

Syntheses and EPR spectral studies of manganese(II) complexes derived from pyridine-2-carbaldehyde based *N*(4)-substituted thiosemicarbazones: Crystal structure of one complex

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Abstract

Five manganese(II) complexes {[MnL¹]₂·H₂O·EtOH (1), [Mn(L¹(HL¹)]OAc (2), [MnL²]₂·3H₂O (3), [MnL³]₂·3H₂O (4) and [Mn(HL³)₂](SCN)₂·MeOH (5)} of three NNS donor *N*(4)-substituted thiosemicarbazone ligands {pyridine-2-carbaldehyde *N*(4)-*p*-methoxyphenyl thiosemicarbazone [HL¹], pyridine-2-carbaldehyde *N*(4)-2-phenethyl thiosemicarbazone [HL²] and pyridine-2-carbaldehyde *N*(4)-methyl, *N*(4)-phenyl thiosemicarbazone [HL³]} were synthesized and physico-chemically characterized. Compound 1 crystallized as [MnL¹]₂·H₂O and its structure has been determined by X-ray diffraction studies. It is found to have a distorted octahedral geometry. EPR spectra in DMF solutions at 77 K show hyperfine sextets with low intensity forbidden lines lying between each of the two main hyperfine lines.

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1. Introduction

Coordination chemistry of thiosemicarbazones has been a subject of enthusiastic research since they show a wide range of biological properties, especially those derived from heterocyclic aldehydes or ketones. Thiosemicarbazones are versatile ligands having *p*-delocalization of charge and configurational flexibility of the molecular chain that can give rise to a great variety of coordination modes. Owing to the interest they generate through a variety of biological properties ranging from anticancer, antitumor, antifungal antibacterial, antimalarial, antifilarial, antiviral and anti-HIV activities [1], thiosemicarbazones and their metal complexes have been extensively studied. Reports on *N*(4)-substituted thiosemicarbazones have concluded that the biological activity depends on the parent aldehyde or ketone, the presence of a bulky group at the terminal nitrogen and the presence of an additional potential bond-

ing site [2,3]. There are only a few reports on Mn(IV) and Mn(II) complexes of thiosemicarbazones and previous reports on the crystal structures of Mn(II) complexes of thiosemicarbazones are few in number [4–6]. In continuation of our investigations on the complexing properties of *N*(4)-substituted thiosemicarbazones, we synthesized the ligands pyridine-2-carbaldehyde *N*(4)-*p*-methoxyphenyl thiosemicarbazone (HL¹), pyridine-2-carbaldehyde *N*(4)-2-phenethyl thiosemicarbazone (HL²) and pyridine-2-carbaldehyde *N*(4)-methyl *N*(4)-phenyl thiosemicarbazone (HL³). The copper(II) and cobalt(III) complexes of these ligands have been reported recently [7,8]. Here, we report the syntheses and the structural and spectral characteristics of five manganese(II) complexes of these three ligands.

2. Experimental

2.1. Materials

Manganese(II) chloride tetrahydrate, manganese(II) acetate tetrahydrate, manganese(II) perchlorate hexahydrate

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and potassium thiocyanate (Merck) were used as supplied and solvents were purified by standard procedures before use. *Caution:* Perchlorate complexes of metals with organic ligands are potentially explosive and should be handled with care.

2.2. Syntheses of ligands

The thiosemicarbazone ligands (Scheme 1) were synthesized by adopting and modifying a reported procedure of Scovill et al. [9]. The syntheses of HL¹ [7], HL² [10] and HL³ [7] have been published earlier.

2.3. Syntheses of complexes

2.3.1. Syntheses of $[MnL^1_2] \cdot H_2O \cdot EtOH$ (1) and $[MnL^1_2] \cdot 3H_2O$ (3)

To a solution of the respective ligand (2 mmol) in hot ethanol (25 ml) was added $MnCl_2 \cdot 4H_2O$ (1 mmol), and the resulting solution was heated at reflux for 2 h and then kept at room temperature (overnight). The complexes formed were filtered, washed thoroughly with water, ethanol and then ether and dried *in vacuo* over P_4O_{10} . However compound **1** crystallized as $[MnL^1_2] \cdot H_2O$ (**1a**) on slow evaporation of its solution in ethanol in air.

2.3.2. Synthesis of $[Mn(L^1)(HL^1)]OAc$ (2)

To a solution of HL² (2 mmol) in hot ethanol (25 ml) was added $Mn(OAc)_2 \cdot 4H_2O$ (1 mmol), and the resulting solution was heated at reflux for 2 h and then kept at room temperature (overnight). The complex formed was filtered, washed thoroughly with water, ethanol and then ether and dried *in vacuo* over P_4O_{10} .

2.3.3. Synthesis of $[MnL^3_2] \cdot 3H_2O$ (4)

To a solution of HL³ (2 mmol) in hot ethanol (25 ml) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and the resulting solution was heated at reflux for 2 hours and then kept at room temperature (overnight). The complex formed was filtered, washed thoroughly with water, ethanol and then ether and dried *in vacuo* over P_4O_{10} .

2.3.4. Synthesis of $[Mn(HL^3)_2](SCN)_2 \cdot MeOH$ (5)

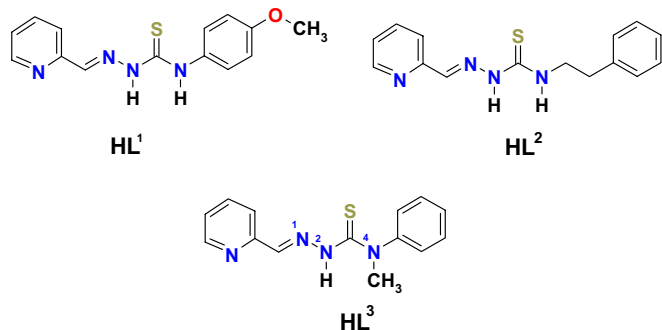
To a solution of HL³ (2 mmol) in hot ethanol (25 ml) was added $MnCl_2 \cdot 4H_2O$ (1 mmol), and the resulting solution was heated at reflux for 2 h. The mixture was then cooled and stirred with KCNS for 30 min and kept at room temperature (overnight). The complex formed was filtered, washed thoroughly with water, ethanol and then ether and dried *in vacuo* over P_4O_{10} .

2.4. Physical measurements

Elemental analyses of the ligands and the complexes were done on a Heracus elemental analyzer at the CDRI, Lucknow, India and on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR spectrophotometer with KBr pellets at the SAIF, Kochi. Electronic spectra of the complexes were recorded on a Cary 5000, version 1.09 UV–Vis–NIR spectrophotometer from solutions in $CHCl_3$. The EPR spectra of the complexes in the solid state at 298 K and in DMF solution at 77 K were recorded on a Varian E-112 spectrometer using TCNE as the standard, with 100 kHz modulation frequencies and 0.2 mT modulation amplitude at the SAIF, IIT, Bombay, India. The magnetic susceptibility measurements were carried out at the Indian Institute of Technology, Roorkee, India, at room temperature in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 kOe field strength. The molar conductivities of the complexes in dimethylformamide solutions (10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

2.5. X-ray crystallography

Single crystals of compound $[MnL^1_2] \cdot H_2O$ (**1a**) of X-ray diffraction quality were grown from a solution of **1** in ethanol by slow evaporation at room temperature in air. The crystallographic data and structure refinement parameters are given in Table 1. Intensity data and cell parameters were recorded at room temperature (293 K) on a Nonius, MACH3 diffractometer equipped with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. A single crystal of dimensions $0.35 \times 0.30 \times 0.30$ mm³ was used for data collection. The Maxus (Nonius software) was used for data reduction [11]. The trial structure was solved using SHELXS-97 [12] and refinement was carried out by full-matrix least squares on F^2 (SHELXL) [12]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms, with the exception of those on N4, were geometrically fixed and refined using a riding model. The hydrogen atoms of the N4 atoms were located from difference Fourier maps. However, the hydrogen atoms of the water molecule could not be located and were ignored. The molecular graphics employed were ORTEP-III [13] and PLATON [14].



Scheme 1. The thiosemicarbazones HL¹, HL² and HL³. The numbering scheme used is shown for HL³.

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