



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

Suja Krishnan, K. Laly, M.R. Prathapachandra Kurup*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682022, Kerala, India

ARTICLE INFO

Article history:

Received 28 March 2009

Received in revised form

10 November 2009

Accepted 10 November 2009

Keywords:

2,6-Diacetylpyridine

Bis(thiosemicarbazones)

Manganese(II) complexes

EPR studies

ABSTRACT

Five Mn(II) complexes of bis(thiosemicarbazones) which are represented as $[\text{Mn}(\text{H}_2\text{Ac4Ph})\text{Cl}_2]$ (1), $[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$ (2), $[\text{Mn}(\text{H}_2\text{Ac4Cy})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (3), $[\text{Mn}(\text{H}_2\text{Ac4Et})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (4) and $[\text{Mn}(\text{H}_2\text{Ac4Et})(\text{OAc})_2]\cdot 3\text{H}_2\text{O}$ (5) have been synthesized and characterized by elemental analyses, electronic, infrared and EPR spectral techniques. In all the complexes except $[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$, 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 $[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$, 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 $[\text{Mn}(\text{Ac4Ph})\text{H}_2\text{O}]$ showing zero field splitting.

© 2009 Elsevier B.V. All rights reserved.

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-substituted thiosemicarbazones) and their Mn(II) complexes are investigated with the help of physico-chemical techniques.

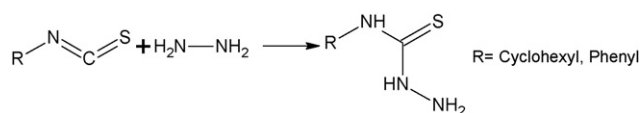
2. Experimental

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.

* Corresponding author. Tel.: +91 484 2862423; fax: +91 484 2575804.

E-mail addresses: mrp@cusat.ac.in, mrp.k@yahoo.com
(M.R. Prathapachandra Kurup).



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)

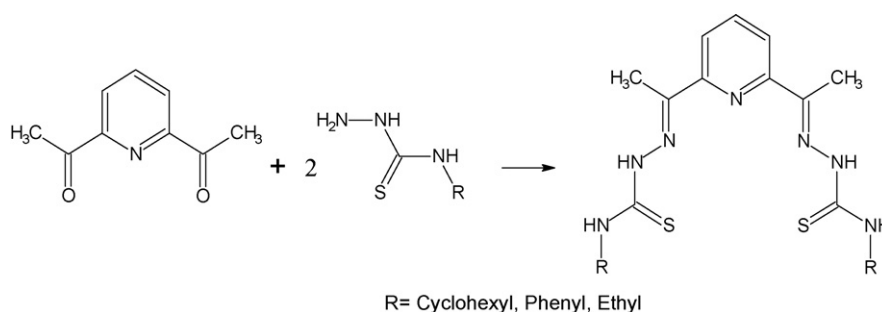
A hot solution of the thiosemicarbazide in 25 ml of ethanol and 2,6-diacetylpyridine in 25 ml of ethanol were mixed in 2:1 ratio with constant stirring. The above mixture was slowly refluxed for 5 h. After cooling, the compounds obtained as pale yellow solids, were filtered, washed with ethanol and dried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



R = Cyclohexyl, Phenyl, Ethyl

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 $4000\text{--}400\text{ cm}^{-1}$. The far IR spectra were recorded using polyethylene pellets in the $500\text{--}100\text{ cm}^{-1}$ 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

Download English Version:

<https://daneshyari.com/en/article/1237188>

Download Persian Version:

<https://daneshyari.com/article/1237188>

[Daneshyari.com](https://daneshyari.com)