Monomeric and dimeric manganese(II) complexes of N,N,N',N'-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanedi­amine and its derivatives

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Two types of manganese(II) complexes of N, N, N', N'-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine (EDTB) and its N-methyl (Me-EDTB) and N-ethyl (Et-EDTB) derivatives have been synthesized and characterised. Solution EPR of the [Mn₂(EDTB)(OAc)₄] in methanol at 142 K indicates that there are the equivalent Mn(II) ions coupled by an exchange interaction, fostered by bridging acetates. This is evidenced by a nearly isotropic 11-line hyperfine structure for ⁵⁵Mn with a coupling constant |A| = 45 ± 5 G. The room temperature magnetic moment of 4.86 B.M. per Mn atom indicates a clear quenching of the magnetic moment below that of a monomeric Mn(II) ion. The [Mn(L)](ClO₄)₂ type complexes show EPR spectra typical of monomeric Mn(II) complexes, in a tetragonal prismatic environment; their room temperature magnetic moments of 5.99, ([Mn(EDTB)](ClO₄)₂), 5.88, ([Mn(Me-EDTB)](ClO₄)₂) and 5.46 ([Mn(Et-EDTB)](ClO₄)₂) per Mn(II) atom are in the range found for d⁵ monomeric Mn(II) complexes. Thus a bridging inner sphere anion-like acetate makes it difficult for the ligand to coordinate to a metal ion with all its six donor atoms, and hence a second metal ion is coordinated by the ligand, whilst a weakly coordinating anion-like perchlorate (ClO₄⁻) makes it easy to bind only one metal ion.

In the recent past, several studies have been reported on the metal complexes of multidentate ligands containing rigidly incorporated benzimidazoles. These metal complexes are important as they simulate a strained low symmetry metal environment that could be imposed by the protein backbone structure. Reports of manganese complexes with these multi-dentate ligands are very few; thus there is compelling interest in the synthesis and characterization of such systems. Herein we report the synthesis, spectral and EPR properties of mono-nuclear and binuclear manganese(II) complexes formed with N,N,N',N'-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanedi­amine (EDTB) and its N-methyl and N-ethyl derivatives (abbreviated as Me-EDTB and Et-EDTB respectively). Earlier work has established the suitability of this ligand for binuclear metal complexes.

Materials and Methods
All the chemicals used were AR grade and used as received except acetonitrile which was dried by distillation from phosphorus pentoxide and Mn(II) acetate which was recrystallised from hot acetic acid.

Preparations
N, N, N', N'-Tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine (EDTB) was synthesized as described before. Its methyl and ethyl derivatives were synthesized by the procedure of Reed et al. These were characterized by ¹H NMR.

EDTB (DMSO-d₆): δ 7.5 (8H, m), 7.1 (8H, m), 4.1 (8H, s), 2.9 (4H, s).
Me-EDTB (CDCl₃): δ 7.5-7.3 (16H, m), 4.1 (8H, m), 3.6 (12H, s), 2.9 (4H, s).
Et-EDTB (CDCl₃): δ 7.4 (16H, m), 4.0 (8H, m), 3.9 (8H, q), 2.95 (4H, s), 1.1 (12H, t).

[Mn(L)](ClO₄)₂ (where L = EDTB (1), MeEDTB (2), EtEDTB (3))

The ligand (0.33 mmol) was suspended in acetonitrile, pH adjusted around 7 using tetramethylammonium hydroxide and Mn(ClO₄)₂ (0.66 mmol) solution (5 ml) in acetonitrile added to the suspension. The ligand suspension went into solution and a colourless solution resulted. This solution was stirred for 30 min at room temperature, concentrated to a small volume on rotary evaporator. On adding ether to the colourless solution, the compound precipitates as a white powder. This was collected and recrystallised from acetonitrile-ether (1:5). [Found: C, 47.0; H, 3.8; N, 16.0; Mn, 7.0. C₃₄H₃₂O₇N₁₀Cl₂-Mn.H₂O (1) requires: C, 47.8; H, 4.0; N, 16.4; Mn, 6.4%]. The above procedure was also used for preparing the
Table 1 – X-band EPR spectra of the manganese complexes (Values in gauss).

<table>
<thead>
<tr>
<th>[Mn(acac)]</th>
<th>[Mn(Et-EDTB)(ClO₄)]</th>
<th>[Mn(Me-EDTB)(ClO₄)]</th>
<th>[Mn(EDTB)(ClO₄)]</th>
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<tbody>
<tr>
<td>300</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>850</td>
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<td>1100</td>
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<tr>
<td>5250</td>
<td>5350</td>
<td>5250</td>
<td>5310</td>
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</table>


complexes 2 and 3 of MeEDTB and Et-EDTB, respectively.

For 2: [Found: C, 48.4; H, 4.5; N, 14.7; Mn, 6.4. C₃₈H₄₀O₁₀N₁₀Cl₂M₂H₂O requires: C, 49.2; H, 4.8; N, 15.1; Mn, 5.9%].

For 3: [Found: C, 52.3; H, 5.3; N, 14.0; Mn, 5.7. C₄₂H₄₈O₁₀N₁₀Cl₂M₂H₂O requires: C, 52.0; H, 5.2; N, 14.4; Mn, 5.5%].

[Mn₂(EDTB)(OAc)₄]
The ligand EDTB (0.33 mmol) was suspended in methanol/ethanol and manganese acetate (0.66 mmol) solution (5 ml) in methanol was added to the ligand. A colourless clear solution was obtained and the solution was stirred for 1 hr at room temperature. The solution was reduced to a small volume on a rotatory evaporator and small amount of acetonitrile was added to precipitate the crude product. The compound was purified by recrystallization from methanol-acetonitrile (1:5) [Found: C, 51.0; H, 4.9; N, 13.9; Mn, 11.5. C₄₂H₃₂O₈N₁₀Mn₂3H₂O requires: C, 51.4; H, 5.1; N, 14.3; Mn, 11.3%] (C, H, N analysis were obtained from Punjab University, Chandigarh, India). Manganese was estimated spectrophotometrically in our laboratory. It is not unusual for these complexes to crystallise as hydrates, since related benzimidazole complexes also showed similar behaviour.

Instrumentation
IR spectra were taken on a Shimadzu IR-435 spectrophotometer, electronic spectra on a Perkin Elmer-554 UV-Vis spectrophotometer, X-band EPR on a Jeol JES-FE 3XG ESR spectrometer with a variable temperature liquid nitrogen cryostat and ¹H NMR on a 90 MHz Perkin-Elmer R-32 instrument.

Results and Discussion

EPR spectroscopy
Figure 1 illustrates the 9.5 GHz EPR spectra of
The magnetic susceptibilities of manganese complexes in solution were determined by the Evans method at 300 K in acetonitrile for [Mn(EDTB)] (ClO$_4$)$_2$ and [Mn(Me-EDTB)] (ClO$_4$)$_2$, and in DMSO for [Mn(Et-EDTB)] (ClO$_4$)$_2$, and [Mn$_2$(EDTB) (OAc)$_4$]. The diamagnetic correction for each complex was estimated using Pascal's constants and was incorporated in the experimental solution susceptibility. It is found that the monomeric complexes [Mn(EDTB)] (ClO$_4$)$_2$, [Mn(Me-EDTB)] (ClO$_4$)$_2$, and [Mn(Et-EDTB)] (ClO$_4$)$_2$ show magnetic moments ($\mu_{\text{eff}}$ per manganese atom) of 5.99, 5.88, and 5.46 B.M., respectively. The experimental $\mu_{\text{eff}}$ lie in the range found for other $d^5$ Mn(II) complexes.
Table 2 – Observed optical bands (nm) and their extinction coefficients

<table>
<thead>
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<th>Compound</th>
<th>Solvent</th>
<th>λ_max (nm)</th>
<th>log ε</th>
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<td>EDTB</td>
<td>Butanol</td>
<td>246</td>
<td>3.98</td>
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<td>4.05</td>
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<td></td>
<td></td>
<td>280</td>
<td>4.04</td>
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<td>[Mn(EDTB)]ClO₄·2H₂O</td>
<td>Acetonitrile</td>
<td>243</td>
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<td></td>
<td></td>
<td>272</td>
<td>4.68</td>
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<td></td>
<td>279</td>
<td>4.67</td>
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<tr>
<td>[Mn₂(EDTB)(OAc)₄]·3H₂O</td>
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<td>4.41</td>
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<td></td>
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<td>272</td>
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<td>279</td>
<td>4.54</td>
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<tr>
<td>Me-EDTB</td>
<td>Chloroform</td>
<td>255</td>
<td>3.98</td>
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<td>268</td>
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<td>276</td>
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<td>285</td>
<td>3.87</td>
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<td>253</td>
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<td></td>
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<td>281</td>
<td>4.65</td>
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<tr>
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<td>Chloroform</td>
<td>257</td>
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<tr>
<td>[Mn(Et-EDTB)]ClO₄</td>
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<td>4.36</td>
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<td>281</td>
<td>4.40</td>
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Complexes. The magnetic moment of the dimeric complex [Mn₂(EDTB)(OAc)₄] is found to be 4.86 B.M. per Mn(II) atom. This indicates a clear quenching of magnetic moment below that of a monomeric manganese complex. This is suggestive of an exchange interaction between the two manganese atoms bound to the hexadentate ligand.

Electronic and IR spectroscopy

The ligands and their manganese complexes show characteristic UV spectra of the benzimidazolyl group. The absorption bands and respective extinction coefficients are reported in Table 2. The UV bands are all blue shifted upon coordination and enhance in intensity as evidenced by extinction coefficients. This includes the band at 246 nm in EDTB and 255 nm in Me-EDTB, Et-EDTB ligands, which is associated with the imidazole ring showing clear evidence of C=N coordination to manganese centre.

IR spectra were taken in nujol mull. In the free ligand, a strong band appears in the region of 1420-1435 cm⁻¹ with two other weaker bands at around 1445 and 1480 cm⁻¹. On the basis of the analogy with the assigned bands for imidazole, the 1435 cm⁻¹ band is attributable to νₛ (−C=N−C=C−) while the other two are overtone or combination bands. In our case we find that the shift is of the order of 20 cm⁻¹ in the complex (Table 3). This implies direct coordination of all four imine nitrogen atoms to Mn(II). These are the preferred nitrogen atoms for coordination as found in other metal complexes with benzimidazoles. In all the complexes, a strong band for the perchlorate anion appears in the region of 1080-1110 cm⁻¹ suggesting the presence of ionic perchlorate.

In the IR spectrum of [Mn₂(EDTB)(OAc)₄], new bands arise at 1590 and 1400 cm⁻¹. These are indicative of bridging acetate group whilst bands at 1620 and at 1375 cm⁻¹ are assigned to a unidentate mode of binding of acetato group. Thus the IR spectra of dimeric complex provides evidence for the presence of both bridging and unidentate acetate groups. All the above noted IR bands are absent in the analogous [Mn(EDTB)](ClO₄)₂ complex.
Table 3 – Observed IR frequencies (cm^{-1}) and proposed modes of assignments for the ligand and the complexes

<table>
<thead>
<tr>
<th></th>
<th>[Mn(EDTB)][ClO_4]_2</th>
<th>[Mn_2(EDTB)(OAc)_2]</th>
<th>Assignments</th>
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<tr>
<td>EDTB</td>
<td></td>
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<tr>
<td>1620 vw</td>
<td>1615 w</td>
<td>1620 s</td>
<td>v(C=N), v(C=O)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Unidentate acetate</td>
</tr>
<tr>
<td>1480 vw sh</td>
<td>1490 sh</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1590 m</td>
<td>v(C=O) bridging</td>
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<tr>
<td></td>
<td></td>
<td>1400 m</td>
<td>v(C=O) acetate</td>
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<tr>
<td>1435 s, sh</td>
<td>1455 vs</td>
<td>1450 vs</td>
<td>v(C=N=C=C-)</td>
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<td></td>
<td>1465 s, sh</td>
<td>1460 s</td>
<td>L</td>
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<td></td>
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<td>1375 m</td>
<td>v(C=O)</td>
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<tr>
<td></td>
<td>1110 s v_3</td>
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<td>v_3(ClO_4)^-</td>
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<tr>
<td>1090 m</td>
<td>1085</td>
<td>1080 m</td>
<td>L</td>
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<tr>
<td>1040 m</td>
<td>1060 m</td>
<td>1030 m</td>
<td>L</td>
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<tr>
<td>1020 m</td>
<td>1025 m</td>
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<td>L</td>
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<td>930 m, v_1</td>
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<tr>
<td>740 m</td>
<td>740 m</td>
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<tr>
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<tr>
<td>1620 w</td>
<td>1020 w</td>
<td>v(C=N)</td>
<td>L</td>
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<tr>
<td>1470 sh</td>
<td>1480, 1495 s</td>
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<tr>
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<td>1445 m</td>
<td>v(C=N=C=C-)</td>
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<td>v_1 &amp; v_3 &amp; v_4(ClO_4)^-</td>
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<td>620 m v_4</td>
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<td>740 m</td>
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Acknowledgement

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References
TRIPATHI et al.: MANGANESE(II) COMPLEXES