Formation of an infinite interpenetrating three-dimensional network by tris(*N,N′*-butylenebisimidazole)manganese(II) tetrafluoroborate

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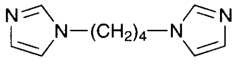
The structure of the complex Mn(*N,N′*-butylenebisimidazole)$_3$(BF$_4$)$_2$ comprises two equivalent, mutually interpenetrating three-dimensional networks of 44-membered rings.

A particularly interesting subset of the rapidly developing field of self-assembling framework materials is the class of compounds which form interpenetrating networks. These can involve two- or three-dimensional arrays, and doubly or triply interpenetrating lattices with a range of types of network 'building blocks'.[1] In the case of interpenetrating metal complexes, as distinct from purely organic compounds such as trimesic acid,[2] building blocks based on essentially rigid cyanide or bi- or tri-pyridyl ligand bridges have been frequently used.[1,3] Whereas this rigidity can assist in the design of predimensioned networks, it frequently limits their ability to accommodate ionic or non-ionic guest species. To this end we have been exploring the use of conformationally flexible bridging ligands to generate large-ring frameworks which have the ability to 'breathe' and thereby generate more adaptable receptor arrays.[4]

One of the consequences, however, of the formation of large-ring structures is that, in the absence of appropriate guest species, such macrocycles tend to collapse in on themselves so as to be self-filling. A way of preserving an open network is for the voids that would inevitably be present to be occupied by a process of mutual interpenetration so as to form polycatenane arrays.[5] The majority of these are two-dimensional and examples of three-dimensional interpenetrating networks comprising flexible bridging ligands are comparatively rare.[1] We now report that the flexible, extended-reach ligand *N,N′*-butylenebisimidazole (**I**, bbi) can be used to form not only large metallamacrocyclic rings, but also a continuous interpenetrating three-dimensional network.



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Reactions between bbi[6] and hydrated MnX$_2$ (X = I, BF$_4$) in methanol gave the compounds Mn(bbi)$_3$(BF$_4$)$_2$ **1** and Mn(bbi)$_3$I$_2$·2H$_2$O **2**,† with X-band EPR spectra comprising a single band at $g_{\mathrm{eff}} = 2$, consistent with Mn$^{\mathrm{II}}$ in an essentially O_h environment. In contrast, when X = Cl, Br, 2 : 1 complexes were obtained with X-band spectra showing very pronounced zero-field splitting characteristic of tetragonal MnN$_4$X$_2$ systems.[7] Compound **2** was obtained only as a powder but **1** formed crystals suitable for X-ray diffraction.‡

The X-ray analysis of **1** reveals that each manganese atom is octahedrally coordinated by six imidazole nitrogen atoms, each of which is from a different bbi ligand (Fig. 1). There are no statistically significant distortions from O_h coordination geometry about the Mn atom, which lies on a crystallographic S_6 centre.

Each bbi ligand has an extended geometry in which the N(CH$_2$)$_4$N chain has an all *anti* geometry and has its plane steeply inclined, by 72°, to the imidazole ring planes. Each ligand serves to bridge adjacent Mn centres forming a rhombohedral array of Mn···Mn edge length of 14.28 Å and acute inter-edge angle of 57.7° (Fig. 2). The approximate volume of this open rhombohedral 'box' is *ca.* 1950 Å^3, a volume grossly in excess of that required to accommodate the BF$_4^-$ anions. However, instead of forming an open, microporous structure the potential voids are filled *via* mutual interpenetration of two equivalent three-dimensional frameworks. The interpenetration of two rhombohedra is represented schematically in Fig. 3; the vertex of the rhombohedron within one lattice lies at the body centre of the other. The shortest Mn···Mn distances within this interpenetrating framework are 9.92 Å.

The region bounded by the all-acute vertices [depicted by Mn(a) and Mn(b) in Fig. 3] of the two interpenetrating rhombohedra forms a cavity that is occupied by a pair of BF$_4^-$ anions (Fig. 4). These anions are displaced from the cavity centre towards the manganese atoms Mn(a) and Mn(b), possibly by virtue of weak CH···F hydrogen bonds, which may be responsible for the contraction of the rhombohedral angle to 57.7°. It is clear that the cavity has the potential to include larger anions and we are currently exploring the effects of anion size and organic ligand chain length in controlling the formation of this type of interpenetrating structure.

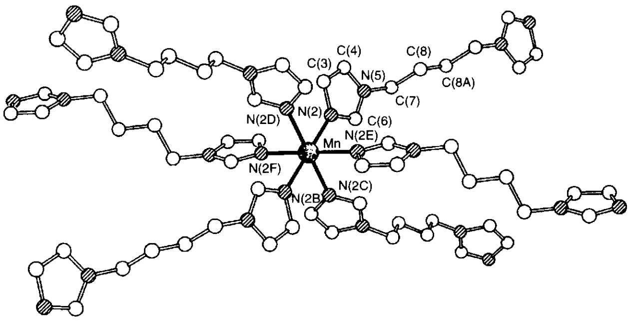

Fig. 1 The S_6 symmetric coordination at Mn in the structure of **1**: Mn–N 2.270(5) Å; N–Mn–N 89.9(3), 90.1(3)°

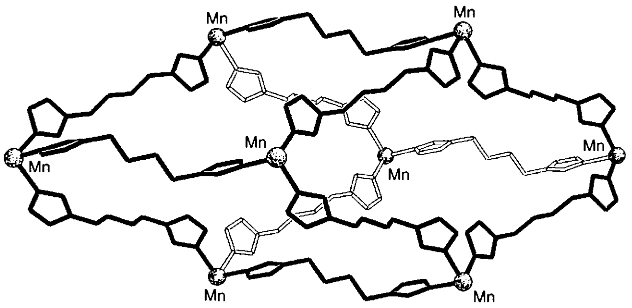

Fig. 2 The rhombohedral array formed by the bridging of Mn centres by the bbi ligands

We thank the Nuffield Foundation for an Undergraduate Research Bursary (to P. C. M. D.), the BBSRC for a postdoctoral fellowship (to S. M.) and the EPSRC for equipment.

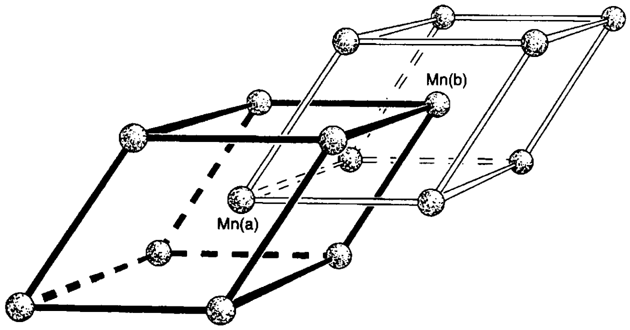

Fig. 3 Schematic representation of the interpenetration of a pair of the Mn_8 rhombohedral units in the contiguous interpenetrating three-dimensional network formed by **1**

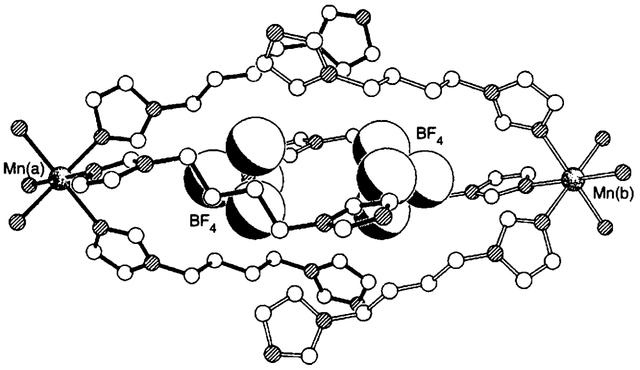

Fig. 4 The anion-containing cavity formed by the intersection of the two rhombohedra

Footnotes

† Satisfactory analyses were obtained.

‡ *Crystal data*: **1**; $C_{30}H_{42}N_{12}B_2F_8Mn$, crystal dimensions 0.23 × 0.15 × 0.15 mm, rhombohedral, space group $R\bar{3}$, a = 13.783(1), c = 17.777(2) Å, γ = 120°, U = 2924.7(4) Å^3, Z = 3, M = 799.3, D_c = 1.361 g cm^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 0.416 mm^{-1}, T = 293 K. Siemens P4/PC diffractometer, graphite-monochromated Mo-Kα radiation, ω scans; 1004 reflections were measured of which 689 were independent. The structure was solved by the heavy-atom method and refined[8] anisotropically (using $|F^2|$) to give R_1 = 0.056 (wR_2 = 0.148) for 634 independent observed reflections [2θ = 4–50°, $|F_o| > 4\sigma(|F_o|)$, 81 parameters]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/207.

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Received, 12th July 1996; Com. 6/04889G