. Water molecules were determined by heating the sample at ca. 110, 130 and 1800°C respectively while pyridine, 2-picoline, 3-picoline and 4-picoline molecules were determined by heating the sample at 2200°C and estimating the weight loss. Fluoride was determined as lead chlorofluoride [19]. The molar conductance of the complexes at 10^{-3} $molL^{-1}$ dilution in DMSO was measured using a Direct Reading 303Systronics Conductivity meter with a dip-type conductivity cell. The magnetic susceptibilities were determined by the Faraday method using Hg [Co(NCS)4] as the calibrant. IR spectra were recorded on a Perkin-Elmer-983 Spectrophotometer in the range 4000-180 cm^{-1} using KBr discs. Electronic spectra of the complexes were recorded on a Milton-Roy Spectronic-21 Spectrophotometer in CH3CN in the range 800-300 nm. The EPR spectra of the complexes in powdered form and in DMSO–CH3CN (30:70) solution at RT and LNT were recorded at X-band frequency on a Varian E–112 X/Q-band spectrometer using DPPH (g=2.0037) as an internal field marker.

Preparation of the Complexes

Preparation of [Mn(sloh)(H_2O)2].2H_2O(1):
Oxaloyldihydrazine(ODH) (1.00 g, 8.47 mmol) was dissolved in distilled water (40 mL). To this solution, Mn(OAc)2.4H_2O(2.00 g, 8.17 mmol) dissolved in ethanol (120 mL) was added slowly accompanied by gentle heating and stirring and the resulting solution was stirred for 30 min. This solution was then added dropwise to 2.7 ml of salicylaldehyde in ethanol (120 mL) at 700°C over a period of 30 min accompanied by vigorous stirring. This reaction mixture was then refluxed for 3 h. This precipitated a orangish brown compound which was filtered hot, washed with hot ethanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 82.5%.

Table 1: Complex, colour, decomposition point, molecular weight and analytical data

No	Complex (color)	D.P (°C)	Elemental analyses: Found (calcd)(%)					
			Mn	K	F	C	H	N
1	[Mn(sloh)(H_2O)2]2H_2O (Orangish brown)	>300	12.53	-	-	42.97	4.09	12.76
			-12.25			-42.76	-4.01	-4.01
2	[Mn(sloh)(py)2]	>300	9.85	-	-	54.47	4.14	15.01
	(Reddish brown)		-9.63			-54.64	-4.2	-14.71
3	[Mn(sloh)(2-pic)2] 2H_2O	>300	9.5	-	-	55.82	4.62	14.31
	(Brown)		-9.18			-56.09	-4.67	-14.02
4	[Mn(sloh)(3-pic)2] 2H_2O	>300	9.46	-	-	56.28	4.73	14.22
	(Brown)		-9.18			-56.09	-4.67	-14.02
5	[Mn(sloh)(4-pic)2] 2H_2O	>300	9.01	-	-	56.34	4.62	13.75
	(Brown)		-9.18			-56.09	-4.67	-14.02
6	K[Mn(sloh)F(H2O)]2H_2O	>300	11.52	8.14	3.85	39.56	3.23	11.18
	(Dark brown)		-11.25	-7.97	-3.88	-39.26	-3.27	-11.45

Preparation of [Mn(sloh)(D)2].2H_2O{Where D = pyridine(py)(2), 2-picoline(2-pic)(3), 3-picoline(3-pic)(4) and 4-picoline (4-pic)(5)}:
In order to prepare [Mn(sloh)(py)2].2H_2O(2), about 1.00 g (2.23 mmol) of [Mn(sloh)(H_2O)2].2H_2O(1) was suspended in ethanol(50 mL) with constant stirring to make a homogeneous suspension. To this suspension 1.79 mL (22.3 mmol) of pyridine was added dropwise over a period of 30 min accompanied by constant stirring. The mixture was then subjected to reflux for 3 h when a reddish brown compound precipitated, was filtered hot and washed with hot ethanol and dried over anhydrous $CaCl_2$. Yield: 80.3%. The complexes (3), (4) and (5) were also prepared by the above procedure using 2.10 mL of picolines instead of 1.79 mL of pyridine. Yield: 77-78%.

Preparation of K[Mn(sloh)F(H_2O)].2H_2O(6):
The complex[Mn(sloh)(H_2O)2].2H_2O(1) (1.00 g, 2.23 mmol) was suspended in methanol (30 mL) and stirred gently for 10-15 min.To this homogeneous suspension, KF solution (1.03 g, 17.84 mmol) in water (100 mL) was added slowly and stirred for about 20 min at 70-75°C. The reaction mixture was then refluxed for 6 h, which precipitated the darkbrown coloured complex. The complex so obtained was filtered in hot condition, washed with hot water, methanol and dried over anhydrous $CaCl_2$. Yield: 80%.

RESULTS AND DISCUSSION

The manganese (IV) complex 1 was synthesized by template method by reacting oxaloyldihydrazine, Mn(OAc)-2.4H_2O and salicylaldehyde in 1:1:3 molar ratio in ethanol under reflux. It appears that aerial oxygen probably acts as an oxidising agent in this reaction. Further, complexes 2-6 were prepared by reacting 1 with pyridine bases in 1:10 molar ratio in ethanol and with KF in 1:8 molar ratio in methanol under reflux. These complexes are orangish brown, reddish brown, brown, dark brown and air stable, decomposing above 300°C without melting. All the complexes are insoluble in water and common organic solvents such as methanol, ethanol, chloroform, carbon tetrachloride, ether, benzene etc. but soluble in highly coordinating solvents such as DMF and DMSO. Effort to crystallize the complexes either from a saturated solution or by diffusion into saturated solutions in DMSO and DMF in a closed system led to the precipitation of amorphous products, preventing analysis by X-ray crystallography. The complexes together with their colours, decomposition points, molecular weights and analytical data are presented in Table 1.

Thermal Studies

All of the complexes showed weight loss corresponding to expulsion of two water molecules in the temperature range 100‒120°C. Further, the complexes 1 and 6 showed loss of weight in the temperature range 160-180°C corresponding to two and one water molecules. The vapour evolved in these temperature range turned the anhydrous copper sulphate blue, confirming water. The loss of weight from 100°C to 120°C indicates lattice water and from 160°C to 180°C indicates coordinated water [20]. Complexes 2-5 showed weight loss in the temperature range 220-230°C corresponding to two pyridine, 2-picoline, 3-picoline and 4-picoline molecules respectively. The vapour evolved in this temperature range in 2 turned a solution of CHCl3 containing a drop of 5 molL^{-1} NaOH solution red, confirming that they originated from a pyridine base [21]. Further, the vapour evolved in 5 in this temperature range turned the cyanogen bromide solution green violet on treatment with phloroglucinol solution, suggesting its origin from 4-picoline molecule [21]. The expulsion of pyridine and 4-picoline molecules at such a high temperature indicates that they are coordinated to the metal centre.

Molar Conductance

The molar conductance values for the complexes 1-5 in DMSO at 10.3 mol L^{-1} dilution falls in the range 10.3 - 11.0 Ω^{-1} cm 2 mol^{-1} suggesting their nonelectrolytic nature in this solvent [22]. A value of 35.0 Ω^{-1} cm 2 mol^{-1} for complex 6consistent with electrolytes [22].

Magnetic Moment

All of the complexes have µB values in the range 3.90-4.10 BM. These values are consistent with the mononuclear manganese (IV) complexes adopting a d3 electronic configuration (S =3/2) [6,23].

Electronic Spectra

All of the complexes have been analysed by electronic spectroscopy, the important spectral bands are listed in Table 2. The electronic spectrum of the ligand H4sloh shows two bands at 303 and 340 nm which arise from intraligand $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition [8,9]. In addition to the intraligand bands, all of the manganese (IV) complexes show a band in the region 610-635 nm. For octahedral manganese (IV) complexes, three spin allowed transitions are expected. The absorption band found in the region 610-635 nm cannot be assigned to the spin-allowed d‒ d transitions because their molar extinction coefficients are very large(εmax: 2130-2710 dm^{3}mol^{-1}cm^{-1}) and their frequencies are lower than expected from the crystal field splitting [24]. Cooper et al. [25] reported an intense band at ~585 nm with molar extinction coefficient equal to 4500 dm^{3}mol^{-1}cm^{-1} in manganese(IV) complexes derived from catecholate ligands. They assigned this band to a catechol →Mn(IV) LMCT band on the basis of its high molar extinction coefficient. Okawa et al. [26] reported a band at 650nm with molar extinction coefficient in the region 2090-3020 dm^3 mol^{-1} cm^{-1} in manganese (IV) complexes derived from 2-substituted(salicylideneamino)phenol. They assigned this band to charge transfer transition from phenolic oxygen to manganese (IV) ion. The absorption spectra of the mononuclear manganese (IV) complexes 1-6 are in fair agreement with those reported by Okawa et al. [26,27]. Hence these bands may be assigned to charge transfer transition from the phenolate oxygen(s) to the d‒orbital of the manganese (IV) ion.

Table 2: Electronic spectral bands, magnetic moment,molar conductance and EPR spectral data of manganese (IV) complexes

Dihydrazone/ Complex	**ν(OH)+ ν(NH)**	**ν(C=O)**	**ν(C=N)**	**Amide(II) + ν(c-o) (phenolic)**	**ν(C-O)**	**ν(N-N)**	**ν(M-O)**	**Other bands**
H4sloh	3278(s) 3204(s)	1667(s)	1627(s) 1603(s)	1534(s)	1262(s)	1035(w)	-	-
1	3410(s)	1678(s)	1628(s) 1605(s)	1540(s)	1278(s)	1045(w)	574(w)	-
2	3419(s)	1679(s)	1627(s) 1604(s)	1539(s)	1277(s)	1046(w)	572(w)	1070(w)
3	3421(s)	1677(s)	1630(s) 1603(s)	1538(s)	1278(s)	1043(w)	573(w)	1056(w)
4	3420(s)	1679(s)	1627(s) 1603(s)	1541(s)	1276(s)	1042(w)	572(w)	1052(w)
5	3419(s)	1678(s)	1629(s) 1604(s)	1540(s)	1277(s)	1047(w)	574(w)	1054(w)
6	3415(s)	1679(s)	1628(s) 1604(s)	1538(s)	1277(s)	1044(w)	572(w)	513(w)

EPR Spectra

All of the complexes have been characterized by EPR spectroscopy in the polycrystalline phase as well as CH3CN-DMSO glass (LNT), the related parameters are listed in Table 2. All of the complexes exhibit similar spectral features. The complexes show featureless spectra at RT. In the polycrystalline phase at LNT, two resonances are observed, a strong one near $g\approx2.0$ and a weak one near $g\approx4.9$. In the magnetically dilute glassy state, the 55 Mn hyperfine structure is well resolved for the resonance near g=2.0. Between every adjacent pair of the six hyperfine lines of the g=2.0 resonances, there is a pair of relatively weak forbidden(ΔMs= ±1, ΔMI= ±1) transitions. Interestingly, the 55Mn hyperfine coupling constant for the g=2.0 signal is equal to 78G which is closer to the values observed for manganese (IV) [28,29], than for Mn(II). In a crystal field of strict octahedral symmetry, a d3 ion has the 4A2gground state leading to an isotropic resonance at g ca 2.0. Distortion and spin-orbit coupling split the ground state quartet into two Kramer’s doublets separated by 2(D2+E2) where D and E are respectively axial and rhombic zero field splitting parameters. The complexity of an EPR spectrum of a d3 ion in an axial field (E/D=0) is dependent on the magnitude of the zero field splitting parameters [28]. The two limiting cases are when the value of the axial zero field splitting parameter 2D is either much larger or much smaller than hν (0.31 cm^{-1} at X-band frequencies). In the first case, the feature at low field is predicted to be strong while the $g\approx2$ component is weak. When D is small, the $g\approx2$ component should dominate with relatively weak signals in the low field region. The spectral features observed in the present study(strong $g\approx2.0$ and weak $g\approx4.0$ resonances) are characteristic of small axial distortion[6], 2D << hν.

IR Spectra

Some structurally significant IR bands for free dihydrazone H4sloh and complexes are listed in Table 3. The free oxaloyldihydrazine(ODH) shows relatively strong bands at 3292, 1651 and 1588 cm^{-1}. The band at 3292 cm^{-1} is characteristic of νNH while the band at 1651 and 1588 cm^{-1} are characteristic of >C=O and bending of NH2.The essential features of these bands suggest that >C=O and $-NH_2$ of ODH are involved in strong intramolecular H-bonding. The IR spectral features of complexes show entirely different from that of ODH yet similar to that of uncoordinated dihydrazone, H4sloh. The complexes show a strong band at ca 1679 cm^{-1} is similar to the band at 1651 cm^{-1} in ODH and at 1667 cm^{-1} in the preformed dihydrazone H4sloh. Hence, this band is assigned to stretching vibration of >C=O. The position of this band is higher than ν(C=O) in ODH and dihydrazone. This rules out the possibility of coordination of >C=O group to the metal centre and suggests the absence of intramolecular H-bonding involving >C=O as in free ODH molecule.

Table 3: Infrared spectral data for the free dihydrazone and its mononuclear manganese (IV) complexes

Complex	Electronic spectral band λ_{max} (nm)(ε_{max}) ($dm^3mol^{-1}cm^{-1}$)	Magneatic moment μ_{eff} (BM)	Molar conductance Λ_M ($\Omega^{-1}cm^2mol^{-1}$)	EPR spetral data at LNT		
				State	g-value	A-value
1	338(8450), 420(5755) 624(2510)	4.1	10.8	Solid CH3CN-DMSO	2.015, 4.933 2.007, 4.818	78G
2	340(8658), 415(5940) 615(2270)	3.93	11	Solid CH3CN-DMSO	2.027, 4.897 2.015, 4.791	78G
3	339(8650), 410(5995) 620(2360)	3.96	10.3	Solid CH3CN-DMSO	2.017, 4.834 2.006, 4.920	78G
4	335(8635), 412(5970) 610(2130)	3.9	10.5	Solid CH3CN-DMSO	2.035, 4.915 2.027, 4.897	78G
5	338(8435), 415(5925) 620(2420)	3.93	10.4	Solid CH3CN-DMSO	2.018, 4.841 2.026, 4.936	78G
6	335(8670), 430(5870) 635(2710)	3.98	35	Solid CH3CN-DMSO	2.001, 4.010 2.002, 4.815	78G

Further, the complexes show two strong bands of almost equal intensity in the 1627-1630 cm^{-1} and 1603-1605 cm^{-1} regions which are attributed to the stretching vibration of the >C=N−group [9]. The appearance of these bands indicates condensation of the –NH2 group of oxaloyldihydrazine with the >C=O group of salicylaldehyde leading to the formation of >C=N−linkages. Such features in the IR spectra of these complexes indicate the generation of disalicylaldehyde oxaloyldihydrazone. The appearance of the ν(C=N) stretching frequencies as a couple of bands in these complexes indicative of coordination of dihydrazone to the metal centre in the anti-cis-configuration [30,31]. The free dihydrazone shows two strong bands at 3278 and 3204 cm^{-1} due to ν(OH)(Phenolic) and ν(NH) stretching vibrations. The complexes do not show any band in these regions. The absence of band due to ν(OH) in all of the complexes indicates deprotonation and involvement in bonding to the metal centre. The absence of the ν(NH) band in the complexes in combination with the presence of a ν(C=O) band suggests coordination of the dihydrazone through the deprotonated secondary nitrogen atom to the metal centre [32,33]. A weak band observed at 1035 cm^{-1} due to ν(N-N) in the free dihydrazone shifts to higher frequency by 7-12 cm^{-1} in the complexes indicating coordination of the hydrazinic nitrogen atom to the metal centre. The magnitude of this shift suggests that only one hydrazinic nitrogen atom is involved in bonding [31]. In all of the complexes a very strong band appears in the region 1538-1541 cm^{-1}. This band is similar in nature to ones observed in many complexes derived from phenol-containing ligands [34,35]. Hence, this bands is assigned to ν(C−O)(phenolic). The position of the band is consistent with the occurrence of bonding through phenolate oxygen atoms. This is also confirmed by the occurrence of weak nonligand bands at 572-574 cm-1assigned to ν(M−O)(phenolate) [36,37]. The strong band at ca 1277 cm^{-1} is assigned to ν(C−O)(phenolic) in all of the complexes as against the band at 1262 cm^{-1} in free dihydrazone. This also indicates bonding of phenolic oxygen to the metal centre. All of the complexes show a strong bond in the region 3410-3421 cm^{-1} might be due to ν(OH) of either lattice or coordinated water or due to ν(OH) of moisture absorbed by KBr during pellet preparation. In order to decide whether bands in this region arise due to water or due to moisture absorbed by KBr pellets, the compounds were subjected to thermal analysis. The thermo-analytical data suggest the presence of band at 3410-3421 cm^{-1} due to the presence of lattice as well as coordinated water in complexes 1 and 6 whereas in the rest of the complexes the band in this region arises due to lattice water. The appearance of a very weak band at 1052-1070 cm^{-1} confirms the presence of a coordinated pyridine, or substituted pyridine [10] in the complexes 2-5. The complex (6) shows an additional weak band at 513 cm^{-1} which is not present in free dihydrazone and other complexes. This band is assigned to ν(M−F) [38-40].

CONCLUSION

A mononuclear manganese (IV) complex $[Mn(sloh)(H_2O)2].2H_2O$ has been synthesized by template method from the reaction of oxaloyldihydrazine, $Mn(OAc)2.4H_2O$ and salicylaldehyde in 1:1:3 molar ratio in ethanol. Further, using this complex as a precurson, five mononuclear manganese (IV) complexes have been synthesized and characterized them on the basis of data obtained from physico-chemical and spectroscopic studies. In all of the complexes, the dihydrazone coordinates to the metal centre through deprotonated secondary nitrogen atoms and phenolate oxygen atoms as a tetradentate NNOO donor. The >C=O groups remain uncoordinated. Water, pyridine, substituted pyridine and fluoride ion are coordinated to the metal centre. In all of the complexes, the dihydrazone ligand is coordinated to the metal centre in keto form in the anti-cis-configuration. The manganese centre has six coordinate octahedral geometry in all of the complexes. The tentative structures for the complexes are shown in Figures 2 and 3.

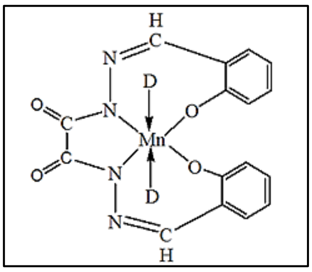


Figure 2: Sugessted structure of [Mn(sloh)(D)$_2$].2H$_2$O [where, D=H$_2$O(1), pyridine(2), 2-picoline(3), 3-picoline(4), 3-picoline(4)]

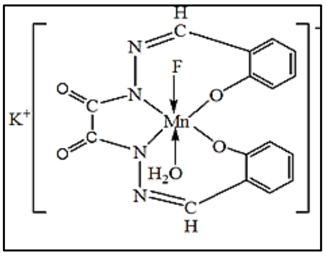


Figure 3: Sugessted structure of K [Mn(sloh)F(H$_2$O)2].2H$_2$O(6)

ACKNOWLEDGMENT

Authors are thankful to the Head, RSIC, NEHU, Shilong, for providing IR and electronic spectra and magnetic moment data, the Head, RSIC,IIT Madras for EPR spectral data, the Head RSIC,CDRI, Lucknow for C,H and N analysis. One of the authors (S. Adhikari) is thankful to the University Grant Commission, Govt of India for financial assistance in the form of a MRP.

REFERENCES

[1] MW Lynch; DN Hendrickson; BJ Fitzgerald; CG Pierpant. *J Am Chem Soc*. **1984**, 106, 2041.
[2] S Mukhopadhyay; HJ Mok; RJ Staples; WH Armstrong. *J Am Chem Soc.* **2004**, 126, 9202.
[3] ML Luduring, KA Puttrudge, WC Stallings. In Manganese in Metabolism and Enzyme Functions, 1st Edition, **1986**, 21, 405.
[4] GC Dismukes. *Chem Rev*. **1986**, 96, 2909.
[5] MJ Baldwin; LT Stemmler; PJ Riggs Gelasco; JE Penner Hahn; VL Pecoraro. *J Am Chem Soc*. **1994**, 116, 11349.
[6] SK Chanra; A Chakraborty. *Inorg Chem*. **1992**, 31, 760.
[7] PA Goodson; LJ Glerup; DJ Hodgson; K Michelsen; E. Pedersen. *Inorg Chem.* **1990**, 29, 503.
[8] RL Dutta; MM Hossain. *J Sci Ind Res*. **1985**, 44, 635.
[9] A Kumar; R Borthakur; A Koch; OB Chanu; S Choudhury. *J Mol Structure.* **2011**, 999, 89.
[10] RA Lal; S Adhikari; A Pal; AN Siva; A Kumar. *J Chem Res.* **2001**, 4, 749.
[11] M Husain; SS Bhattacharjee; KB Singh; RA Lal. *Polyhedron.* **1997**, 10, 779.
[12] A Kumar; RA Lal; OB Chanu; R Borthakur; A Koch; A Lemtur; S Adhikari; S Choudhary. *J Coord Chem.* **2011**, 64, 1729.
[13] S Gopinathan; SS Tavale; VG Puranik; MP Degaonkar. *Bull Chem Soc*. **1994**, 41, 1797.
[14] B Ji; Q Du; K Ding; Y Li; Z Zhou. *Polyhedron*. **1996**, 15, 403.
[15] PA Vigato; J Jamburini; DE Fenton. *Coord Chem Rev*. **1990**, 25, 106.
[16] W Levason; MD Spicer. *Coord Chem Rev*. **1987**, 76, 45.
[17] RA Lal; S Adhikari; A Kumar; J Chakraborty; S Bhaumik. *Synth React Inorg Met-Org Chem*. **2002**, 32, 81.
[18] MK Singh; NK Kar; RA Lal. *J Coord Chem*. **2008**, 61, 3158-3171.
[19] NK Kar; MK Singh; RA Lal. *Arab J Chem*. **2012**, 5, 67-72.
[20] RA Lal; S Bhaumik; A Lemtur; MK Singh; D Basumatari; S Choudhary; A Dey; A Kumar. *Inorg Chem. Acta*. **2006**, 359, 3105-3110.
[21] AI Vogel. A Text Book Of Quantitative Inorganic Analysis, Including Elementary Instrumentation Analysis, 5th Edition, ELBS and Longman, London, **1989**.
[22] RA Lal; AN Siva; S Adhikari; MK Singh; US Yadav. *Synth React Inorg Met-Org Chem*. **1996**, 26, 321.

[23] F Feigl, V Anger, RE Oesper. Spot Tests in Organic Analysis. Elsevier Publishing Company, **1996**, 173.
[24] WJ Geary. *Coord Chem Rev*. **1971**, 7, 81.
[25] H Adams; DE Fenton; G Minardi; AM Pistudi; C Solinas. *Inorg Chem Commun*. **2000**, 3, 24.
[26] ABP Lever. Inorganic Electronic Spectroscopy, 2nd Edition. Elsevier, New York, **1984**, 430.
[27] JR Hartman; BM Foxman; SR Cooper. *Inorg Chem*. **1984**, 23,1381.
[28] H Okawa, M Nakamura, S Kida, *Bull Chem Soc*. **1982**, 55, 466.
[29] BP McGarvey. In Transition Metal Chemistry, A series of Advances RL. Carlin Eds, Marcel Dekker, New York, **1966**, 3, 89.
[30] PG Rasmussen; KM Beem; EJES Hornyak. *J Chem Phys*. **1969**, 50, 3647.
[31] E Pedersen; H Toftlund. *Inorg Chem*. **1974**, 13, 1603.
[32] S Pal; P Ghosh; A Chakraborty. *Inorg Chem*. **1985**, 24, 3704.
[33] RA Lal; S Adhikari; A Kumar; J Chakraborty. *Synth React Inorg Met-Org Chem*. **2001**, 65.
[34] RA Lal; A Kumar. *Indian J Chem*. **1999**, 38A, 839.
[35] AD Ahmad; PK Mandal; NR Choudhary. *J Inorg Nucl Chem*. **1966**, 28, 2951.
[36] NK Dutta; A Sengupta. *J Inorg Nucl Chem*. **1971**, 31, 4185.
[37] R Gup; B Kirkan. *Spectrochim Acta*. **2005**, 62, 1188.
[38] S Purohit; AP Koley; LS Prasad; PT Manohoran; S Ghosh. *Inorg Chem*. **1989**, 28, 3935.
[39] GC Percy. *Spectrochim Acta*. **1976**, 32, 1287.
[40] K Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds. **1986**, 4th Edition, P 153, John Wiley and Sons, New York.