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Manganese(II) β-Diketonate Complexes with Pyridin-4-one, 3-Hydroxypyridin-2-one and 1-Fluoropyridine Ligands: Molecular Structures and Hydrogen-bonded Networks

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Abstract

Manganese(II) bis(4,4,4-trifluoro-1-phenylbutane-1,3-dionate) complexes with pyridin-4-one (pyon), 3-hydroxyopyridin-2-one (hpyon), 1-fluoropyridine (pyF) and methanol were prepared and the solid-state structures were determined by single-crystal X-ray analysis. The coordination of the metal center in all complexes was found to be octahedral. In compounds [Mn(tfpb)$_2$(pyon)$_2$] (1) and [Mn(tfpb)$_2$(hpyon)$_2$] (2) extended hydrogen bonding is present facilitating the formation of a three-dimensional supramolecular structure in 1 and a layered structure in 2 through N–H···O hydrogen bonding enhanced by C–H···π interactions as well as C–F···π interactions. In [Mn(tfpb)$_2$(pyF)$_2$] (3) a layered structure is formed through C–H···O and C–H···F interactions as well as π···π and C–F···π interactions. In [Mn(tfpb)$_2$(MeOH)$_2$] (4) a layered structure is formed through a combination of O–H···O and C–F···π interactions.

Keywords: β-Diketonates; manganese; pyridines; crystal structure; π···π interaction

1. Introduction

Inorganic–organic hybrids, metal–organic coordination polymers and especially metal–organic frameworks (MOFs) are currently an extremely important topic and an active area of research because of their intriguing architectures and topologies, as well as due to their potential applications in catalysis, chemical separation processes, wastewater treatment, gas storage, magnetism and as sensors. Control of the solid-state arrangement of molecules within a crystal is the central challenge of materials chemistry. In metal–organic frameworks and coordination polymers, covalent bonding using bridging organic linkers for creation of robust polymeric structures is of prime importance. Various kinds of these materials have been designed with special attention dedicated to the geometry of the metal ions as well as flexibility, bridging potential and coordination preferences of different organic linkers. On the other hand, in inorganic–organic hybrids non-covalent bonds adjust the dimensionality and enable new topologies to arise. Non-covalent forces, such as hydrogen bonding, C–H···π/F interactions, π···π stacking, and halogen bonding are much weaker compared to the covalent bonds, however, their multitude makes them a powerful tool in the crystal engineering. Also, a great variety of non-covalent donors–acceptors and their numbers, their unique directionality and simple introduction into structures make them a particularly good choice for the construction of self-assemblies.

Here we report the influence of pyridin-4-one (4-pyridone; pyon), 3-hydroxyopyridin-2-one (hpyon), and 1-fluoropyridine (pyF) ligands on the molecular and supramolecular structure in the cases of [Mn(tfpb)$_2$(pyon)$_2$] (1), [Mn(tfpb)$_2$(hpyon)$_2$] (2), [Mn(tfpb)$_2$(pyF)$_2$] (3) complexes as well as the structure of [Mn(tfpb)$_2$(MeOH)$_2$] (4), where tfpb is the 4,4,4-trifluoro-1-phenylbutane-1,3-dionate (or 4,4,4-trifluoro-3-oxo-1-phenylbutan-1-olate) ligand. The tfpb ligand was selected because it is not symmetric and possesses phenyl and trifluoromethyl groups enabling also the formation of C–H···F , F···F and C–F···π interactions besides the π···π and C–H···π interactions. Pyridin-4-one and 3-hydroxyopyridin-2-one were selected since the tautomeric equilibrium between the lactam and lactim forms enables various coordination modes and also
due to their different hydrogen bond formation abilities when coordinated in lactam/lactim form. On the other hand, 1-fluoropyridine was selected in order to be able to study the influence of an additional fluorine substituent on the formation of supramolecular aggregation in the absence of the competing strong hydrogen bond donors.

2. Experimental

2.1. Materials and Characterization

Reagents and chemicals were obtained as reagent grade from commercial sources and were used as purchased without any further purification. [Mn(tfpb)_2(H_2O)_2] was prepared according to the literature procedure. Infrared (IR) spectra (4000–600 cm\(^{-1}\)) of the samples were recorded using a Perkin–Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. Elemental (C, H, N) analyses were obtained using a Perkin–Elmer 2400 Series II CHNS/O Elemental Analyzer.

2.2. Synthesis

Synthesis of [Mn(tfpb)_2(pyon)_2] (1)

[Mn(tfpb)_2(H_2O)_2] (0.065 g, 0.125 mmol) was dissolved in warm methanol (12 mL) and then pyon (0.024 g, 0.250 mmol) was added. The reaction mixture was stirred for 15 min at ~60 °C and then allowed to stand at room temperature. Orange crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent over a few days. Yield: 0.040 g, 58%. Anal. Calcd. [Mn(tfpb)_2(pyon)_2] (C_{30}H_{20}F_8MnN_2O_4) (MW = 679.42): C 53.92, H 2.97, N 4.12; Found C 53.92, H 2.97, N 4.10.

Synthesis of [Mn(tfpb)_2(MeOH)_2] (4)

[Mn(tfpb)_2(H_2O)_2] (0.065 g, 0.125 mmol) was dissolved in warm methanol (12 mL) and then pyon (0.024 g, 0.250 mmol) was added. The reaction mixture was stirred for 15 min at ~60 °C and then allowed to stand at room temperature. Orange crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent over a few days. Yield: 0.040 g, 58%. Anal. Calcd. [Mn(tfpb)_2(MeOH)_2] (C_{22}H_{20}F_8MnO_6) (MW = 549.32): C 48.10, H 3.67; Found C 47.94, H 3.38. IR (ATR, cm\(^{-1}\)): 2538br, 1928w, 1876w, 1644m, 1609w, 1597m, 1574s, 1532m, 1490m, 1458m, 1318m, 1281s, 1248m, 1182s, 1129s, 1096m, 1075m, 1025w, 941w, 798w, 768m, 718m, 699s, 635s.

Synthesis of [Mn(tfpb)_2(Hpyon)_2] (2)

[Mn(tfpb)_2(H_2O)_2] (0.065 g, 0.125 mmol) was dissolved in warm ethanol (12 mL) and then hpyon (0.024 g, 0.250 mmol) was added. The reaction mixture was stirred for 15 min at ~60 °C and then allowed to stand at room temperature. Orange crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent over a few days. Yield: 0.036 g, 43%. Anal. Calcd. [Mn(tfpb)_2(Hpyon)_2] (C_{30}H_{20}F_8MnN_2O_4) (MW = 679.42): C 53.92, H 2.97, N 4.12; Found C 53.92, H 2.97, N 4.10.

Synthesis of [Mn(tfpb)_2(pyF)_2] (3)

[Mn(tfpb)_2(H_2O)_2] (0.065 g, 0.125 mmol) was dissolved in pyF (2 mL). The reaction mixture was stirred for 15 min at ~60 °C and then allowed to stand at room temperature. Orange crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent over a few days. Yield: 0.045 g, 53%. Anal. Calcd. [Mn(tfpb)_2(pyF)_2] (C_{30}H_{20}F_8MnN_2O_4) (MW = 679.42): C 53.02, H 2.97, N 4.12; Found C 52.55, H 2.81, N 3.99.

2.3. X-ray Crystallography

Single-crystal X-ray diffraction data were collected at room temperature (1, 2, 4) or 150 K (3) on a Nonius Kappa CCD diffractometer or an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å). The data were processed using DENZO\(^6\) or Crysalis Pro.\(^7\) The structures were solved by direct methods implemented in SHELXS\(^8\) and SIR-97\(^9\) and refined by a full-matrix least-squares procedure based on \(F^2\) with SHELXL\(^8\). All non-hydrogen atoms were refined anisotropically. All H atoms were initially located in a difference Fourier maps. The hydrogen atoms on carbon atoms were treated as riding atoms in geometrically idealized positions. Hydrogen atoms attached to nitrogen and oxygen atoms were refined fixing the bond lengths and isotropic temperature factors as \(U_{eq}(H) = kU_{eq}(N,O)\), where \(k = 1.5\) for OH groups, and 1.2 for NH groups. In 1 and 4 the CF\(_3\) groups are disordered for NH groups. In 1 and 4 several attempts of its synthesis other solvents were used instead. Compounds 1 and 2 were obtained by the reaction of...
shows two bands at 3244 and 3080 cm\(^{-1}\) and the spectrum at room temperature over a few days. The IR spectrum of analyses were obtained by slow evaporation of the solvent as a solvent and as a ligand. Crystals suitable for X-ray respectively. Compound (hpyon) in 1:2 molar ratio in warm ethanol or acetone, re-
gands pyridine-4-on (pyon) and 3-hydroxypyridine-2-on [Mn(tfpb)\(_2\)] in warm 1-fluoropyridine (pyF) acting
bands in the frequency range 1609–1527 cm\(^{-1}\) characteris-
tive for the \(\nu(C=O)\) and \(\nu(C=C)\) stretching of the tfpb li-
ger. In all four compounds, there are
strong hydrogen bonding. In all four compounds, there are
volvement of the O–H groups of methanol ligands in
shows one broad band at 3381 cm\(^{-1}\) that suggests the in-
gands in strong hydrogen bonding. The spectrum of
volvement of the O–H and N–H groups of pyridone li-
[C=O] and [C=C] stretching of the tfpb li-
[Mn(tfpb)\(_2\)](pyon)\(_2\)] and the corresponding heteroaromatic
licands pyridine-4-on (pyon) and 3-hydroxypyridine-2-on (hpyon) in 1:2 molar ratio in warm ethanol or acetone, re-
ions being 14.48(6) and 16.47(6)\(^{\circ}\). In both com-
axes are oriented in the opposite direction (Fig. 2) with pyon
ring and the plane of the equatorial MnO4 core deviates
from 90\(^{\circ}\) being 78.60(5)° (for A) and only 44.51(5)° (for B).
Superposition of both complexes shows that pyon ligands
oriented in the opposite direction (Fig. 2) with pyon
ring in complex B inclined toward the phenyl ring of the
tfpb ligand. Complex A is stabilized by an intramolecular
molecular C22–H22–O2\(^{\circ}\) interaction between pyon and tfpb ligand
Table 3) and C1–F3a/b–π interactions between –CF\(_3\)
angles of 130.4(5) and
Cg3 distances of 3.769(10) and
3.82(4)\(^{\circ}\) and C–F–Cg3 angles of 130.4(5) and
128.3\(^{\circ}\), respectively, where Cg3 is N1/C21–C25 ring cen-
troid (Fig. 3). Complex B is stabilized by an intramolecular

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**Table 1.** Crystallographic and refinement data for 1–4.

| Parameter | [Mn(tfpb)\(_2\)](pyon)\(_2\)] \((1)\) | [Mn(tfpb)\(_2\)](hpyon)\(_2\)] \((2)\) | [Mn(tfpb)\(_2\)](pyF)\(_2\)] \((3)\) | [Mn(tfpb)\(_2\)](MeOH)\(_2\)] \((4)\) |
| --- | --- | --- | --- | --- |
| Formula | C\(_{30}\)H\(_{22}\)F\(_6\)MnN\(_2\)O\(_6\) | C\(_{30}\)H\(_{22}\)F\(_6\)MnN\(_2\)O\(_8\) | C\(_{30}\)H\(_{20}\)F\(_8\)MnN\(_2\)O\(_4\) | C\(_{22}\)H\(_{20}\)F\(_6\)MnO\(_6\) |
| \(M_r\) | 675.43 | 707.43 | 679.42 | 549.32 |
| \(T\) (K) | 293(2) | 293(2) | 150(2) | 293(2) |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | \(P_{2}_1/n\) | \(P\)–1 | \(P_{2}_1/c\) | \(P\)–1 |
| \(a\) (Å) | 16.1805(3) | 7.3146(2) | 11.8720(3) | 10.4921(4) |
| \(b\) (Å) | 10.5318(2) | 9.9367(2) | 8.8105(2) | 10.5763(4) |
| \(c\) (Å) | 17.8217(3) | 10.7440(2) | 14.5507(4) | 12.4197(5) |
| \(\alpha\) (°) | 90 | 90 | 90 | 90 |
| \(\beta\) (°) | 91.558(2) | 100.589(2) | 108.628(3) | 70.893(2) |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 |
| Volume (Å\(^3\)) | 3035.87(10) | 726.16(3) | 1442.24(7) | 1195.92(8) |
| \(Z\) | 4 | 1 | 2 | 2 |
| \(D_{calc}\) (Mg/m\(^3\)) | 1.478 | 1.618 | 1.565 | 1.525 |
| \(\mu\) (mm\(^{-1}\)) | 0.517 | 0.549 | 0.549 | 0.634 |
| \(F(000)\) | 1372.0 | 359.0 | 1378.9 | 9395 |
| Reflections collected | 6949/2/471 | 3298/2/220 | 3311/0/205 | 5457/2/353 |
| Data/restraints/parameters | 28841 | 5959 | 13789 | 9395 |
| \(R\) | 0.0416, 0.1040 | 0.0328, 0.0882 | 0.0399, 0.0961 | 0.0459, 0.1073 |
| \(R_{int}\) | 0.0322 | 0.0133 | 0.0333 | 0.0291 |
| \(R\) | 0.0416, 0.1040 | 0.0328, 0.0882 | 0.0399, 0.0961 | 0.0459, 0.1073 |
| \(R\) | 0.0322 | 0.0133 | 0.0333 | 0.0291 |
| \(S\) & \(GOF\), \(\overline{S}\) | 1.051 | 1.074 | 1.044 | 1.012 |
| Max/min \(\Delta\rho\) (e/Å\(^3\)) | 0.21/–0.21 | 0.31/–0.34 | 0.83/–0.27 | 0.32/–0.27 |

\(a\) \(R = \sum_{}|F_o| – |F_c|/\sum_{}|F_o|\). \(b\) \(wR_2 = \sum_{}(w(F_o^2 – F_c^2)^2)/\sum_{}w(F_o^2)^2\)\(^{1/2}\). \(c\) \(S = \{(\sum_{}(F_o^2 – F_c^2)^2)/n/p\}^{1/2}\) where \(n\) is the number of reflections and \(p\) is the total number of parameters refined.
C27–H27···O4ii interaction between pyon and tfpb ligand. The NH groups of the pyon ligands of both independent complexes act as hydrogen-bond donors interacting with the tfpb carbonyl oxygens of the adjacent complexes, facilitating the formation of a hydrogen-bonded tree-dimensional supramolecular structure (Fig. 3). Complex A interacts with two complexes B through N1–H1···O6iii bonding enabling the formation of an ABAB chain. Complex B interacts with two complexes A through N2–H2···O3 bonding enhanced by C26–H26···O1i interaction with R22(7) ring motif11 enabling the formation of an ABAB chain in the second dimension. Furthermore, complex B interacts with two adjacent complexes B through the centrosymmetric C29–H29···F6aiv interactions with R22(18) ring motif forming a BBB chain in the third dimension (Table 3).

Table 2. Selected bond distances and angles for 1.

| Distance (Å)                  | Angle (°)            |
|-------------------------------|----------------------|
| Mn1–O1                        | 2.1365(14)           | O1–Mn1–O2                           | 84.10(5)   |
| Mn1–O2                        | 2.1233(13)           | O1–Mn1–O3                           | 85.43(5)   |
| Mn1–O3                        | 2.2358(12)           | O2–Mn1–O1                           | 86.91(5)   |
| Mn2–O4                        | 2.1245(13)           | O2–Mn1–O2                           | 94.57(5)   |
| Mn2–O5                        | 2.1467(13)           | O2–Mn1–O3                           | 93.09(5)   |
| Mn2–O6                        | 2.2035(12)           | O3–Mn1–O1                           | 94.18(5)   |
| O1–Mn2–O5                     | 85.38(5)             | O3–Mn1–O2                           | 94.80(5)   |
| O4–Mn2–O6                     | 85.82(5)             | O3–Mn1–O3                           | 94.18(5)   |
| O4–Mn2–O6i                    | 94.18(5)             | O4–Mn2–O6                          | 94.80(5)   |
| O4–Mn2–O6ii                   | 95.90(5)             | O5–Mn2–O6                          | 94.80(5)   |
| O4–Mn2–O6iv                   | 94.62(5)             | O5–Mn2–O6                          | 94.80(5)   |
| O4–Mn2–O6v                    | 94.62(5)             | O5–Mn2–O6                          | 94.80(5)   |
| O4–Mn2–O6vii                  | 95.90(5)             | O5–Mn2–O6                          | 94.80(5)   |
| O4–Mn2–O6vi                   | 94.80(5)             | O5–Mn2–O6                          | 94.80(5)   |

Symmetry codes: (i) 1 – x, −y, −z; (ii) 1 – x, −y, 1 – z.

Figure 1. Crystallographically independent molecules in 1. Disorder on CF3 groups has been omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.

Figure 2. Superposition of crystallographically independent molecules A (green) and B (orange) in 1. Disorder on CF3 groups has been omitted for clarity.
The supramolecular structure is further stabilized also by C11–F4a···π interaction between –CF3 group of complex B and pyon ring of complex A with F···Cg3 distance of 3.806(11) Å and C–F···Cg3 angle of 139.1(5)°.

Compound 2 crystallizes in the triclinic P–1 space group. Selected bond distances and angles are summarized in Table 4. The asymmetric unit contains one half of the complex, with the MnII atom sitting on the inversion center. Octahedrally coordinated manganese(II) atom is surrounded by four oxygen atoms positioned in the equatorial plane, stemming from two chelating tfpb ligands in a trans arrangement, with Mn–O distances 2.1132(10) and 2.1218(9) Å (Fig. 4). The Mn(tfpb)2 fragment deviates from planarity, the angle between the mean plane formed by the equatorial MnO4 core and that of the tfpb chelate C3O2 moiety being 15.91(4)°. The axial positions are occupied by two hpyon ligands bonded to the metal center through the O3 atom, with Mn1–O3 distance of 2.2768(10) Å and Mn1–O3–C11 angle of 128.19(9)°. The hpyon ligand is inclined toward the tfpb moiety, with the angle between the plane of the hpyon ring and that of the equatorial MnO4 core being 43.25(6)°. The hydroxy group of the hpyon ligand is involved in intramolecular hydrogen bonding with the tfpb ligand through O4–H4···O1i interaction (Table 3). The NH group of the hpyon ligand acts as a hydrogen bond donor, facilitating the formation of a centrosymmetric hydrogen-bonded motif via N1–H1···O3ii interactions with the ligated carbonyl O3 atom enhanced by C15–H15···O2iv interactions with the graph set motifs R22(8) and R22(7), respectively (Fig. 5 and Table 3). This interaction is further stabilized by C1–F3···π interaction between CF3 group and the hpyon ring with d(F3···Cg3) = 3.2278(17) Å and <(C1–F3···Cg3) = 135.64(11)°, where Cg3 is N1/C11–C15 ring centroid. Consequently, a chain is formed along the a axis. The chains are further connected into layers along the ac plane via centrosymmetric C13–H13···O4iii hydrogen bonding between hypon CH moiety and the hydroxy group of the adjacent molecule (Fig. 5). There are no significant π···π interactions.

The supramolecular structure is further achieved by hydrogen bonding around a) molecule A and b) molecule B through a series of N1–H1···O6iii, N2–H2–O3, C26–H26–O1i and C29–H29–F6aiv interactions. Blue dashed lines indicate hydrogen bonds. For the sake of clarity, intramolecular interactions, disorder on CF3 groups and H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.

### Table 3. Hydrogen bonds for 1–4 [Å and °]

| D–H···A | d(D–H)  | d(H···A)  | d(D···A)  | <(DHA) |
|---------|---------|---------|---------|-------|
| 1       | N1–H1···O6iii | 0.872(17) | 1.854(17) | 2.720(2) | 172(3) |
| N2–H2···O3  | 0.888(16) | 1.859(17) | 2.723(2) | 164(2) |
| C22–H22···O2i | 0.93     | 2.36     | 3.119(3) | 139.1 |
| C26–H26···O1i | 0.93     | 2.48     | 3.322(2) | 151.1 |
| C27–H27···O4ii | 0.93    | 2.47     | 3.206(2) | 136.6 |
| C29–H29···F6aiv | 0.93   | 2.47     | 3.394(7) | 175.7 |
| 2       | O4–H4···O1i | 0.814(17) | 1.952(18) | 2.7495(16) | 166(3) |
| N1–H1···O3iii | 0.882(14) | 2.009(15) | 2.8829(15) | 170.2(18) |
| C13–H13···O4ii | 0.93    | 2.58     | 3.4770(19) | 162.9 |
| C15–H15···O2iv | 0.93    | 2.42     | 3.2428(19) | 147.3 |
| 3       | C13–H13···F2ii | 0.95     | 2.42     | 3.287(3) | 151.6 |
| C14–H14···O1i | 0.95    | 2.58     | 3.493(3) | 161.3 |
| 4       | O5–H5···O1i | 0.822(10) | 1.966(14) | 2.772(2) | 167(4) |
| O6–H6···O3i | 0.813(10) | 2.001(13) | 2.801(2) | 168(4) |

Symmetry codes for 1: (i) 1 – x, –y, –z; (ii) 1 – x, 1 – y, 1 – z; (iii) –½ + x, ½ – y, –½ + z; (iv) 1 – x, 1 – y, 1 – z; for 2: (i) 2 – x, 2 – y, –z; (ii) 2 – x, 1 – y, 1 – z; (iii) 2 + x, 2 – y, 1 – z; (iv) 1 + x, y, 0; for 3: (i) –½ + x, ½ – y, –½ + z; (ii) x, ½ + y, ½ + z; for 4: (i) 2 – x, 1 – y, 1 – z; (ii) 2 – x, –y, 1 – z.

Figure 3. Three-dimensional supramolecular structure in 1 is achieved by hydrogen bonding around a) molecule A and b) molecule B through a series of N1–H1···O6iii, N2–H2–O3, C26–H26–O1i and C29–H29–F6aiv interactions. Blue dashed lines indicate hydrogen bonds. For the sake of clarity, intramolecular interactions, disorder on CF3 groups and H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.
In the solid state, pyridin-4-one and 3-hydroxypyridin-2-one are in the lactam form. Also in metal complexes, pyridin-4-one, in its lactam form, is bonded to the metal center. For comparison, metal complexes with pyridine-2-one were more often investigated than complexes with pyridin-4-one and 3-hydroxypyridin-2-one and a variety of coordination modes has been observed. Compound 3 crystallizes in the monoclinic $P2_1/c$ space group. Selected bond distances and angles of Table 5. Initial attempts to collect XRD data at room temperature failed due to slow decomposition of the crystal when exposed to the air. Most probably 1-fluoropyridine molecule is eliminated from the complex and the crystal lattice is being thus destroyed. Similar loss of pyridine bonded in zinc picolinato complexes has been previously observed.21,23,24

The asymmetric unit contains one half of the complex, with the Mn$^{11}$ atom sitting on the inversion center. The manganese(II) atom in compound 3 is octahedrally coordinated (Fig. 6). In the equatorial plane, Mn$^{11}$ atom is surrounded by four oxygen atoms where pyridin-4-one, in its lactam form, is bonded to the metal center through the N1 atom, while two pyF ligands bonded to the metal center through the O3 atom. Superposition of both crystallographic independent molecules in 1 as well as mole-
Figure 5. a) Hydrogen-bonded layer along the ac plane in 2 is formed by b) centrosymmetric N1–H1···O3, C15–H15···O2, and C1–F3···Cg3 interactions and c) C13–H13···O4 interactions; d) packing of layers (arbitrary colors). Blue and green dashed lines indicate hydrogen bonds and C–F···π interactions, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.

Figure 6. Structure of 3. Displacement ellipsoids are drawn at 50% probability level.
In the case of molecule B in 1 and molecule 2 also the phenyl rings of tfpb are evidently inclined toward pyridone moieties.

Compound 4 crystallizes in the triclinic P–1 space group. Selected bond distances and angles of 4 are summarized in Table 6. The asymmetric unit contains one complex molecule with cis-octahedral arrangement of methanol ligands on the manganese(II) central atom (Fig. 9). Two methanol ligands are bonded to the metal center with Mn1–O5 and Mn1–O6 distances of 2.1714(18) and 2.173(2) Å, respectively, and O5–Mn1–O6 angle of 88.54(8)°. The Mn–O bond lengths with four oxygen atoms of the two chelating tfpb ligands are asymmetric with the longer ones of 2.1821(18) and 2.1751(17) Å at the trifluoromethyl substituent and the shorter ones of 2.1266(18) and 2.1315(18) Å at the phenyl substituent. The Mn(tfpb) fragments deviate from planarity, the tfpb ligands being in-

**Table 5.** Selected bond distances and angles for 3.

| Distance   | Å       | Angle  | °     |
|------------|---------|--------|-------|
| Mn1–N1     | 2.3425(17) | N1–Mn1–O1  | 94.36(6) |
| Mn1–O2     | 2.1337(14) | N1–Mn1–O1i | 85.64(6) |
| N1–Mn1–O1  | 94.36(6)  | N1–Mn1–O1i | 85.64(6) |
| N1–Mn1–O2  | 88.31(6)  | N1–Mn1–O2ii | 91.69(6) |
| O1–Mn1–O2  | 85.12(5)  | O1–Mn1–O2ii | 94.88(5) |

Symmetry code: (i) –x, –y, –z.

**Figure 7.** a) Hydrogen-bonded layer along the ac plane in 3 is formed by C13–H13–O1iii and centrosymmetric C14–H14–F2ii interactions as well as centrosymmetric π–π interactions and C–F–π interactions; b) packing of layers (arbitrary colors). Blue and green dashed lines indicate hydrogen bonds and π–π and C–F–π interactions, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.

**Figure 8.** a) Hydrogen-bonded layer along the ac plane in 3 is formed by C13–H13–O1iii and centrosymmetric C14–H14–F2ii interactions as well as centrosymmetric π–π interactions and C–F–π interactions; b) packing of layers (arbitrary colors). Blue and green dashed lines indicate hydrogen bonds and π–π and C–F–π interactions, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.

**Figure 7.** a) Hydrogen-bonded layer along the ac plane in 3 is formed by C13–H13–O1iii and centrosymmetric C14–H14–F2ii interactions as well as centrosymmetric π–π interactions and C–F–π interactions; b) packing of layers (arbitrary colors). Blue and green dashed lines indicate hydrogen bonds and π–π and C–F–π interactions, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.

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Figure 8. Two views on superposition of crystallographically independent molecules A (green) and B (orange) in 1, 2 (blue) and 3 (violet). Disorder on CF$_3$ groups has been omitted for clarity.

Figure 9. Structure of 4. Disorder on both CF$_3$ groups has been omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.

Figure 10. a) Hydrogen-bonded chain along $b$ axis in 4 formed by centrosymmetric O5–H5–O1' and O6–H6–O3' interactions; b) chains are linked into a layer through C–F–π interactions. Blue and green dashed lines indicate hydrogen bonds and C–F–π interactions, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted. For symmetry codes see Table 3.
clined by 25.94(8) and 23.51(8)°. Each methanol ligand is involved in a centrosymmetric hydrogen-bonded motif via O5–H5⋯O1 and O6–H6⋯O3 interactions with the carboxyl oxygen atom at the trifluoromethyl substituent of the adjacent complex. Both centrosymmetric hydrogen bonds have the graph-set motif R2(3) (Fig. 10 and Table 3) and enable the formation of a hydrogen-bonded chain along the b axis. A centrosymmetric Cl–F3⋯π interaction between CF3 group and the benzene ring of tpb ligand of the adjacent molecule is present with d(F3–Cg3) = 3.661(4) Å and <(C1–F3–Cg3) = 121.9(3)°, where Cg3 is C5–C10 ring centroid, connecting chains into a layer along the bc plane (Fig. 10). There are no significant π⋯π interactions.

Table 6. Selected bond distances and angles for 4.

| Distance   | Å      | Angle | °      |
|------------|--------|-------|--------|
| Mn1–O1     | 2.1821(18) | Mn1–O2 | 2.1266(18) |
| Mn1–O3     | 2.1751(17) | Mn1–O4 | 2.1315(18) |
| Mn1–O5     | 2.1714(18) | Mn1–O6 | 2.173(2) |

4. Conclusion

We have prepared and structurally characterized four manganese(II) bis(4,4,4-trifluoro-1-phenylbutane-1,3-dionate) complexes with pyon, hpyon, pyF and methanol ligands. In all prepared compounds the coordination of crystal aggregation due to the absence of the competing strong hydrogen bond donors. A layered structure is formed through C–H⋯O and C–H⋯F interactions as well as π⋯π and C⋯F⋯π interactions. In 4 a layered structure is formed through a combination of O–H⋯O and C⋯F⋯π interactions.

Supplementary Material

CCDC 2024368–2024371 (1–4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Povzetek

Sintetizirali smo manganove(II) bis(4,4,4-trifluoro-1-fenilbutan-1,3-dionato) komplekse s piridin-4-onom (pyon), 3-hidroksipiridin-2-onom (hpyon), 1-fluoropiridinom (pyF) in metanolom ter določili strukture z monokristalno rentgen- sko difrakcijo. V vseh kompleksih je koordinacija kovinskega centra oktaedrična. Pri spojinah [Mn(tfpb)₂(pyon)]₂ (1) in [Mn(tfpb)₂(hpyon)]₂ (2) so prisotne številne vodikove vezi, ki omogočajo tvorbo tridimenzionalne supramolekularne strukture v 1 in plastovite strukture v 2 z N–H···O vodikovimi vezmi ojačane z C–H···O interakcijami ter tudi C–F···π interakcije. Pri [Mn(tfpb)₂(pyF)]₂ (3) je prisotna plastovita struktura z C–H···O in C–H···F interakcijami ter tudi z π···π in C–F···π interakcijami. Pri [Mn(tfpb)₂(MeOH)]₂ (4) je prisotna plastovita struktura s kombinacijo O–H···O in C–F···π interakcij.

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