Synthesis and characterisation of manganese(II) complexes with bis(2-benzimidazolyl)propane and bis(2-benzimidazolyl) butane

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Flexible bidentate ligands 1,3-bis(2-benzimidazolyl)propane [GAB] and 1,4-bis(2-benzimidazolyl)butane [AAB] have been synthesized and a series of manganese (II) complexes of general composition [MnL₂X₂]nH₂O have been prepared where (L = GAB, AAB) and X is an exogenous anionic ligand (X = HCOO⁻, CH₃COO⁻, Cl⁻, SCN⁻). Using low temperature EPR studies, D and E parameters have been calculated for these complexes, which indicate a rhombic distortion of the six co-ordinated complexes. The ligand AAB provides a larger D, E implying a greater ligand field distortion in comparison to the ligand GAB. Cyclic voltammetric results show an irreversible oxidation of Mn(II) to Mn(III) for all complexes except the complexes [Mn(AAB)₂(SCN)₂] and [Mn(GAB)₂Cl₂]. The CV data indicate that the SCN⁻ anion tends to stabilize the Mn(II) oxidation state relative to the Cl⁻.

Due to their steric requirements, bidentate ligands carrying pendant benzimidazole groups simulate a strained low symmetry metal environment, as could be imposed by the protein backbone structure in Mn (II) containing metalloenzymes. Further it has been recently found that bis-benzimidazoles are used as DNA fluorophores and that they exhibit potent activity against several microorganisms including those that produce AIDS-like infections. Based on the above pieces of information, we were prompted to synthesize and study the Mn(II) complexes with bis-benzimidazole ligands.

Materials and Methods

All chemicals were of AR grade and used as received. Elemental analyses were obtained from the Micro-analytical laboratory of CDRI, Lucknow and RSIC, Chandigarh. IR spectra were taken on a Shimadzu IR-435 spectrophotometer and electronic spectra were taken on a Perkin-Elmer 554 spectrophotometer. X-band EPR spectra were taken on a VARIAN E-112 ESR spectrometer with a variable temperature liquid nitrogen cryostat at IIT, Madras (India). ¹H NMR spectra were taken on a 90 MHz Perkin-Elmer R-32 spectrometer. Cyclic voltammetric measurements were done on a BAS CV 50W instrument. A mixed solvent system DMSO:CH₃CN (2:8) was employed for the CV studies with 0.1 M NaClO₄ as the supporting electrolyte. Magnetic susceptibilities of complexes were determined at 29°C in the solid state at USIC, University of Roorkee.

Preparation of ligands GAB and AAB: Ligands 1,3-bis(2-benzimidazolyl)propane (GAB) and 1,4-bis(2-benzimidazolyl)butane (AAB) were prepared as described earlier.

Preparation of [MnL₂X₂]nH₂O (where L = GAB and AAB, X = SCN⁻, Cl⁻, CH₃COO⁻): Complexes with both the ligands GAB and AAB were synthesized following a common procedure as described below:

(i) X = Cl⁻, CH₃COO⁻.

To a solution of the ligand (2 mmol) in methanol (25 cm³) was added a methanolic solution (10 cm³) of the corresponding manganese salt (1 mmol). The resulting colourless solution was stirred for about 1 hour at room temperature after which the volume reduction was done using a rotary evaporator. To this a small amount of ether was added to precipitate the product. The product so obtained was redissolved in B₂O₃:MeOH mixed solvent (2:1 v/v) and was kept in refrigerator for a day. The white product so obtained was filtered and dried in vacuo over P₂O₅.

(ii) X = SCN⁻.

Mn(SCN)₂ solution was prepared by adding methanolic solution of potassium thiocyanate dropwise to methanolic solution of MnCl₂·4H₂O (2 mmol). KCl thus precipitated was filtered off and
the clear filtrate was used as Mn(SCN)$_2$ solution (2 mmol). This was then added to a methanolic solution (25 cm$^3$) of ligand (2 mmol) and worked up in a manner similar to that described in (i).

The complexes were characterized by elemental analysis as given in Table 1.

**Results and Discussion**

The EPR spectrum can be described in terms of the spin Hamiltonian:

$$g\beta H.S + D[S_x^2 - S_y^2] + E(S_x^2 - S_y^2) + A.S.I.$$  \(\ldots\) (1)

The above equation has been employed to get an estimate of the zero field splitting parameter $D$ and $E$. It is found that the resonance position can be fitted with $|D| = 0.032$ cm$^{-1}$ and $|E| = 0.011$ cm$^{-1}$, giving $\lambda = 0.31$ for the complex [Mn(GAB)$_2$(OAc)$_2$] (Fig. 1(A)). The value is very close to 1/3 indicating rhombic distortion of the six coordinated complex, while the major resonance positions for the complex [Mn(AAB)$_2$Cl$_2$] (Fig. 1(B)) can be fitted with $|D| = 0.108$ cm$^{-1}$ and $|E| = 0.03$ cm$^{-1}$ with $\lambda = 0.277$, again a departure from purely axial to rhombic symmetry can be concluded. It is interesting to note that the

![Fig. 1](image-url)

**Fig. 1**—5000 G scan, X-band EPR spectra of (A) [Mn(GAB)$_2$(OAc)$_2$].2H$_2$O (B) [Mn(AAB)$_2$Cl$_2$].2H$_2$O in solid state, microwave power 20 mW, microwave frequency 8.99 GHz, modulation amplitude (A) 0.5x10$^{-3}$ G (B) 3.2 G, receiver gain (A) 2.5x10$^2$ (B) 2.5x10$^2$ at liquid N$_2$ temperature.

**Table 1**—Microanalytical, magnetic and electrochemical data of Manganese(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (cal.)%</th>
<th>(\mu_{\text{eff}}) (BM)</th>
<th>(E_{\text{pK}}) (V)</th>
<th>(E_{\text{p'K}}) (V)</th>
<th>(E_{\text{1/2}}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(GAB)$_2$Cl$_2$].2H$_2$O</td>
<td>56.3(57.1) 4.8(5.0) 15.1(15.7)</td>
<td>7.7(7.7)</td>
<td>5.24</td>
<td>+0.98</td>
<td>+0.75</td>
</tr>
<tr>
<td>[Mn(GAB)$_2$(CH$_3$COO)$_2$].2H$_2$O</td>
<td>60.8(59.9) 4.9(5.5) 14.2(14.7)</td>
<td>6.9(7.2)</td>
<td>5.98</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Mn(GAB)$_2$(SCN)$_2$].2H$_2$O</td>
<td>56.2(56.9) 4.1(4.7) 17.8(18.4)</td>
<td>7.1(7.2)</td>
<td>5.64</td>
<td>+1.21</td>
<td>—</td>
</tr>
<tr>
<td>[Mn(AAB)$_2$Cl$_2$].2H$_2$O</td>
<td>58.6(58.2) 4.9(5.4) 14.6(15.1)</td>
<td>7.7(7.4)</td>
<td>6.03</td>
<td>+0.96</td>
<td>—</td>
</tr>
<tr>
<td>[Mn(AAB)$_2$(CH$_3$COO)$_2$].3H$_2$O</td>
<td>59.4(59.5) 5.1(5.9) 13.1(13.9)</td>
<td>6.3(6.8)</td>
<td>6.16</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Mn(AAB)$_2$(SCN)$_2$].3H$_2$O</td>
<td>58.9(59.3) 3.8(4.9) 17.7(18.2)</td>
<td>6.8(7.1)</td>
<td>5.56</td>
<td>+1.02</td>
<td>+0.88</td>
</tr>
</tbody>
</table>

*Error bar equals ± 0.05 BM*
ligand AAB provides a larger D,E implying a greater ligand field distortion in comparison to the ligand GAB.

A single one-line spectrum has been observed for complexes [Mn(AAB)_2(OCCH)], [Mn(GAB)_2(SCN)_2], [Mn(GAB)_2Cl_2] and [Mn(AAB)_2(SCN)_2] at 9.5 GHz in solid state (Table 2). The spectrum reveals the presence of a strong signal in the g =2.0 region. No other signal is observed in the 5.000 gauss scan spectra, as would have been expected for non-cubic Mn(II) complexes with an appreciable zero field splitting. Such a single one-line spectrum devoid of any hyperfine structure has been interpreted as arising from a Mn(II) complex with a neighbouring atom magnetic interaction.

The UV spectra of ligands GAB and AAB in methanol show three prominent bands at \( \lambda_{\text{max}} \) 278, 272 and 242 nm. All manganese complexes show absorption spectra typical of the benzimidazole nucleus. Small shifts are observed for bound benzimidazole. None of the manganese complexes absorbs in the visible region as is typical for other Mn(II) complexes.

The cyclic voltammetric data for manganese (II) complexes are presented in Table 1. Cyclic voltammograms of all the complexes were taken in DMSO:CH\(_3\)CN (2:8) solution under dried nitrogen atmosphere at room temperature. The complex [Mn(GAB)_2Cl_2] shows Mn(II)/Mn(III) oxidation wave at +0.98 V and the corresponding reduction wave at +0.75 V. The \( E_{1/2} \) for this complex is +0.86 V while the complex [Mn(AAB)_2Cl_2] shows Mn(II)/Mn(III) irreversible oxidation wave at +0.96 V. The complex [Mn(GAB)_2(SCN)_2] shows an irreversible one-electron oxidation of Mn(II)/Mn(III) and Mn(III)/Mn(IV), two-step oxidation at +0.98 V and +1.21 V respectively. No reverse corresponding reduction peaks were observed. So the oxidations are irreversible, while the complex [Mn(AAB)_2(SCN)_2] shows an oxidation wave at +1.02 V with a corresponding reduction wave at +0.88 V. The \( E_{1/2} \) value for this couple is +0.95 V. The two thiocyanato complexes also show a wave at 0.6V, which is ascribed to bound thiocyanate. The free SCN\(^{-}\) ion shows an oxidation wave at 0.782 V under identical solvent/scan rate conditions.

The \( E_{1/2} \) (0.95 V) for thiocyanato complexes is more positive as compared to that for chloro complexes (0.86 V), hence SCN\(^{-}\) anion stabilizes the Mn(II) state while Cl\(^{-}\) destabilizes it. The acetato complexes of Mn(II) did not show well-defined voltammograms due to their limited solubility in mixed solvent system.

The magnetic susceptibility data of all the manganese complexes were determined in solid state at room temperature. The diamagnetic correction for each complex was estimated using Pascal’s constant and incorporated in experimental susceptibility. The magnetic moment data are given in Table 1. The magnetic susceptibility data in all cases support the formulation based on the EPR. The room temperature magnetic moment data for all these Mn(II) complexes lie in the range of 5.96 – 6.16 B.M. The experimental \( \mu_{\text{eff}} \) data match with those for other \( d^{5} \) Mn(II) complexes. This is apparent from the ground state of Mn(II) ion, which in the presence of nearly octahedral
field gives a $^6A_{1g}$ ground state that has no orbital angular momentum.

IR spectra were taken in KBr. In the free ligand (GAB, AAB), a strong band appears in the region of 1420-1470 cm$^{-1}$. On the basis of analogy with the assigned bands for imidazole the 1430 cm$^{-1}$ band is attributed to stretching mode of $\nu_s (-C=\text{N}=-C=\text{C}-)$ while the others are overtone or combination bands$^5$. In Mn(II) complexes of these ligands, a shift of the order of 10 cm$^{-1}$ is observed. This implies direct coordination of all the imine nitrogen atoms to Mn(II). These are the preferred nitrogen atoms for coordination as found in other metal complexes with benzimidazoles$^9$. The peak observed around 1620-1630 cm$^{-1}$ is assigned to C=N stretching vibration primarily. The peak observed at 1590 cm$^{-1}$ is due to the ortho-substituted benzene ring$^{10}$. These frequencies do not change appreciably in the spectra of chelates. The peak observed at 1000-1030 cm$^{-1}$ arises due to benzene ring-breathing vibration$^{11}$. The remaining peaks at around 1260 cm$^{-1}$ are assigned to imidazole ring vibration. The N-H stretching frequency appears at 3200-3350 cm$^{-1}$. In acetaato complexes of Mn(II) bands at 1560 ($\nu_{as}$ COO$^-$) and 1340 cm$^{-1}$ ($\nu_s$ COO$^-$) have been assigned. These bands show the unidentate mode of binding of acetate group to the metal center.

A bidentate mode would have resulted in a lower difference between $\nu_s$ and $\nu_{as}$ ($< 144$ cm$^{-1}$). Our results indicate convincingly that the acetate is bound in a monodentate fashion as $\nu_s-\nu_{as} = 220$ cm$^{-1}$. The (-C=N-) stretching frequency for coordinated SCN$^-$ is generally low for typically N-bonded complexes (near or below 2100 cm$^{-1}$) than that for the S-bonded complexes (more than 2100 cm$^{-1}$). For our thiocyanato complexes a sharp singlet at 2020 cm$^{-1}$ is observed. This represents a high energy absorption for a terminally bound thiocyanate group and could be due to nitrogen bonded thiocyanate$^{12}$.

The presence of water molecules in Mn(II) complexes was confirmed by IR and thermogravimetric analysis. The observed weight loss corresponding to dehydration is consistent with the theoretical values.

References
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