Crystal Structure of a New Quasi-Two-Dimensional Compound Containing 1,4-Bis(imidazol-1-ylmethyl)-benzene (bix) and Mn^{II} ions

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The construction of solid-state architectures and crystal engineering has become an area of increasing interest over recent years.\(^1,2\) Much study has been centered upon the use of supramolecular contacts and in particular hydrogen bonding between suitable organic molecules to generate multi-dimensional arrays and networks. The design of inorganic networks is less well developed, but recent examples have helped to extend the understanding of this developing area.\(^3-6\) Recently, Robson et al. have reported two two-dimensional (2D) polyrotaxanes derived from Zn^{II} and Ag^{I} with the ligand of the title.\(^7,8\) However, in both the examples, Zn^{II} and Ag^{I} have the d^{10} configuration, and bix [1,4-bis(imidazol-1-ylmethyl)benzene] was only used as bridging ligand connecting the two metal ions. In addition, bix is a suitable candidate for studying the maximum distance for the magnetic interaction of metal ions bridged by a long-distance ligand, which attracts many scientists' interest. We report here the structure of Mn\_\(bix\)_\(2\)\((\text{NO}_3)_4\)\cdot4\(H_2\)\(O\), which has a quasi-2D structure with bix as both terminal and bridging ligands. It provides the first example that bix can act as both terminal and bridging ligand concurrently in a complex.

**Experimental**

**Starting materials and physical measurements.** All chemicals were commercial products of reagent grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer analyzer model 240. Infrared spectroscopy on KBr pellets was performed on a Nicolet 5DX FT-IR spectrophotometer in the 4000–400 cm\(^{-1}\) region. Magnetic susceptibility measurements of a crystalline sample were carried out in the temperature range 1.4–296 K on a model CF-1 vibrating sample magnetometer.

**Preparation of \(\alpha,\alpha'-\text{dibromo-p-xylene.}\)** \(\alpha,\alpha'-\text{Dibromo-p-xylene was obtained in the following way. A stirred mixture of p-xylene (10.6 g, 0.1 mol), N-bromo-succinimide (NBS) (0.39 g), azobis(isobutyronitrile) (AIBN) (ca. 50 mg), and newly distilled HCOOCH\(_3\) (100 mL) was refluxed under illumination (a 500 W incandescent bulb) for 14 h. The white solid was separated by filtering, washed with newly distilled HCOOCH\(_3\) and water, and recrystallized from CHCl\(_3\). Yield: 18 g (74\%), m.p. 142–143 °C. (Found: C, 36.52; H, 3.08; C\(_9\)H\(_8\)Br\(_2\) requires: C, 36.40; H, 3.05%).**

**Preparation of bix.** Bix was obtained as described in Ref. 8 except for the use of \(\alpha,\alpha'-\text{dibromo-p-xylene} instead of \(\alpha,\alpha'-\text{dichloro-p-xylene} in the synthesis processing. M.p. 128–131 °C. (Found: C, 70.65; H, 6.02; N, 22.89; C\(_{14}\)H\(_{14}\)N\(_4\) requires: C, 70.57; H, 5.92; N, 23.5%).**


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Preparation of Mn(bix)$_2$(NO$_3$)$_2$·4H$_2$O. The titled compound obtained by the following method. A solution of bix (123 mg, 0.5 mmol) in methanol (10 mL) was added dropwise to a stirred aqueous solution (2 mL) of Mn(OAc)$_2$ (49 mg, 0.2 mmol); then NaNO$_3$ (27.6 mg, 0.4 mmol) dissolved in water (2 mL) was added slowly. The clear yellow solution was left to stand undisturbed at room temperature. A week later, X-ray-qualified light yellow single crystals were obtained, which were filtered, washed with water, methanol, and ether, and dried in a vacuum. Yield 62%. (Found: C, 49.52; H, 4.88; N, 22.02.  C$_{24}$H$_{50}$MnNi$_4$O$_8$, requires: C, 49.71; H, 4.91; N, 21.85%; m.p. 162–163°C.

Crystallographic data collection and structure determination. Crystal data: C$_{24}$H$_{50}$MnNi$_4$O$_8$, light yellow crystals of dimension 0.15 x 0.3 x 0.3 mm, M = 933.89, triclinic, space group P1, a = 9.037(2), b = 11.498(2), c = 12.404(2) Å, α = 110.09(3), β = 109.62(3), γ = 93.05(3), V = 1119(1) Å$^3$. D$_m$ = 3.185 g cm$^{-3}$. T = 299(1) K. F(000) = 489. Mo-Kα radiation (λ = 0.71073 Å), μ = 0.3472 mm$^{-1}$. Δρ$_{max}$ = 0.48 e Å$^{-3}$. Δρ$_{min}$ = -0.47 e Å$^{-3}$.

The structure was solved by direct methods and refined by the full-matrix least-squares method with use of SDPLUS and Siemens SHXTEL-PC program package. A total of 3171 reflections were mounted on a computer-controlled Enraf-Nonius CAD4 diffractometer. Cell parameters were determined by a least-squares calculations based on the setting angles and 25 reflections with θ angles ranging from 7.92 to 12.10°. The intensities of the unique hkl reflections were measured up to θ$_{max}$ = 23°; the 0-2θ scan technique was employed, with an ω-scan width equal to (0.6 + 0.35 tan θ)$^o$, and a scan speed of 0.92–5.49° min$^{-1}$. A total of 2868 independent reflections was measured, giving 2399 observed reflections (I$\geq 3σ$(I)) used in the refinement. Three standard reflections monitored every 60 min showed no intensity variation during the data collection. An absorption correction was made with DIFABS during processing. The final refinement was by full-matrix least-squares, with the function minimized being Σ(|I$_{hkl}$| - |F$_{hkl}$|)$^2$, where w$^{-1}$ = σ$^2$(F), goodness of fit = 1.15. Non-hydrogen atomic coordinates are listed in Table 1.

Results and discussion

Crystal structure. An ORTEP drawing of the complex is shown in Fig. 1. The selected bond distances and angles with the estimated standard deviations are listed in Table 2.

In this crystal structure, the Mn coordination environment can be considered as a distorted octahedron. Mn$^{II}$ is situated at a center of symmetry, which is coordinated with four nitrogen atoms from two bridging bix groups, two terminal bix groups, and two coordinating waters, forming a chain, as shown in Fig. 1. Mn(1)–O(1) = Mn(1)–O(1a) = 2.207(4) Å, Mn(1)–N(1) = Mn(1)–N(1a) = 2.274(5) Å, Mn(1)–N(5) = Mn(1)–N(5a) = 2.251(4) Å. The coordination environment is similar to the previously reported compound Mn(im)$_2$(H$_2$O)$_2$Cl$_2$ (im = imidazole). The three rings (two imidazole rings and one benzene) of both bridged and terminal bix are not in a plane. In the terminal bix, the dihedral angle between the plane of the coordinated imidazole and the benzene plane is 88.9°, and the one between the plane with the free imidazole and the benzene plane is 77.4°, while the dihedral angle between the two imidazole planes of the terminal bix is 39.1°; in the bridged bix, the dihedral angles between imidazole plane and the benzene plane are 106.0 and 91.4°, respectively. The two NO$_3$$^-$ ions, two coordinating waters and the two crystal waters form hydrogen bonds to produce a two-dimensional network, as shown in Figs. 2 and 3: O(11)–O(11) = 2.633 Å, O(11)–O(62) = 2.860 Å, O(11)–O(61) = 2.728 Å. The possible hydrogen-bond distances and angles are listed in Table 3. The metal-metal separation across the bridging bix is 12.659 Å for Mn(1)···Mn(1b), while the distance through the hydrogen bond is 14.22 Å for two manganese(II) ions.

In comparison with the two complexes of Ag$_2$(bix)$_3$(NO$_3$)$_2$ and Zn(bix)$_2$(NO$_3$)$_2$·4.5H$_2$O previously reported, the bix ligands in the present complex have different coordination modes in which bix is used.
**Fig. 1.** The ORTEP drawing of Mn(bix)$_3$(NO$_2$)$_2$·4H$_2$O.

Table 2. Selected bond distances (in Å) and angles (in °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
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<tr>
<td>Mn(1)–O(1)</td>
<td>2.207(4)</td>
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</tr>
<tr>
<td>Mn(1)–N(5)</td>
<td>2.251(4)</td>
<td></td>
</tr>
<tr>
<td>O(1)–Mn(1)–N(1)</td>
<td>92.2(2)</td>
<td>90.1(2)</td>
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<td>N(1)–Mn(1)–N(5)</td>
<td>94.1(2)</td>
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<tr>
<td>N(1)–Mn(1)–O(1a)</td>
<td>87.8(2)</td>
<td>89.9(2)</td>
</tr>
<tr>
<td>N(5)–Mn(1)–N(5a)</td>
<td>180.0</td>
<td></td>
</tr>
<tr>
<td>N(1)–Mn(1)–N(1a)</td>
<td>95.9(2)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry code: \(a = -x, -y, 1-z; b = 1-x, 1-y, 1-z,\)

**Fig. 2.** The hydrogen bond of Mn(bix)$_3$(NO$_2$)$_2$·4H$_2$O.

as both terminal and bridging ligands. This difference may be due to the fact that the electronic configuration of the metal ions (d$^5$ for Mn$^{II}$, d$^{10}$ for Zn$^{II}$ and Ag$^+$ and counter-ions have a significant effect on the coordination modes of bix.

**IR spectrum.** The IR spectrum of the compound exhibits several characteristic strong bonds. The strong and broad absorption in the region 3600–3000 cm$^{-1}$ of the complex can be assigned to the presence of water. Strong bands at 1670–1600 cm$^{-1}$ were observed, which are attributed to C=O stretching modes of imidazol rings. The absorption in the region 1540–1430 cm$^{-1}$ of the complex is assignable to the stretch of the benzenes and imidazol rings. The strong band at 800 cm$^{-1}$ are due to the C=C and C=N stretches of the bix molecules.

**Magnetic behavior.** The magnetic behavior of the compound is represented in Fig. 4 in the form of $\mu_{\text{eff}}$ vs. $T$. The observed $\mu_{\text{eff}}$ value is 6.06 B.M. at 295 K, which is slightly higher than the spin-only value of 5.92 B.M. for Mn$^{II}$ (S = 5/2) and $g_{\text{spin}} = 2$. When the temperature is
lowered, $\mu_{\text{eff}}$ remains almost constant until 5 K and then decreases sharply to 2.53 B.M. at 1.5 K, indicating the presence of a zero-field splitting effect within the $S=5/2$ local ground states of the Mn$^{III}$ ions or a magnetic interaction between the Mn$^{III}$ ions. Because the Mn$^{II}$–Mn$^{II}$ separations of 14.22 and 12.659 Å, through hydrogen bonds and across the bridging bix, respectively, are too long to mediate a magnetic interaction, we attempted to interpret the phenomenon employing the zero-field splitting effect within the $S=5/2$ local ground states of the Mn$^{II}$ ions. The theoretical expression of $\chi_{\text{dfs}}^{13}$ [eqn. (1)] is then

$$\chi_{m} = \chi_{\text{dfs}} = \frac{N_{\text{Sdd}} \beta^{2}}{4KT} \left( 1 + 9 \exp(-2D/KT) + 25 \exp(-6D/KT) \right)$$

where $D$ is the axial zero-field splitting parameter for Mn$^{II}$. Least-squares fitting gave rise to $g=2.05$ and $D=0.9968$ cm$^{-1}$. The agreement factor, defined as $F = \Sigma(x_{\text{obs}}-x_{\text{calcld}})^{2}/x_{\text{obs}}^{2}$, is $1.437 \times 10^{-3}$ for all of the 86 observations.

If we compare this system with our previously reported complex with 4,4’-bipy bridging ligand, we see that a dominant zero-field splitting within the $S=5/2$ local ground states of the Mn$^{III}$ ions is in the present compound. This may be due to the fact that the Mn$^{II}$–Mn$^{II}$ separation of 12.659 Å is clearly too large to permit a larger overlap between magnetic orbitals. The existence of a Mn$^{II}$–(bix)–Mn$^{II}$ pathway is not a sufficient condition for superexchange.

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References


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