



Synthesis and spectral investigations of Mn(II) complexes of pentadentate bis(thiosemicarbazones)

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ABSTRACT

Five Mn(II) complexes of bis(thiosemicarbazones) which are represented as [Mn(H₂Ac4Ph)Cl₂] (1), [Mn(Ac4Ph)H₂O] (2), [Mn(H₂Ac4Cy)Cl₂].H₂O (3), [Mn(H₂Ac4Et)Cl₂].3H₂O (4) and [Mn(H₂Ac4Et)(OAc)₂].3H₂O (5) have been synthesized and characterized by elemental analyses, electronic, infrared and EPR spectral techniques. In all the complexes except [Mn(Ac4Ph)H₂O], the ligands act as pentadentate neutral molecules and coordinate to Mn(II) ion through two thione sulfur atoms, two azomethine nitrogens and the pyridine nitrogen, suggesting a heptacoordination. While in compound [Mn(Ac4Ph)H₂O], the dianionic ligand is coordinated to the metal suggesting six coordination in this case. Magnetic studies indicate the high spin state of Mn(II). Conductivity measurements reveal their non-electrolyte nature. EPR studies indicate five g values for [Mn(Ac4Ph)H₂O] showing zero field splitting.

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1. Introduction

The synthesis and study of coordination complexes with unusual geometry and coordination number is a challenging task for the practical chemist. The most important factor in this objective is probably the design of ligands with an appropriate structural backbone that can coerce the metal ion into the desired coordination geometry. Though tridentate ligands with mixed NS donor points at strategic positions of the donor-framework are common [1,2], such pentadentate ligands are seldom encountered in coordination chemistry. The chelating properties of 2,6-diacetylpyridine bis(thiosemicarbazone), have been investigated and several coordination modes have been found [3–6]. There are reports on heptacoordinated bis(thiosemicarbazones) of 2,6-diacetylpyridine [7]. This type of coordination is commonly found in metals like Sn(IV) [8], Mn(II) [9] and indium(III) [10]. As previous research [11] show, these ligands tend to form pentagonal bipyramidal complexes in which the ligand acts as a pentacoordinated chelate and the two arms (thiosemicarbazide groups) of the ligand have remained protonated [12].

Transition metal complexes of bis(thiosemicarbazone) ligands have been investigated as metallodrugs for a number of years. It has been reported that α -diketone and α -ketoaldehyde bis(thiosemicarbazones) and their metal complexes show anti-

tumor activity [13,14]. Spectral and biological studies have been carried out on metal complexes of 2,6-diacetylpyridine bis(*N*4-substituted thiosemicarbazones)[15]. Manganese coordination chemistry with a diverse range of ligands has much relevance in biological systems with a number of model manganese complexes. Manganese coordination compounds are also of growing importance as homogeneous catalysts in oxidation reactions [16,17]. In such studies manganese complexes in different oxidation states were obtained and their magnetic and spectral properties were studied in depth. The absence of ligand field stabilization energy for high spin Mn(II) complexes leads to the possibility to obtain various coordination geometries and a lower stability of Mn(II) complexes compared with those of other divalent 3d metals.

In the present article, synthesis and characterization of some 2,6-diacetylpyridine bis(*N*4-substitutedthiosemicarbazones) and their Mn(II) complexes are investigated with the help of physico-chemical techniques.

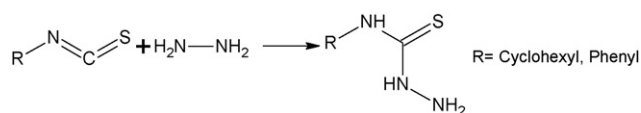
2. Experimental

2.1. Materials

2,6-Diacetylpyridine (Aldrich), hydrazine hydrate, *N*4-phenyl isothiocyanate, *N*4-cyclohexyl isothiocyanate, *N*4-ethylthiosemicarbazide, manganese(II) chloride tetrahydrate and manganese(II) acetate tetrahydrate were used as supplied for the preparation of complexes. Solvents used were methanol, ethanol, dimethylformamide and chloroform.

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Scheme 1.

2.2. Synthesis of bis(thiosemicarbazones)

2,6-Diacetylpyridine bis(*N*4-phenylthiosemicarbazone) (H_2Ac4Ph) and 2,6-diacetylpyridine bis(*N*4-cyclohexylthiosemicarbazone) (H_2Ac4Cy)

Step 1. Preparation of *N*4-phenylthiosemicarbazide/*N*4-cyclohexylthiosemicarbazide

The thiosemicarbazides were synthesized by stirring equimolar amounts of the corresponding isothiocyanate in ethanol and hydrazine hydrate in methanol for half an hour. The product (*N*4-phenylthiosemicarbazide/*N*4-cyclohexylthiosemicarbazide) formed was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10} (Scheme 1).

Step 2. Synthesis of thiosemicarbazone (H_2Ac4Ph)/(H_2Ac4Cy)/(H_2Ac4Et)

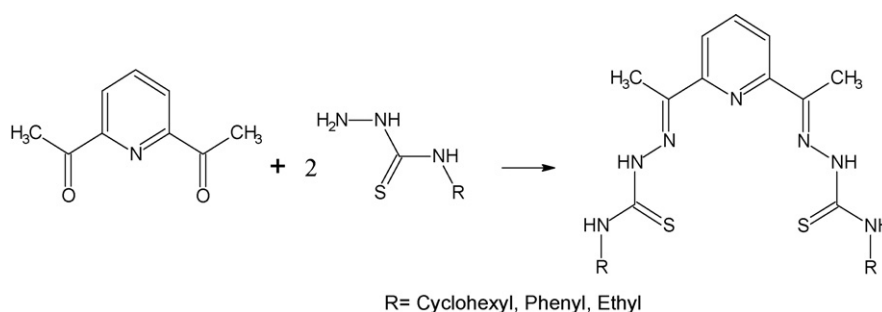
A hot solution of the thiosemicarbazide in 25 ml of ethanol and 2,6-diacetylpyridine in 25 ml of ethanol were mixed in 2:1 ratio with constant stirring. The above mixture was slowly refluxed for 5 h. After cooling, the compounds obtained as pale yellow solids, were filtered, washed with ethanol and dried *in vacuo* over P_4O_{10} (Scheme 2).

Elemental Anal. Found (Calcd.) (%): H_2Ac4Ph : C, 59.44 (59.84); H, 4.75 (5.02); N, 21.87 (21.24). H_2Ac4Cy : C, 58.70 (58.32); H, 7.75 (7.45); N, 20.55 (20.70). H_2Ac4Et : C, 49.05 (49.29); H, 6.93 (6.34); N, 26.64 (26.82).

2.3. Synthesis of complexes

$[Mn(H_2Ac4Ph)Cl_2]$ (**1**) and $[Mn(Ac4Ph)H_2O]$ (**2**) were prepared by refluxing 1 mmol each of $MnCl_2 \cdot 4H_2O/Mn(OAc)_2 \cdot 4H_2O$ in methanol and H_2Ac4Ph in DMF for 4 h. $[Mn(H_2Ac4Cy)Cl_2] \cdot H_2O$ (**3**) was prepared by refluxing 1 mmol each of methanolic solution of $MnCl_2 \cdot 4H_2O$ and H_2Ac4Cy in chloroform. The complexes $[Mn(H_2Ac4Et)Cl_2] \cdot 3H_2O$ (**4**) and $[Mn(H_2Ac4Et)(OAc)_2] \cdot 3H_2O$ (**5**) were prepared by refluxing 1 mmol of $MnCl_2 \cdot 4H_2O/Mn(OAc)_2 \cdot 4H_2O$ in methanol and 1 mmol of H_2Ac4Et in chloroform for 4 h. The compounds formed were filtered, washed with methanol and ether and dried *in vacuo* over P_4O_{10} .

Elemental Anal. Found (Calcd.) (%): $[Mn(H_2Ac4Ph)Cl_2]$ (**1**): C, 46.87 (47.02); H, 4.08 (3.95); N, 16.61 (16.69). $[Mn(Ac4Ph)H_2O]$ (**2**): C, 52.94 (52.77); H, 4.17 (4.24); N, 18.84 (18.73). $[Mn(H_2Ac4Cy)Cl_2] \cdot H_2O$ (**3**): C, 45.39 (44.73); H, 5.81 (6.04);



Scheme 2.

Table 1

Colors, magnetic susceptibilities and molar conductivities of the Mn(II) complexes.

Compound	Color	μ (B.M.)	χ_{M}
$[Mn(H_2Ac4Ph)Cl_2]$ (1)	pale yellow	5.91	33
$[Mn(Ac4Ph)H_2O]$ (2)	yellow	5.83	29
$[Mn(H_2Ac4Cy)Cl_2] \cdot H_2O$ (3)	pale yellow	5.84	14
$[Mn(H_2Ac4Et)Cl_2] \cdot 3H_2O$ (4)	yellow	5.78	10
$[Mn(H_2Ac4Et)(OAc)_2] \cdot 3H_2O$ (5)	yellow	6.08	20

^a Molar conductivity, 10^{-3} M DMF at 298 K.

N, 15.99 (15.88). $[Mn(H_2Ac4Et)Cl_2] \cdot 3H_2O$ (**4**): C, 33.54 (33.03); H, 5.59 (5.36); N, 18.21 (17.98). $[Mn(H_2Ac4Et)(OAc)_2] \cdot 3H_2O$ (**5**): C, 39.07 (38.51); H, 6.14 (5.95); N, 17.03 (16.55).

2.4. Physical measurements

Elemental analyses of ligands and the complexes were done on a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT/IR-4100 type Fourier Transform Infrared Spectrometer using KBr pellets in the range $4000-400\text{ cm}^{-1}$. The far IR spectra were recorded using polyethylene pellets in the $500-100\text{ cm}^{-1}$ region on a Nicolet Magna 550 FTIR instrument at the SAIF, Indian Institute of Technology, Bombay. Electronic spectra were recorded on a Cary 5000 version 1.09 UV-Vis-NIR spectrophotometer from solutions in DMF. The magnetic susceptibility measurements were done in the polycrystalline state at room temperature on a Vibrating Sample Magnetometer at the Indian Institute of Technology, Roorkee, India. EPR spectra of complexes in solid state at 298 K and in frozen DMF at 77 K were recorded on a Varian E-112 spectrometer at X-band, using TCNE as a marker with 100 kHz modulation frequency and 9.1 GHz microwave frequency at SAIF, IIT Bombay, India. The molar conductivities of the complexes in dimethylformamide solutions (10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

3. Results and discussion

Condensation reaction of 2,6-diacetylpyridine and *N*4-substituted thiosemicarbazides in a molar ratio of 1:2 resulted in ligand systems 2,6-diacetylpyridine bis(*N*4-substitutedthiosemicarbazones). All the five Mn(II) complexes were prepared by the reaction of corresponding ligands with metal salts in 1:1 ratio. Unfortunately, attempts to grow crystals for structural studies of these metal complexes have failed to date. While the present work was in progress, a dianionic Mn(II) complex of H_2Ac4Et was reported [18]. Colors, molar conductivities and magnetic susceptibilities are listed in Table 1. Conductivity measurements were done in 10^{-3} M DMF solutions and these values, although indicate extensive dissociation of these complexes in DMF, are much lower than that observed for 1:1 electrolytes in this solvent. They can, therefore, be considered

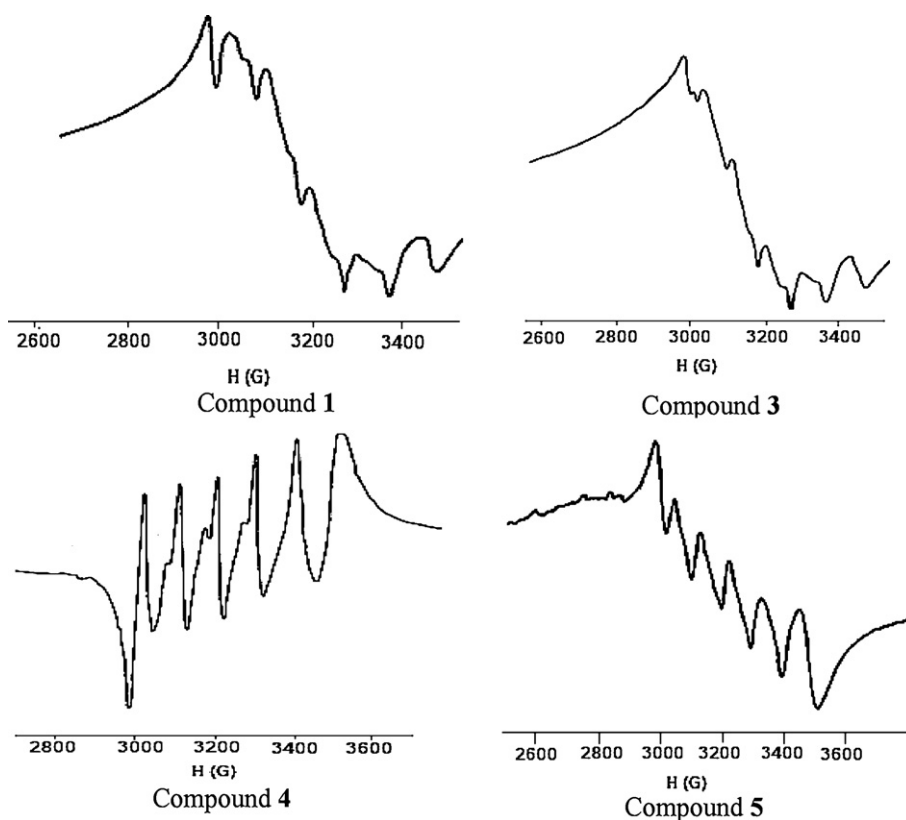


Fig. 1. EPR spectra of Mn(II) compounds in DMF at 77 K.

Table 2

Selected IR bands (cm^{-1}) with tentative assignments of manganese(II) complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu/\delta(\text{C}=\text{S})$	$\nu(\text{Mn}-\text{N})$	$\nu(\text{N}-\text{N})$	py(ip)
$\text{H}_2\text{Ac4Ph}$	1597	1322,808	–	1028	628
$[\text{Mn}(\text{H}_2\text{Ac4Ph})\text{Cl}_2]$ (1)	1562	1320,802	486	1047	663
$[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$ (2)	1560	1205,710	434	1095	676
$\text{H}_2\text{Ac4Cy}$	1596	1307,857	–	1013	601
$[\text{Mn}(\text{H}_2\text{Ac4Cy})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (3)	1555	1208,802	460	1068	680
$\text{H}_2\text{Ac4Et}$	1541	1305,857	–	1050	639
$[\text{Mn}(\text{H}_2\text{Ac4Et})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (4)	1527	1289,726	427	1068	652
$[\text{Mn}(\text{H}_2\text{Ac4Et})(\text{OAc})_2]\cdot 3\text{H}_2\text{O}$ (5)	1526	1293,806	489	1086	663

as non-electrolytes in this solvent. Because of the additional stability of the half filled d shell, Mn(II) generally forms high spin complexes with an orbitally degenerate ${}^6\text{S}$ ground state term and the spin only magnetic moment of 5.92 B.M. The magnetic moments of the present complexes indicate them to be of high spin type.

Table 3

Electronic spectral assignments (nm) of manganese(II) complexes.

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	LMCT
$\text{H}_2\text{Ac4Ph}$	310	346	–
$[\text{Mn}(\text{H}_2\text{Ac4Ph})\text{Cl}_2]$ (1)	310	353	456
$[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$ (2)	311	351	452
$\text{H}_2\text{Ac4Cy}$	308	342	–
$[\text{Mn}(\text{H}_2\text{Ac4Cy})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (3)	310	345	438
$\text{H}_2\text{Ac4Et}$	310	340	–
$[\text{Mn}(\text{H}_2\text{Ac4Et})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (4)	311	343	444
$[\text{Mn}(\text{H}_2\text{Ac4Et})(\text{OAc})_2]\cdot 3\text{H}_2\text{O}$ (5)	310	346	455

* Antibonding orbital.

3.1. Infrared and electronic spectra

The bands assigned in the spectra of ligands and complexes, because of coordination are illustrated in Table 2. The IR spectra of the free ligands show bands in the $3300\text{--}3000\text{ cm}^{-1}$ region, attributable to stretching modes of two NH groups each in the two arms of the ligand. A considerable downfield shift in compound 2 can be due to shifting of NH protons resulting in enolisation followed by deprotonation. The pyridine nitrogen coordination is evidenced by the positive shift of pyridine ring deformation mode in all the complexes. The $\nu(\text{C}=\text{N})$ bands of ligands are found to be shifted to lower wavenumbers in the spectra of all complexes suggesting the coordination of the azomethine nitrogen to the metal [19]. Due to this the $\nu(\text{N}-\text{N})$ band of the spectra enjoy a shift to higher frequencies. The presence of a new band in the range $450\text{--}470\text{ cm}^{-1}$, assignable to $\nu(\text{Mn}-\text{Nazo})$ confirm coordination of azomethine nitrogen in these complexes [1].

The stretching and bending vibrations of the C=S group of the ligands are shown in the $1305\text{--}1322$ and $807\text{--}857\text{ cm}^{-1}$ regions. If coordinated in the neutral form, there is no considerable negative shift in the case of $\nu(\text{C}=\text{S})$ band. But in compound 2 there is considerable shift in $\nu/\delta(\text{C}=\text{S})$ bands and that may be due to the formation of strong metal-sulfur bonds [20]. Bands observed at $ca\ 247\text{ cm}^{-1}$ in the far IR spectra have been assigned to terminal $\nu(\text{Mn}-\text{Cl})$ bands in compounds 1, 3 and 4. Bands at 1526 and 1484 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of the acetate group, consistent with the presence of a monodentate acetate group in the complex 5 [21]. For a d^5 complex, transitions from the ${}^6A_{1g}$ ground state are doubly forbidden and hence electronic transition intensities are found to be very low. In the present compounds, d-d bands could not be identified due to their low intensity. However the broad band at $ca. 450\text{ nm}$ in the complexes may be probably due to charge transfer bands. The electronic spectral assignments are summarized in Table 3

Table 4
EPR spectral data for complexes in polycrystalline state at 298 K and DMF solution at 77 K.

Compound	g values		^a A in G
	Polycrystalline state (298 K).	DMF solution (77 K)	
[Mn(H ₂ Ac4Ph)Cl ₂] (1)	2.027	2.012	92
[Mn(Ac4Ph)H ₂ O] (2)	2.005	5.69, 3.22, 2.65, 2.23, 1.82	
[Mn(H ₂ Ac4Cy)Cl ₂].H ₂ O (3)	2.050	1.996	96
[Mn(H ₂ Ac4Et)Cl ₂].3H ₂ O (4)	2.040	1.992	96
[Mn(H ₂ Ac4Et)(OAc) ₂].3H ₂ O(5)	2.070	2.021	92

^a Expressed in units of cm⁻¹ multiplied by a factor of 10⁻⁴.

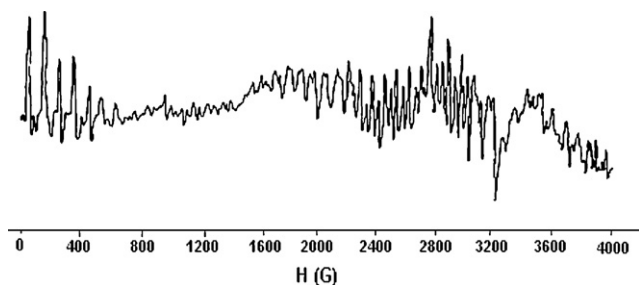


Fig. 2. EPR spectrum of compound [Mn(Ac4Ph)H₂O] (2) in DMF at 77 K.

3.2. EPR spectra

EPR spectra of all Mn(II) complexes were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K. The values are given in Table 4. All compounds at 298 K, in polycrystalline state exhibited a broad signal with a g value at ca 2.027 with no hyperfine splittings. Broadening of the signal is due to dipole–dipole interactions and random orientation of the Mn(II) ions [21].

In the spectra of DMF solutions at 77 K of complexes **1**, **3**, **4** and **5** a hyperfine sextet with g_{iso} values 2.012, 1.996, 1.992, 2.021 and A values 92, 96, 96, 92 were obtained (Fig. 1). A single transition at $g_{\text{eff}} \approx 2$ observed for weak ligand like this is found to be split into six hyperfine lines by the ⁵⁵Mn nuclear spin ($I = 5/2$). Due to negligible zero field splitting D , all of the $\Delta M_s = \pm 1$ transitions are degenerate. The low intensity forbidden lines in between two hyperfine lines are due to quadrupolar interactions.

The solution EPR spectrum of compound **2** in DMF at 77 K exhibiting a spectrum with five g values of 5.69, 3.22, 2.65, 2.23 and 1.82 (Fig. 2). For a small but finite value of D the degeneracy is removed and the spectrum exhibits a 5-fold fine structure each with six hyperfine splitting. Hence we get a spectrum with five sets of lines corresponding to five transitions with different energy, appear at different positions, each with six hyperfine splittings.

The observed g values are very close to free electron spin value suggestive of the absence of spin orbit coupling in the ground state for complexes **1**, **3**, **4** and **5**. The A_{iso} values are same as the values reported earlier for Mn(II) complexes. The complexes containing neutral ligands gave EPR spectra with single g value with hyperfine

splitting. However complexes containing anionic ligand showed zero-field splitting also.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.11.022.

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