Manganese(II) complexes having pseudohalide coordination: Synthesis, IR spectroscopy and X-ray crystal structures of [Mn(L\textsuperscript{1})(NCS)\textsubscript{2}] and [Mn(L\textsuperscript{2})(NCS)\textsubscript{2}] compounds involving Schiff bases

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The synthesis, characterisation and properties of two manganese(II) complexes with thiocyanate coordination [Mn(L\textsuperscript{1})(NCS)\textsubscript{2}] (1) and [Mn(L\textsuperscript{2})(NCS)\textsubscript{2}] (2) (L\textsuperscript{1} and L\textsuperscript{2} = tetradentate ligand, derived from bis condensation of pyridine-2-carboxaldehyde and 1,3-diaminopropane, and 2-benzoyl pyridine and 1,3-diaminopropane, respectively) is described. The magnetic moments of 1 and 2 are respectively 5.95 and 5.86 BM at 298 K, indicating high-spin (idealised $t_2^2e_g^5, S = 5/2$) electronic configuration. The X-band EPR in 1:1 DMF-toluene glass (77 K) shows the $^{55}$Mn hyperfine structure at $g = 2$ with peak-to-peak separation of about 85 G. The structures 1 and 2 have been determined by single crystal X-ray diffraction studies, showing thereby that the manganese atom is hexacoordinated with an unusual distortion in the coordination sphere of this type of linear tetradentate ligand and thiocyanato anion acting as a terminal donor.

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The chemistry of manganese compounds has received considerable attention in recent years\textsuperscript{1} due to their significant role as redox active site in several biochemical processes, the diversity of their magnetic properties\textsuperscript{2-4} and building units of supramolecular architecture through variety of non-covalent intermolecular interactions\textsuperscript{5}. Designed synthesis of suitable polydentate ligands for generating numerous transition metal coordination compounds for their powerful stabilizing potential has also gained importance\textsuperscript{6,7}. Pseudohalide anions (N\textsubscript{3} -, NCS -, NCO -) have been well documented for their versatile coordination abilities leading to variety of species\textsuperscript{8,9}.

We report here the synthesis, characterisation and properties of two bivalent manganese complexes [Mn(L\textsuperscript{1})(NCS)\textsubscript{2}] (1) and [Mn(L\textsuperscript{2})(NCS)\textsubscript{2}] (2) (L\textsuperscript{1} and L\textsuperscript{2} = tetradentate ligand, derived from bis condensation between pyridine-2-carboxaldehyde and 1,3-diaminopropane, and 2-benzoyl pyridine and 1,3-diaminopropane, respectively). The synthesis, characterisation including X-ray structure, EPR and magnetic properties of these two new compounds 1 and 2 are described here.

**Materials and Methods**

1,3-Diaminopropane, pyridine-2-carboxaldehyde, 2-benzoyl pyridine and ammonium thiocyanate were purchased from Lancaster Chemical Company Inc. and used as received. All other solvents and chemicals were of analytical grade. The tetradeinate ligands [N,N'-bis(pyridine-2-yl)]propane-1,3-diamine (L\textsuperscript{1}) and [N,N-bis(pyridine-2-yl)benzylidene]propane-1,3-diamine (L\textsuperscript{2}) were synthesized adopting a procedure as reported previously\textsuperscript{10}.

**Physical measurements**

Elemental analyses for carbon, hydrogen and nitrogen were performed at IACS, Kolkata, using a Perkin-Elmer 2400II elemental analyzer. Manganese was determined titrimetrically. IR spectra (4000-400 cm\textsuperscript{-1}) were recorded on (KBr pellets) at 298 K using a JASCO FT/IR-420 spectrometer. Magnetic susceptibilities were measured at 298 K using a magnetometer (Sherwood Scientific Model MK1). Pascal's constants were utilized to estimate diamagnetic correction, which was subtracted from the experimental susceptibility data to give corrected molar magnetic susceptibility ($\chi_m$). EPR spectra were measured in the X-band using Varian 109C spectrometer fitted with quartz dewar. Calibration was done with DPPH ($g = 2.0037$). Solution (ca. $10^{-3}$ mol dm\textsuperscript{-3}) electrical conductivities were measured with a Philips PR 9500 bridge.
Preparation of [Mn(L1)(NCS)2], 1

A methanolic solution (6 cm³) of the L1 ligand (0.063 g, 0.25 mmol) was added dropwise to a methanolic solution (6 cm³) of Mn(ClO4)2·6H2O (0.091 g, 0.25 mmol) with constant stirring for 0.5 h at room temperature. To the resulting yellowish colour solution, a methanolic solution (6 cm³) of ammonium thio­cyanate was added slowly. The yellow solution was then left for slow evaporation and after 3-5 days, a yellowish green crystalline compound suitable for X-ray analysis of 1 was obtained. Yield: 0.080 g, 76% (Anal. Found: C, 48.1; H, 3.7; N, 19.7; Mn, 12.7. Calcd for C17H16N6S2Mn: C, 48.2; H, 3.8; N, 19.8, Mn, 12.9%). IR data: 1633, 1583 cm⁻¹. Preparation of [Mn(L2)(NCS)2], 2

This compound was synthesised following the same procedure as for 1 except that L2 was replaced with equimolar quantity of L2. Yield: 0.130 g, 91% (Anal. Found: C, 60.4; H, 4.1; N, 14.5; Mn, 9.4. Calcd for C29H24N6S2Mn: C, 60.5; H, 4.2; N, 14.6, Mn, 9.5%). IR data: 2071, 1633, 1583 cm⁻¹.

Perchlorate salts and azido complexes are potentially explosive especially in presence of organic ligands. They must be prepared and handled in small quantities, and with special care.

Crystal structure determination and refinement

Single crystals of suitable dimensions of 1 and 2 were collected on a Bruker APEX CCD diffractometer at 100(2) and 296(2) K respectively with graphite-monochromated MoKα radiation (λ = 0.71073 Å) in an o-2θ scan mode. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were made based on azimuthal scans. The structures were solved by direct methods and the structure solution and refinement was based on |F|². All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions when possible and given isotropic U values 1.2 times that of the atom to which they are bonded. Hydrogen atoms bonded to hetero-atoms were located in the Fourier map and their coordinates fixed to ride on the bonded atom with isotropic U values 1.2 times that of the atom to which they are bonded. All crystallographic calculations were carried out using SHELX-97 and ORTEP-3 program packages. The crystal data and data collection details are given in Table 1.

Results and Discussion

Synthesis

The reaction of ligand L1 or L2 and with manganese(II) perchlorate hexahydrate and ammonium thiocyanate, a methanolic solution (6 cm³) of L1 ligand was added slowly to a methanolic solution (6 cm³) of Mn(ClO4)2·6H2O (0.091 g, 0.25 mmol) with constant stirring for 0.5 h at room temperature. To the resulting yellowish colour solution, a methanolic solution (6 cm³) of ammonium thiocyanate was added slowly. The yellow solution was then left for slow evaporation and after 3-5 days, a yellowish green crystalline compound suitable for X-ray analysis of 1 was obtained. Yield: 0.080 g, 76% (Anal. Found: C, 48.1; H, 3.7; N, 19.7; Mn, 9.4. Calcd for C17H16N6S2Mn: C, 48.2; H, 3.8; N, 19.8, Mn, 12.9%). IR data: 1633, 1583 cm⁻¹.

Table 1 — The crystal data and data collection summary for [Mn(L1)(NCS)2]1 and [Mn(L2)(NCS)2]2

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Mn(L1)(NCS)2]</th>
<th>[Mn(L2)(NCS)2]</th>
</tr>
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<tbody>
<tr>
<td>Formula weight</td>
<td>423.44</td>
<td>575.62</td>
</tr>
<tr>
<td>Space group</td>
<td>C17H16N6S2Mn</td>
<td>C29H24N6S2Mn</td>
</tr>
<tr>
<td>α (Å)</td>
<td>8.4892(5)</td>
<td>7.8989(8)</td>
</tr>
<tr>
<td>β (Å)</td>
<td>8.8163(6)</td>
<td>13.630(3)</td>
</tr>
<tr>
<td>γ (Å)</td>
<td>25.7149(17)</td>
<td>14.6138(11)</td>
</tr>
<tr>
<td>ρ calc (g cm⁻³)</td>
<td>1.462</td>
<td>1.395</td>
</tr>
<tr>
<td>F(000)</td>
<td>868</td>
<td>594</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.44 X 0.36 X 0.20</td>
<td>0.98 X 0.60 X 0.50</td>
</tr>
<tr>
<td>μ (M0, Kα) (mm⁻¹)</td>
<td>0.916</td>
<td>0.664</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100</td>
<td>296</td>
</tr>
<tr>
<td>2θ max (°)</td>
<td>56.6</td>
<td>50.0</td>
</tr>
<tr>
<td>Reflections</td>
<td>12560</td>
<td>5007</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4685 (Rint = 0.019)</td>
<td>4641 (Rint = 0.010)</td>
</tr>
<tr>
<td>Reflections observed</td>
<td>4253</td>
<td>4299</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>0.88</td>
<td>1.08</td>
</tr>
<tr>
<td>R1 (wF²)</td>
<td>0.0349; 0.1088</td>
<td>0.0344; 0.0963</td>
</tr>
<tr>
<td>Largest difference peak and hole (e Å⁻³)</td>
<td>0.52 and -0.21</td>
<td>0.46 and -0.38</td>
</tr>
</tbody>
</table>
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manganese thiocyanate using a ratio of \( \text{L}^1 \) or \( \text{L}^2 : \text{Mn}^{II} : \text{NCS}^- = 1 : 1 : 2 \) in methanol medium affords yellowish green and orange crystalline compounds respectively having composition \([\text{Mn(L}^1)(\text{NCS})_2] \) (1) and \([\text{Mn(L}^2)(\text{NCS})_2] \) (2). It is interesting to note that by changing ratio of \( \text{L}^1 \) or \( \text{L}^2 : \text{Mn}^{II} : \text{NCS}^- = 1 : 1 : 1 \) or any other ratio to make different thiocyanate bridged bi- or polynuclear compounds leads to the same compounds 1 and 2, respectively. In DMF and acetonitrile these compounds behave as non-electrolyte\(^{14}\), as indicated by their very low \( \Lambda_\infty \) values (5-7 \( \Omega \cdot \text{cm}^2 \cdot \text{mol}^{-1} \)). The magnetic moments in polycrystalline form are 5.95 (for Compound 1) and 5.86 (for Compound 2) BM at 298 K, corresponding to a high-spin (idealised \( \text{t}^2 \text{e}_2^2, S = 5/2 \)) electronic configuration with five unpaired electrons as expected\(^3\). The X-band EPR spectra of the chelates were examined in the polycrystalline phase (300 and 77 K) as well as in 1:1 DMF-toluene glass (77 K). The spectra of the two complexes were similar. In the magnetically dilute glassy state, the \(^{55}\text{Mn} \) hyperfine structures were observed at \( g = 2 \) with peak-to-peak separation of about 85 G\(^{15}\).

**IR spectroscopy**

The IR spectra of 1 and 2 exhibit a very strong absorption at 2063 and 2071 cm\(^{-1}\) respectively corresponding to the asymmetric stretching vibrations of N bonded thiocyanate\(^6\). The absorptions corresponding to the \( v(\text{C}=\text{N}) \) stretches of \( \text{L}^1 \) and \( \text{L}^2 \) are located at 1637 and 1589 cm\(^{-1}\) and 1633 and 1583 cm\(^{-1}\) for compounds 1 and 2 respectively\(^{16,17}\).

**Crystal Structures of \([\text{Mn(L}^1)(\text{NCS})_2] \), 1 and \([\text{Mn(L}^2)(\text{NCS})_2] \), 2**

The ORTEP drawing of the complexes \([\text{Mn(L}^1)(\text{NCS})_2] \) (1) and \([\text{Mn(L}^2)(\text{NCS})_2] \) (2) are shown in Figs 1 and 2, and the selected bond distances and angles are listed in Table 2. Manganese(II) is in a highly distorted octahedral (MnN\(_6\)) coordination environment consisting of two nitrogen atoms (N1 and N2) from the N bonded thiocyanate anion and four nitrogen atoms (N3 to N6) from the tetradentate ligand. The Mn-N distances are ranging from 2.1734(14) to 2.3495(13) Å for complex 1 and 2.172(2) to 2.3770(19) Å for complex 2. The Mn-N(thiocyanate) distances are considerably shorter than Mn-N(ligand) distances as expected due to stronger binding capability of thiocyanate anion compared to that of neutral polydentate ligand\(^8\). All these Mn-N distances are consistent with corresponding values of analogous MnN\(_6\) chromophores\(^18-20\). In these molecules, the distortions in the coordination sphere is so large that the cis and trans angles vary from 71.20(5) to 134.42(5) for 1 and 71.30(6) to 125.49(17) for 2 and 144.84(5) to 153.48(5) for 1 and 143.14(6) to 161.26(8)\(^\circ\) for 2 respectively. The most possible origin of this substantial deformation of the compounds 1 and 2 are the structural constraints imposed by the polydentate ligand backbone. This type of unusual distortion in the coordination sphere was not observed even in topologically constrained pentadentate\(^9\) or
even other constrained macrocyclic ligand systems. But, we observed this type of severe distortion using pentadentate ligand system and thiocyanate anion as terminal donor. Distortions linked to oversized metal ion (for high-spin manganese(II): 0.97 Å) and structural constrained imposed by rigid ligand framework have been noted.

Conclusions
The present study describes the preparation of two high-spin (idealised $t_{2g}^0e_g^2$, $S = 5/2$) mononuclear manganese(II) compounds having composition $[\text{Mn}(L^1)(\text{NCS})_2] \quad \text{(1)}$ and $[\text{Mn}(L^2)(\text{NCS})_2] \quad \text{(2)}$ from tetradentate Schiﬀ base ligands ($L^1$ and $L^2$) while thiocyanate anion acts as terminal donor. Both complexes 1 and 2 have a highly distorted coordination sphere around manganese center. This type of severe distortions and thereby stability is new using linear tetradentate ligand as reported here. The effects of increasing topological, ﬂexibility constraints of macrocyclic ligands and linear pentadentate ligands along with their importance has only recently been recognized. The present ligands, therefore, provide an avenue to get highly distorted stable manganese(II) coordination compounds.

Supplementary Material
Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 259337 and 259338 for Compounds 1 and 2 respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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References
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