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Supramolecular structure of $\{C_6H_2[CH_2OCH_2C(pz)_3]_4[Mn(CO)_3]_4\}(BF_4)_4$ based on tetrametallic organometallic building blocks constructed from a multitopic tris(pyrazolyl)methane ligand

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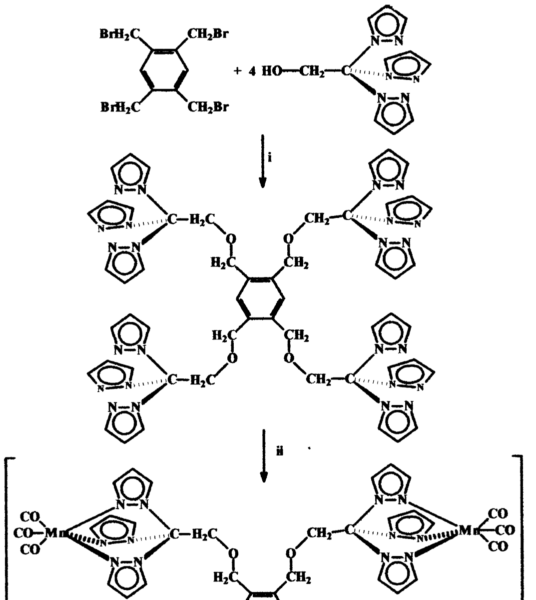
The compound $\{C_6H_2[CH_2OCH_2C(pz)_3]_4[Mn(CO)_3]_4\}(BF_4)_4$ forms a 3D sinusoidal architecture with 16 × 7 Å channels organized by π–π stacking and weak C–H · · · F hydrogen bonds.

Two important organizational tools in supramolecular chemistry are weak hydrogen bonds[1] of the type C–H · · · Y (Y = O, N, F) and π–π stacking.[2] The design of organometallic supramolecular systems that can utilize these forces is a growing field.[3] We are developing supramolecular organometallic chemistry based on new multitopic ligands prepared by linking tripodal tris(pyrazolyl)methane units in a single molecule.[4,5] Specifically, we have prepared multitopic ligands with the general formula $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$, ($n$ = 2, 4, pz = pyrazolyl ring). The reaction of these new ligands with $M(CO)_5Br$ in the presence of AgX (M = Mn and Re, X = BF_4^-, OTf^-) leads to the formation of compounds with the formula $\{C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n[M(CO)_3]_n\}(X)_n$. Reported here is the synthesis, spectral characterization and solid state structure of $\{C_6H_2[CH_2OCH_2C(pz)_3]_4[Mn(CO)_3]_4\}(BF_4)_4$ (**1**), a compound with a 3D sinusoidal architecture containing 16 × 7 Å channels.

Compound **1** was prepared as shown in Scheme 1.† Crystals of the formula $\{C_6H_2[CH_2OCH_2C(pz)_3]_4[Mn(CO)_3]_4\}(BF_4)_4\cdot 6CH_3CN\cdot 2C_4H_{10}O$ were grown by vapor phase diffusion of diethyl ether into an acetonitrile solution of **1**. Single crystal X-ray analysis ‡ shows that each of the tris(pyrazolyl)methane units of the ligand is κ^3-bonded to a $[Mn(CO)_3]^+$ cation, forming a distorted octahedral arrangement around the manganese(I), Fig. 1. The overall structure of the centrosymmetric tetrametallic building block is surprising in that the *ortho*-bonded ligand sidearms are on the *same side* of the connecting arene ring. In the structures of o-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ and 1,2,4,5-$C_6H_2[CH_2OCH_2C(pz)_3]_4$, and the coordination polymers $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ and $\{1,2,4,5\text{-}C_6H_2[(CH_2OCH_2C(pz)_3]_4Ag_2(BF_4)_2\}_n$, adjacent sidearms are on opposite sides of the central arene ring.[5] The driving force for the same side organization observed here is strong intramolecular π–π stacking interactions, shown by dotted lines in Fig. 1, between two pyrazolyl rings located on adjacent arms. The perpendicular distance between the pyrazolyl rings planes is 3.50 Å and the centroid–centroid distance is 3.53 Å, both values significantly below the "cut-off" distance of 3.8 Å for a π–π interaction.[2] The pairs of adjacent arms are on opposite sides of the arene ring, yielding an overall stepped structure for each tetrametallic building block.



Scheme 1 Synthesis of **1**: tris-2,2,2-(1-pyrazoyl)ethanol was prepared as in ref. 4; (i) NaH, thf, reflux, 5 h; (ii) $Mn(CO)_5Br$, $AgBF_4$, acetone, reflux, 2 h.

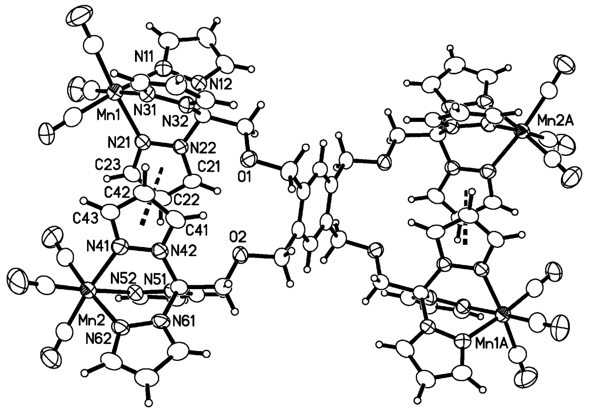


Fig. 1 ORTEP representation and numbering scheme of **1**. Selected bond distances and angles (Å and °): average Mn(1)–C(O) = 1.819; average Mn(2)–C(O) = 1.824; Mn(1)–N(11) = 2.051(3); Mn(1)–N(21) = 2.039(3); Mn(1)–N(31) = 2.035(3); Mn(2)–N(41) = 2.043(3); Mn(2)–N(52) = 2.033(3); Mn(2)–N(62) = 2.046(3); average N–Mn(1)–N = 83.7; average N–Mn(2)–N = 83.7; average (O)C–Mn(1)–C(O) = 90.5; average (O)C–Mn(2)–C(O) = 90.7.

As shown in Fig. 2, the tetrametallic building blocks are organized into a 3D architecture by weak C–H · · · F hydrogen bonds. There are two BF_4^- anions per asymmetric unit; both are involved in weak hydrogen bonds with different organizational functions. One is involved in organizing the tetrametallic building blocks into 2D corrugated sheets and the second organizes the sheets into a 3D network. As shown in the top part of Fig. 3(a), the former BF_4^- ions make a three center-four

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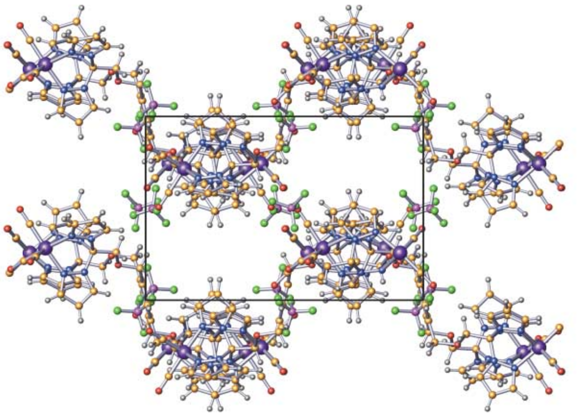

Fig. 2 The supramolecular structure of **1** is a sinusoid-like "function" with respect to the *b* axis; the "wavelength"—measured between three consecutive phenyl centroids from the same sheet—is equal to the *b* axis, 17.6246(13) Å.

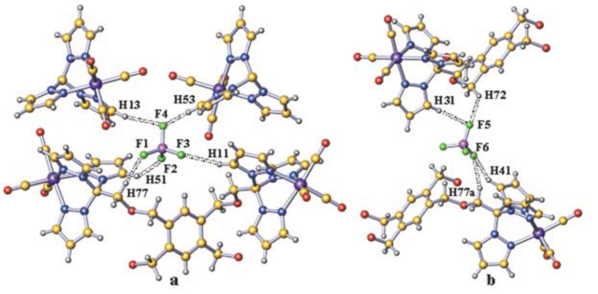

Fig. 3 Non-covalent interactions in **1**: (a) C–H ··· F bonds holding together the corrugated sheets; (b) C–H ··· F bonds involved in the organization of the 3D network.

electron bond that links two $[C(pz)_3Mn(CO)_3]^+$ units from different building blocks. The distances are H(13) ··· F(4) = 2.37 and H(53) ··· F(4) = 2.35 Å, with corresponding C–H ··· F angles of 159 and 158°. The remaining fluorine atoms all bond to a third building block. The bond distances and C–H ··· F angles are: H(77) ··· F(1) = 2.25 Å and 169°; H(51) ··· F(2) = 2.33 Å and 138°; H(11) ··· F(3) = 2.41 Å and 146°. These C–H ··· F interaction link the building blocks into corrugated sheets, two of which are viewed end-on in Fig. 2. The top and bottom rows of six BF_4^- counter-ions in Fig. 2, oriented along the horizontal lines of the unit cell, relate to the one shown in Fig. 3(a).

The second BF_4^- counter-ion is involved in the organization of the corrugated sheets into a 3D architecture. As shown in Fig. 3(b), two of the fluorine atoms are involved in three center-four electron bonds with two building blocks located in separate sheets. Both fluorine atoms make one bond each with a hydrogen from a pz ring and one bond to a methylene group. The distances and C–H ··· F angles are: H(31) ··· F(5) = 2.24 Å and 159° and H(72) ··· F(5) = 2.37 Å and 132° for one fluorine atom and H(41) ··· F(6) = 2.34 Å and 144° and H(77a) ··· F(6) = 2.46 and 141° for the second fluorine atom. All these distances are typical for C–H ··· F weak hydrogen bonds[6] and much shorter than the sum of the van der Waals radii, 2.54 Å.[7] The central row of BF_4^- counter-ions in Fig. 2 relates to the one shown in Fig. 3(b).

The overall 3D structure forms 16 × 7 Å channels defined on four sides by $[C(pz)_3Mn(CO)_3]^+$ octahedra and, additionally, on two sides by central arene rings, alternately left and right. The channels are filled with solvent molecules (acetonitrile and ether), Fig. 4.

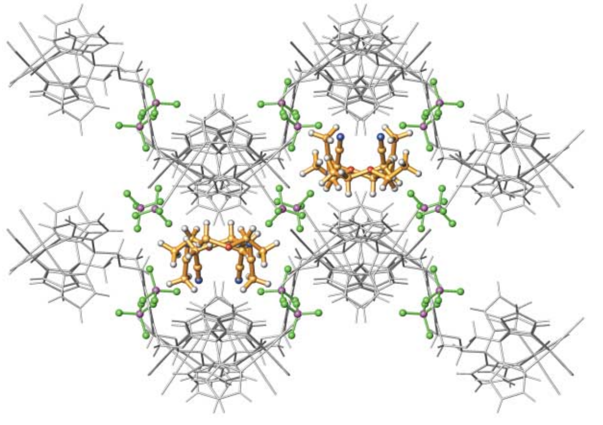

Fig. 4 Solvent molecules in **1**: the 3D architecture is shown as wires, and BF_4^- anions (fluorine in green) and solvent molecules as sticks and balls.

In conclusion, the reaction of $Mn(CO)_5Br$ in the presence of $AgBF_4$ with the new tetratopic ligand $C_6H_2[CH_2OCH_2C(pz)_3]_4$ yields **1**, which was characterized in the solid state by single crystal X-ray diffraction, in solution by ^{1}H and ^{13}C NMR techniques and by ES$^+$-MS spectroscopy. In the solid state, each tetrametallic building block is arranged into a stepped structure by intracation π–π stacking. These building blocks are organized by C–H ··· F weak hydrogen bonds, utilizing the BF_4^- counter-ions, into sinusoidal 2D corrugated sheets. The overall supramolecular structure of **1** is organized by additional C–H ··· F weak hydrogen bonds between the corrugated sheets forming solvent-filled 16 × 7 Å channels.

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Notes and references

† Calcd. for $C_{66}H_{54}B_4F_{16}Mn_4N_{24}O_{16}$: C, 39.51; H, 2.71; found C, 39.16; H, 3.19%; ^{1}H NMR (300 MHz, CD_3CN, all br): δ 8.20, 8.11 (2 × 12H, 3,5-H pz) 7.99 (2H, C_6H_2), 5.95 (12H, 4-H pz), 5.48 (8H, OCH_2Ph), 5.25 (8H, $OCH_2C(pz)_3$); ^{13}C NMR (500 MHz, CD_3CN): δ 220.3 (CO) 148.6, 136.0 (3,5-C pz), 136.7, 135.1 (C_6H_2), 108.8 (4-C pz), 83.6 ($C(pz)_3$), 71.6, 67.4 (CH_2); IR (Nujol) ν/CO: 2051, 1941 cm^{-1}. ES$^+$-MS: *m*/*e* 1919 $\{L[Mn(CO)_3]_4(BF_4)_3\}^+$, 1693 $\{L[Mn(CO)_3]_3(BF_4)_2\}^+$, 1467 $\{L[Mn(CO)_3]_2(BF_4)\}^+$, 1241 $\{L[Mn(CO)_3]\}^+$, where L = $C_6H_2[CH_2OCH_2C(pz)_3]_4$.

‡ Crystal data for $C_{86}H_{92}B_4F_{16}Mn_4N_{30}O_{18}$, **1**: FW = 2400.90; monoclinic; space group $P2_1/c$; a = 11.8441(9); b = 17.6246(13), c = 25.6874(19) Å; β = 99.538(2)°; V = 5288.1(7) Å^3; Z = 2; D_c = 1.508 Mg m^{-3}; μ = 0.573 mm^{-1}; F(000) = 2452; reflections collected = 34997; independent reflections = 10830 [R(int) = 0.0395]. Data were measured at 173(2) K on a Bruker SMART APEX CCD-based diffractometer system (Mo-Kα radiation, λ = 0.71073 Å). The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2 using the SHELXTL software package. The ether molecule of solvation present in the channels displays high thermal motion, reflecting disorder. Six geometric restraints were used to model the average coordinates of this species. GOF on F^2 = 1.042; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0688, $wR2$ = 0.2000; R indices (all data): $R1$ = 0.0938, $wR2$ = 0.2164. CCDC reference number 175724. See http://www.rsc.org/suppdata/dt/b1/b110095e/ for crystallographic data in CIF or other electronic format.

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