

Cis- and trans-derived chain stacking in bis(hexafluoroacetylacetonato)metal(II) tetramethylpyrazine complexes

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Abstract

The reaction of metal(II) hexafluoroacetylacetonates (metal = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)) with tetramethylpyrazine is reported. The X-ray crystal structures of $[\text{Mn}(\text{hfac})_2]_2(\text{tmp})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{hfac})_2(\text{tmp}) \cdot 4\text{H}_2\text{O}$ are reported and reveal the formation of chain polymers through second sphere *cis*- and *trans*-derived stacking, respectively.

Introduction**

The reaction of aquabis(hexafluoroacetylacetonato)-copper(II) $[\text{Cu}(\text{hfac})_2(\text{H}_2\text{O})]$ with pyrazine (pyz) in a 1:1 ratio gave $\text{Cu}(\text{hfac})_2(\text{pyz})$, the crystal structure of which revealed a linear infinite chain polymer with the $\text{Cu}(\text{hfac})_2$ moieties bridged by the pyz rings [1]. An extension of this reaction gave the corresponding $\text{M}(\text{hfac})_2(\text{pyz})$ complexes ($\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II})$) but no crystals were obtained which were suitable for X-ray structural analysis [2]. A further extension using tetramethylpyrazine (tmp) has led to the isolation of a series of compounds $[\text{M}_k\{(\text{hfac})_2\}_l(\text{tmp})_m] \cdot m\text{H}_2\text{O}$, $\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II})$; $k = 1, 2$; $l = 1-3$; $m = 1-4$. The preparation of these compounds and the X-ray crystal structures of $[\text{Mn}(\text{hfac})_2]_2(\text{tmp})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{hfac})_2(\text{tmp}) \cdot 4\text{H}_2\text{O}$ are reported herein.

Experimental

The metal β -diketonates were prepared by literature procedures [3, 4]. Microanalyses were carried out by the University of Sheffield Microanalytical Service.

Synthesis of $[\text{M}_k\{(\text{hfac})_2\}_l(\text{tmp})_m] \cdot m\text{H}_2\text{O}$

Aquated $\text{M}(\text{hfac})_2$ (1 mmol) was suspended in CCl_4 or n-hexane; to this was added a clear solution of

tetramethylpyrazine (1 mmol in $10 \text{ cm}^3 \text{ CCl}_4$ or 2 mmol in $10 \text{ cm}^3 \text{ n-hexane}$). The mixture was stirred at reflux temperature for 2 h and filtered rapidly whilst hot. On cooling the product precipitated and was collected. The yields varied from 40 to 60%. Microanalytical data for the bulk samples are given in Table 1. Samples for X-ray analysis were recrystallised from n-hexane.

X-ray analysis

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet R3 4-circle diffractometer by the omega scan method. The structures were solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Complex scattering factors were taken from ref. 5 and from the program package SHELXTL [6] as implemented on the Data General Nova 3 computer. Unit weights were used throughout the refinement. Table 2 lists the crystallographic data and Tables 3 and 4 list atomic positional parameters with estimated standard deviations. See also 'Supplementary Material'.

For $[\{\text{CF}_3\text{C}(\text{O})\text{C}(\text{H})\text{C}(\text{O})\text{CF}_3\}_2(\text{OH}_2)_2\text{Co}]\{(\text{CH}_3)_4\text{C}_4\text{N}_2\} \cdot 2\text{H}_2\text{O}$ the independent reflections were corrected for Lorentz and polarisation effects and for absorption. Both trifluoromethyl groups were rotationally disordered, and were refined with geometrical constraints which imposed a common carbon-fluorine bond length and local C_{3v} symmetry. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode.

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**Hexafluoroacetylacetonone = 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

TABLE 1. Microanalytical data for the complexes (the calculated values are given in parentheses)

| Ratio of reactants | Complex | C (%) | H (%) | N (%) | Colour |
|--------------------|---|------------------|----------------|----------------|--------------|
| 1:1 | Mn(hfac) ₂ (tmp)·2H ₂ O | 33.90 (33.68) | 3.05 (2.82) | 4.30 (4.36) | yellow |
| 1:2 | [Mn(hfac) ₂] ₂ (tmp) ₃ ·4H ₂ O | 37.20 (37.25) | 3.00 (3.41) | 5.13 (5.90) | yellow |
| 1:1 | Fe(hfac) ₂ (tmpH·hfac) | 34.11 (33.93) | 1.96 (1.98) | 3.37 (3.44) | purple |
| 1:2 | Fe(hfac) ₂ (tmp) ₂ ·3H ₂ O | 39.41 (39.21) | 3.66 (4.04) | 6.62 (7.03) | deep purple |
| 1:1 | Co(hfac) ₂ (tmp)·2H ₂ O | 33.27 (33.40) | 2.98 (2.81) | 4.14 (4.34) | light brown |
| 1:2 | Co(hfac) ₂ (tmp) ₂ ·2H ₂ O | 39.72 (39.96) | 3.77 (3.86) | 6.76 (7.16) | orange-brown |
| 1:1 | Cu(hfac) ₂ (tmp) | 35.65 (35.19) | 2.42 (2.29) | 4.59 (4.56) | deep green |
| 1:2 | [Cu(hfac) ₂] ₂ (tmp) ₃ ·3H ₂ O | 37.19 (37.28) | 3.96 (3.27) | 5.41 (5.93) | light green |
| 1:1 | Zn(hfac) ₂ (tmp)·H ₂ O | 34.35 (34.88) | 3.10 (2.54) | 5.09 (4.42) | white |
| 1:2 | Zn(hfac) ₂ (tmp) ₂ ·2H ₂ O | 39.54 (39.63) | 3.74 (3.83) | 6.93 (7.11) | white |

TABLE 2. Crystal data

| Compound | [(CF ₃ C(O)C(H)C(O)CF ₃) ₂ (OH ₂) ₂ Co]- {(CH ₃) ₄ C ₄ N ₂ }·2H ₂ O | [(CF ₃ C(O)C(H)C(O)CF ₃) ₂ (OH ₂) ₂ Mn]- {(CH ₃) ₄ C ₄ N ₂ } _{1.5} |
|---|---|--|
| Formula | C ₁₈ H ₂₂ F ₁₂ N ₂ O ₈ Co | C ₂₂ H ₂₄ F ₁₂ N ₃ O ₆ Mn |
| <i>M_r</i> | 681.29 | 709.36 |
| Crystal dimensions (mm) | 0.475 × 0.350 × 0.175 | 0.60 × 0.40 × 0.30 |
| Crystal appearance | yellow–orange plates | yellow blocks |
| Solvent used | n-hexane | n-hexane |
| Crystal system | triclinic | triclinic |
| <i>a</i> (Å) | 7.758(10) | 11.148(38) |
| <i>b</i> (Å) | 9.220(13) | 12.149(35) |
| <i>c</i> (Å) | 10.933(12) | 13.424(33) |
| <i>α</i> (°) | 111.23(10) | 98.51(22) |
| <i>β</i> (°) | 94.45(10) | 93.95(24) |
| <i>γ</i> (°) | 97.12(11) | 117.58(21) |
| Volume (Å ³) | 717.0(16) | 1574(7) |
| Space group | <i>P</i> $\bar{1}$ (<i>C</i> ₁ ¹ , No. 2) | <i>P</i> $\bar{1}$ (<i>C</i> ₁ ¹ , No. 2) |
| <i>Z</i> ; <i>D_c</i> (g cm ⁻³) | 1; 1.578 | 2; 1.497 |
| Radiation used (Å) | 0.71069 (Mo K α) | 0.71069 (Mo K α) |
| <i>μ</i> (cm ⁻¹) | 7.11 | 5.07 |
| <i>F</i> (000) | 342.95 | 715.48 |
| No. unique reflections (measured) | 1609 (2541) | 2653 (5420) |
| Criterion | <i>F</i> /σ(<i>F</i>) > 3.0 | <i>F</i> /σ(<i>F</i>) > 3.0 |
| Absorption correction | 7 <i>ψ</i> -scans | not made |
| Transmission coefficients: min, max. | 0.605, 0.705 | |
| <i>R</i> | 0.0926 | 0.1117 |
| No. parameters | 242 | 508 |
| Mean and max. final <i>δ</i> /σ | 0.056, 0.325 | 0.053, 0.217 |
| Residual peaks in final difference Fourier: max., min (e Å ⁻³) | +0.76, -0.73 | +0.57, -0.45 |

For [(CF₃C(O)C(H)C(O)CF₃)₂(OH₂)₂Mn]{(CH₃)₄-C₄N₂}_{1.5} the independent reflections were corrected for Lorentz and polarisation effects, but not for absorption. All four trifluoromethyl groups were rotationally dis-

ordered, and were refined with geometrical constraints which imposed a common carbon–fluorine bond length and local C_{3v} symmetry: in addition the hydrogen atoms of one coordinated water molecule were permitted

TABLE 3. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for $\text{Co}(\text{hfac})_2(\text{tmp}) \cdot 4\text{H}_2\text{O}$

| Atom | x | y | z | U_{eq} |
|-------|-----------|----------|-----------|-----------------|
| Co(1) | 0 | 0 | 0 | 46(1)* |
| O(1) | -1428(7) | 1009(7) | 1531(6) | 65(3)* |
| O(2) | 1701(8) | 2154(7) | 566(6) | 67(3)* |
| O(3) | -1557(8) | 709(8) | -1238(6) | 78(4)* |
| O(4) | -4944(10) | 1151(11) | -766(9) | 112(5)* |
| N(1) | -630(10) | 375(10) | -3781(8) | 69(4)* |
| C(1) | -2371(2) | 2861(1) | 3379(1) | 95(6)* |
| C(2) | -1153(8) | 2438(7) | 2404(5) | 71(4)* |
| C(3) | 276(13) | 3567(12) | 2372(10) | 75(5)* |
| C(4) | 1605(8) | 3482(5) | 1513(5) | 70(4)* |
| C(5) | 2853(4) | 4854(3) | 1613(1) | 100(6)* |
| C(6) | 888(12) | 1167(12) | -3903(9) | 65(4)* |
| C(7) | 1509(12) | 766(12) | -5126(10) | 67(5)* |
| C(8) | 1837(15) | 2463(14) | -2649(11) | 93(6)* |
| C(9) | 3229(14) | 1634(15) | -5303(12) | 103(7)* |
| F(1) | -2085(10) | 2200(5) | 4274(4) | 166(11)* |
| F(2) | -4027(3) | 2339(5) | 2766(6) | 135(8)* |
| F(3) | -2145(6) | 4438(2) | 4004(4) | 129(6)* |
| F(4) | 3328(9) | 5799(6) | 2892(2) | 174(8)* |
| F(5) | 2106(6) | 5654(5) | 961(4) | 160(11)* |
| F(6) | 4286(6) | 4381(8) | 1073(5) | 108(6)* |
| F(1a) | -3645(15) | 3490(21) | 2944(12) | 157(22)* |
| F(2a) | -1506(12) | 3917(18) | 4534(6) | 229(21)* |
| F(3a) | -3085(19) | 1560(7) | 3561(15) | 93(13)* |
| F(4a) | 2888(6) | 4927(9) | 408(3) | 179(17)* |
| F(5a) | 4458(6) | 4725(8) | 2082(4) | 233(25)* |
| F(6a) | 2368(6) | 6174(4) | 2440(5) | 113(10)* |

Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. Both trifluoromethyl groups are rotationally disordered with occupancies of 0.697/0.303 and 0.630/0.370, respectively. Atom O(4) is a water molecule of crystallisation.

limited angular refinement. Otherwise, hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode.

Results and discussion

The reaction of tmp with $\text{M}(\text{hfac})_2$ has given complexes of stoichiometries of 1:1, 1:2 and 1:3 as suggested by the microanalytical data. The IR spectra show the presence of the ligand but are very similar and, with the exception of $\text{Fe}(\text{hfac})_2(\text{tmpH} \cdot \text{hfac})$, do not give any clear indication of any difference in structural type. $\text{Fe}(\text{hfac})_2(\text{tmpH} \cdot \text{hfac})$, shows two $\nu(\text{C}=\text{O})$ stretches, at 1660 and 1640 cm^{-1} , and the complex has been assigned by analogy with $\text{Cu}(\text{hfac})_2(\text{tedH} \cdot \text{hfac})_2$ [7]. The FAB mass spectra show fragmentation patterns for the $\text{M}(\text{hfac})_2$ precursors and so suggest that any ligand liaisons are weak. The crystal structures of two of the complexes, $[\text{Co}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})_{1.5}$, show that the tmp is en-

TABLE 4. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for $[\text{Mn}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})_{1.5}$

| Atom | x | y | z | U_{eq} |
|--------|-----------|----------|---------|-----------------|
| Mn(1) | -807(2) | 3373(2) | 3179(1) | 63(1)* |
| O(1) | -1524(9) | 3703(8) | 1736(5) | 86(6)* |
| O(2) | -2063(9) | 4161(9) | 3751(5) | 90(6)* |
| O(3) | 1049(9) | 5248(8) | 3476(5) | 76(5)* |
| O(4) | 516(9) | 2825(8) | 2337(5) | 90(6)* |
| O(5) | -423(3) | 3170(7) | 4764(5) | 74(5)* |
| O(6) | -2395(8) | 1414(3) | 2808(1) | 73(4)* |
| N(1) | 2112(11) | 633(9) | 6540(6) | 76(6)* |
| N(2) | 1001(10) | 1990(9) | 5719(6) | 75(6)* |
| N(3) | -4095(10) | 511(9) | 892(6) | 75(6)* |
| C(1) | -2782(1) | 4010(1) | 411(1) | 138(15)* |
| C(2) | -2430(5) | 3992(5) | 1474(2) | 103(10)* |
| C(3) | -3226(15) | 4200(15) | 2232(9) | 108(10)* |
| C(4) | -3030(4) | 4325(5) | 3312(4) | 89(9)* |
| C(5) | -3929(1) | 4566(1) | 3944(1) | 102(9)* |
| C(6) | 3181(1) | 6990(1) | 3378(1) | 105(9)* |
| C(7) | 2194(5) | 5642(3) | 3091(4) | 72(7)* |
| C(8) | 2419(14) | 4741(13) | 2424(8) | 82(8)* |
| C(9) | 1676(6) | 3448(4) | 2052(4) | 75(8)* |
| C(10) | 2068(1) | 2689(1) | 1338(2) | 110(12)* |
| C(11) | 2920(15) | 177(14) | 4963(9) | 100(10)* |
| C(12) | 2185(13) | 761(11) | 5581(7) | 72(7)* |
| C(13) | 1640(14) | 1477(12) | 5155(7) | 77(8)* |
| C(14) | 1683(14) | 1633(14) | 4058(8) | 96(10)* |
| C(15) | 230(17) | 2470(14) | 7323(9) | 110(11)* |
| C(16) | 967(13) | 1898(11) | 6706(8) | 75(7)* |
| C(17) | 1552(15) | 1240(13) | 7115(8) | 95(9)* |
| C(18) | 1495(20) | 1062(18) | 8224(9) | 160(17)* |
| C(19) | -5869(14) | 266(15) | 1956(7) | 104(10)* |
| C(20) | -5426(12) | 113(12) | 918(7) | 68(7)* |
| C(21) | -6343(11) | -377(11) | -1(7) | 61(6)* |
| C(22) | -7824(12) | -821(12) | 20(8) | 85(8)* |
| F(1) | -2368(5) | 5213(2) | 306(5) | 162(18)* |
| F(2) | -4149(1) | 3317(3) | 127(4) | 226(21)* |
| F(3) | -2158(4) | 3511(5) | -184(4) | 181(20)* |
| F(1a) | -3539(17) | 2814(3) | -124(5) | 209(25)* |
| F(2a) | -1625(4) | 4602(16) | 15(7) | 251(37)* |
| F(3a) | -3505(16) | 4639(15) | 364(5) | 158(20)* |
| F(4) | -3217(5) | 5256(4) | 4869(2) | 112(9)* |
| F(5) | -4446(4) | 5210(3) | 3498(3) | 185(14)* |
| F(6) | -4959(3) | 3453(3) | 4054(5) | 158(9)* |
| F(4a) | -5241(2) | 3703(3) | 3572(4) | 189(10) |
| F(5a) | -3625(5) | 4482(4) | 4909(2) | 189(10) |
| F(6a) | -3754(5) | 5738(2) | 3932(4) | 189(10) |
| F(7) | 2645(5) | 7662(4) | 3000(3) | 184(16)* |
| F(8) | 3464(5) | 7345(5) | 4402(1) | 139(12)* |
| F(9) | 4342(3) | 7213(6) | 3000(3) | 161(15)* |
| F(7a) | 4446(4) | 7135(8) | 3617(4) | 145(16)* |
| F(8a) | 3158(9) | 7556(6) | 2592(3) | 205(23)* |
| F(9a) | 2853(5) | 7525(5) | 4192(2) | 193(19)* |
| F(10) | 3170(3) | 3459(4) | 956(3) | 116(10)* |
| F(11) | 2379(6) | 1941(6) | 1828(5) | 143(13)* |
| F(12) | 1021(4) | 1959(6) | 572(4) | 144(12)* |
| F(10a) | 1590(4) | 1522(2) | 1549(4) | 157(21)* |
| F(11a) | 1530(4) | 2593(5) | 380(3) | 137(19)* |
| F(12a) | 3443(1) | 3250(4) | 1424(4) | 162(21)* |

Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. Each of the trifluoromethyl groups is rotationally disordered; occupancies are 0.568/0.432, 0.716/0.284, 0.560/0.440 and 0.609/0.391, respectively.

gaged in second sphere coordination leading to chain polymerisation via *trans*- and *cis*-derived stacking, respectively.

The molecular structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp}) \cdot 2\text{H}_2\text{O}$, recrystallised in *n*-hexane from the bulk sample analysing as $\text{Co}(\text{hfac})_2(\text{tmp})_2 \cdot 2\text{H}_2\text{O}$, is shown with atom labelling in Fig. 1. Bond lengths and angles with estimated standard deviations are listed in Table 5. The cobalt(II) ion is *trans* coordinated by two water molecules, with the remaining sites occupied by two bidentate hexafluoroacetylacetonate ligands: the whole complex possesses crystallographically imposed inversion symmetry. The remainder of the crystal structure comprises a centrosymmetric tetramethylpyrazine molecule and two centrosymmetrically related free water molecules. The fragments are linked by the formation of a hydrogen bond between the coordinated water and the nitrogen of the tetramethylpyrazine (Fig. 2; $\text{O} \dots \text{N}$ 2.84 Å) — giving rise to the formation of chains

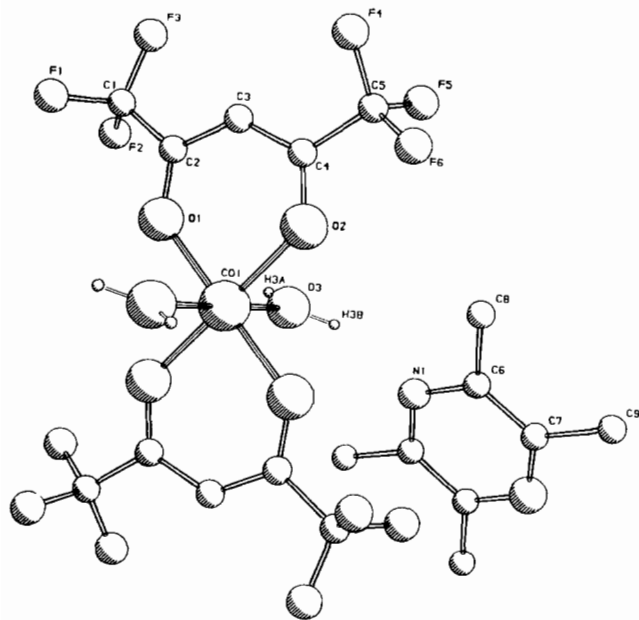


Fig. 1. The structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})$ (some H atoms are omitted for clarity)

TABLE 5. Selected bond lengths (Å) and bond angles (°) for $\text{Co}(\text{hfac})_2(\text{tmp}) \cdot 4\text{H}_2\text{O}$

| | | | |
|--------------------------|----------|----------------------------|----------|
| Co(1)—O(1) | 2.076(7) | Co(1)—O(2) | 2.098(6) |
| Co(1)—O(3) | 2.074(8) | O(4) ..O(4) ^b | 3.141(7) |
| O(3)...N(1) | 2.844(7) | H(O3b)...N(1) | 1.99 |
| O(3)...O(4) | 2.768(6) | H(O3a)...O(4) | 1.87 |
| O(4)...F(6) ^a | 3.092(9) | H(O4b)...F(6) ^a | 2.28 |
| O(4)...O(1) ^b | 3.103(7) | O(4)...F(2) ^b | 3.126(9) |
| O(1)—Co(1)—O(2) | 89.8(2) | O(1)—Co(1)—O(3) | 89.9(3) |
| O(2)—Co(1)—O(3) | 89.0(3) | | |

Symmetry operations: ^a $[-1+x, y, z]$, ^b $[-1-x, -y, -z]$.

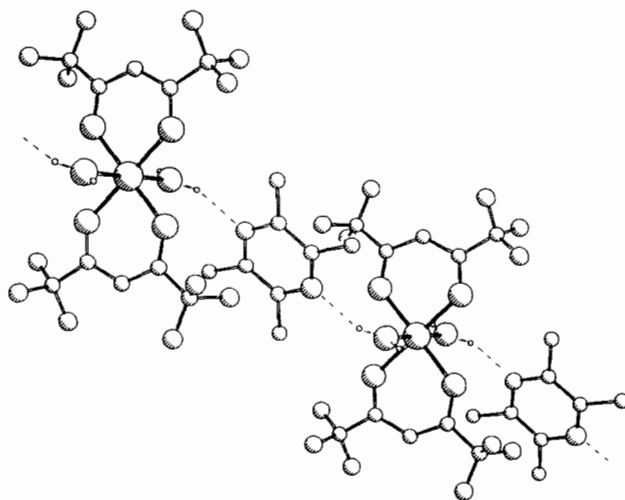


Fig. 2. The polymeric chain of $[\text{Co}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})$.

parallel to the crystallographic *c* axis. The second hydrogen of each coordinated water is hydrogen bonded to the 'free' water molecule of crystallisation ($\text{O} \dots \text{O}$ 2.77 Å): the geometry of Co(1), O(4) and N(1) around O(3) is approximately trigonal, and the hydrogen atoms are positioned to reflect this. This free water shows four similar length contacts, outside the hydrogen bonding range (3.09–3.14 Å), to oxygen or fluorine atoms of other molecules, or to symmetry related free water molecules. However, these did not form a basis for the location of the hydrogen atoms, which were rather positioned on residual electron density peaks and geometrically optimised. One such hydrogen was found to lie approximately along the shortest O(4)...F contact and perhaps represents a weak hydrogen bonding interaction linking together chains which are displaced by a unit cell *a* axis translation.

The coordination polyhedron of the cobalt is a perfect octahedron, with no significant angular distortions: the hexafluoroacetylacetonate ligand also has optimum geometry (r.m.s. deviation of chelate plane 0.034 Å, deviation of cobalt 0.058 Å). The skeleton of the tetramethylpyrazine is planar (r.m.s. deviation 0.004 Å) with maximum deviation of a methyl carbon of only 0.003 Å.

The molecular structure of $[\text{Mn}(\text{H}_2\text{O})_2(\text{hfac})_2](\text{tmp})_{1.5}$, recrystallised in *n*-hexane from the bulk sample analysing as $[\text{Mn}(\text{hfac})_2]_2(\text{tmp})_3 \cdot 4\text{H}_2\text{O}$, is shown with atom labelling in Fig. 3. Bond lengths and angles with estimated standard deviations are listed in Table 6. The manganese(II) ion is coordinated by two *cis* water molecules and by two hexafluoroacetylacetonate ligands. The crystal structure involves the bridging of such manganese complexes by the formation of hydrogen bonds to the nitrogen atoms of tetramethylpyrazine molecules across crystallographic inversion centres. One

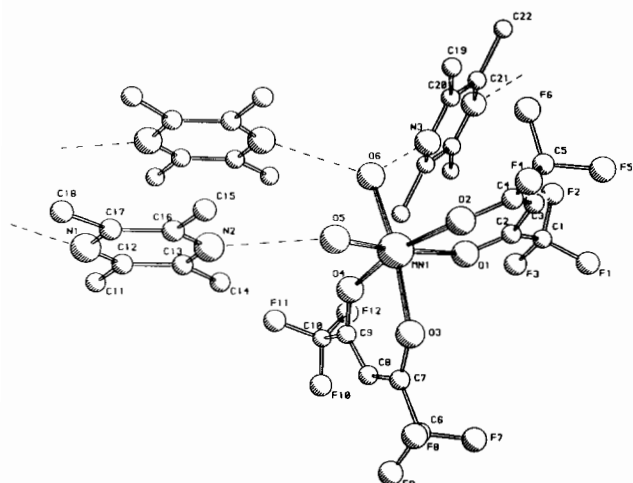


Fig. 3. The structure of $[\text{Mn}(\text{H}_2\text{O})_2(\text{hfac})_2(\text{tmp})_{1.5}]$ (some H atoms are omitted for clarity).

TABLE 6. Selected bond lengths (\AA) and bond angles ($^\circ$) for $[\text{Mn}(\text{H}_2\text{O})_2(\text{hfac})_2(\text{tmp})_{1.5}]$

| | | | |
|---------------------------|-----------|----------------------------|-----------|
| Mn(1)–O(1) | 2.206(11) | Mn(1)–O(2) | 2.152(14) |
| Mn(1)–O(3) | 2.210(10) | Mn(1)–O(4) | 2.194(13) |
| Mn(1)–O(5) | 2.213(9) | Mn(1)–O(6) | 2.162(7) |
| O(5)...N(2) | 2.930(16) | H(5a)...N(2) | 1.97 |
| O(5)...F(9a) ^b | 2.961(10) | H(5b)...F(9a) ^b | 1.96 |
| O(6)...N(3) | 2.825(17) | H(6a)...N(3) | 1.93 |
| O(6)...N(1) ^a | 2.895(16) | H(6b)...N(1) ^a | 1.91 |
| O(1)–Mn(1)–O(2) | 81.4(4) | O(1)–Mn(1)–O(3) | 91.5(3) |
| O(2)–Mn(1)–O(3) | 92.9(4) | O(1)–Mn(1)–O(4) | 87.2(4) |
| O(2)–Mn(1)–O(4) | 167.2(4) | O(3)–Mn(1)–O(4) | 81.6(4) |
| O(1)–Mn(1)–O(5) | 167.0(4) | O(2)–Mn(1)–O(5) | 85.7(3) |
| O(3)–Mn(1)–O(5) | 90.7(3) | O(4)–Mn(1)–O(5) | 105.8(3) |
| O(1)–Mn(1)–O(6) | 90.5(3) | O(2)–Mn(1)–O(6) | 96.8(4) |
| O(3)–Mn(1)–O(6) | 170.3(4) | O(4)–Mn(1)–O(6) | 89.0(3) |
| O(5)–Mn(1)–O(6) | 89.5(2) | | |

Symmetry operations: ^a $[-x, -y, 1-z]$, ^b $[-x, 1-y, 1-z]$.

such bridge is made across the inversion centre at (0, 0, 0.5) via two centrosymmetrically related tetramethylpyrazine ligands utilising one hydrogen atom on each coordinated water ligand on the manganese (O...N 2.93 and 2.83 \AA). A second bridge across the inversion centre at (–0.5, 0, 0) occurs via one centrosymmetric tetramethylpyrazine ligand (O...N 2.90 \AA). The otherwise unused second hydrogen atom on the coordinated water O(5) forms a hydrogen bond to a fluorine atom of one of the lower occupancy components of a disordered trifluoromethyl group of a centrosymmetrically related (through (0, 0.5, 0.5)) complex (O...F 2.96 \AA): rather surprisingly, the shortest contact to the disorder component with higher refined occupancy is much longer at an oxygen–fluorine separation of 3.45 \AA .

The skeletons of the hexafluoroacetylacetonate ligands are each planar (r.m.s. deviations 0.042 and 0.017 \AA) with deviations of the manganese atom by 0.328 and 0.229 \AA , respectively. The aromatic rings are also

planar (r.m.s. deviations 0.021 and 0.009 \AA) with maximum deviations of a methyl group of 0.062 \AA . The deviations of the coordination polyhedron of the manganese from octahedral reflect the reduced ‘bite’ of the β -diketone ligands and the involvement of the water molecules in intermolecular hydrogen bond formation.

There are several reports in the literature of extended chain stacked complexes involving pyrazine [1, 8–11] all of which refer to pyrazine as a first sphere ligand interacting directly with the metal ion. In the complexes reported here the stacking occurs through a second sphere hydrogen-bonding interaction of the tetramethylpyrazine with the first sphere coordinated water molecules on the metal. Tetramethylpyrazine is expected to be a weaker coordinating ligand than pyrazine and there is also the possibility that it is sterically disadvantaged, by the four methyl groups, in interaction with the metal diketonates. It is surprising that the two structures exist in different geometric forms particularly as the structure of $\text{Mn}(\text{hfac})_2(\text{tempo})_2$ [12] (tempo is the cyclic nitrosyl radical ligand 2,2,6,6-tetramethylpiperidinyl-1-oxy) is found in the *trans*-octahedral configuration. The reason for this difference is not obvious. A *cis*-octahedral configuration was found in $\text{Zn}(\text{hfac})_2, 2\text{pyridine}$ in which the hexafluoroacetylacetonate anions were noted to have alternate long and short bonds [13], this is also evident in the *cis*- $\text{Co}(\text{hfac})_2$ complex reported above. It is probable that the remaining complexes also have stacked structures but in the absence of structural analysis there is no obvious direct correlation with the structures described above.

Supplementary material

Tables of anisotropic thermal vibrational parameters with e.s.d.s, hydrogen atom position parameters, observed structure amplitudes and calculated structure factors are available from the authors on request.

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