Synthesis, Magnetochemistry, and Spectroscopy of Heterometallic Trinuclear Basic Trifluoroacetates [Fe$_2$M($\mu_3$-O)(CF$_3$COO)$_6$(H$_2$O)$_3$]·H$_2$O (M = Mn, Co, Ni)


Keywords: Heterometallic complexes / Carboxylate ligands / Magnetic properties / Iron / Manganese / Cobalt / Nickel / Trinuclear complexes

Three new $\mu_3$-oxo(trifluoroacetato) complexes [Fe$_2$IIIM($\mu_3$-O)(CF$_3$COO)$_6$(H$_2$O)$_3$]·H$_2$O (M = Mn (1), Co (2), Ni (3)) have been prepared. Compounds 1 and 2 crystallize in the monoclinic space groups C2/c [a = 22.002(5), b = 13.647(3), c = 24.767(4) Å, β = 98.23(3)] and C2/m [a = 21.426(4), b = 15.100(2), c = 14.815(3) Å, β = 117.99(2)], respectively. The coordination spheres of the metal ions are essentially octahedral, with the Fe–O distances [1.870(5) Å] falling in the usual range for these systems. Magnetochemical studies reveal the presence of antiferromagnetic exchange in the isoceles triangular skeletons of the polynuclear species. Application of the isotropic spin Hamiltonian $H = -2J_{FeM}[S_{Fe1}S_{M} + S_{M}S_{Fe2}] - 2J_{FeFe}[S_{Fe1}S_{Fe2}]$ gives the fitting parameters: $g_{Fe} = 2.00$, $J_{FeM} = -56.50(7)$ and $J_{Fe-Fe} = -16.23(4)$ cm$^{-1}$ (1), $g_{Mm} = 2.09(1)$, $J_{Fe-Fe} = -42.8(3.5)$ cm$^{-1}$, $J_{Fe-Co} = -17.8(1.4)$ cm$^{-1}$ (2) and $g_{Fe} = 2.00$, $g_{Ni} = 2.215(2)$, $J_{Fe-Fe} = -45.60(1)$ and $J_{Fe-Ni} = -16.96(2)$ cm$^{-1}$ (3). A Mössbauer investigation confirms that no electron transfer from Mn$^{III}$ or Co$^{II}$ to Fe$^{III}$ occurs during the syntheses of these complexes.

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Introduction

Polynuclear carboxylates of the 3d transition metals have been attracting renewed interest because of their intramolecular magnetic exchange interactions[1-2] and their application as simple models of oligonuclear active sites in metalloproteins.[3-6] Particular attention is being paid to polynuclear complexes behaving as single-molecular magnets.[7-9] Trinuclear (carboxylato)(oxo) complexes are also found within supramolecular arrays of higher nuclearity, and thus are of interest as building blocks ("molecular Legos") with regard to modern magnetic materials.[10,11]

The first heterometallic trinuclear acetates of tripotitive iron and chromium [X$_2$IIIZIII($\mu_3$-O)(CH$_3$COO)$_6$(H$_2$O)$_3$]$^+$ (where X$_2Z$ = Fe$_2$Cr, Cr$_2$Fe)$^{[12]}$ and of mixed-valence metals [Fe$_2$IIIM($\mu_3$-O)(CH$_3$COO)$_6$(H$_2$O)$_3$]$^+$ (where M = Co, Mn, Ni, Zn)$^{[13]}$ were synthesized by Weiland. Difficulties in the synthesis and in the interpretation of the physicochemical properties of these heterometallic trinuclear carboxylates discouraged their extensive investigation.[14] Nonetheless, the consequences of straightforward variations in their structures, such as substitution of the acetate group by other functionalised carboxylates, appear to be fundamental in the development of new materials derived from them. This class of compounds is also active with respect to alkane activation, the catalytic activity being dependent on the carboxylate and metal identities.[15,16]

Thus, it is attractive to combine this property of super-acidity and catalytic activity of trinuclear (carboxylato)(μ$_3$-oxo) complexes using strong acids such as trifluoroacetic acid as the ligand source. We present here the syntheses, structures and investigation of the spectroscopic and magnetic behaviour of the trinuclear heterometallic basic trifluoroacetates [Fe$_2$IIIM($\mu_3$-O)(CF$_3$COO)$_6$(H$_2$O)$_3$]·H$_2$O (M = Mn (1), Co (2), Ni (3))

Results and Discussion

Synthesis

The heteronuclear basic trifluoroacetates [Fe$_2$IIIM($\mu_3$-O)(CF$_3$COO)$_6$(H$_2$O)$_3$]·H$_2$O (M = Mn (1), Co (2), Ni (3))
were synthesized by metathesis reaction between trifluoroacetate and the acetate trimers. The reactions proceeded smoothly in aqueous trifluoroacetic acid as the solvent without any destruction of the oxo-bridged trinuclear skeleton of the Mn, Co, or Ni complexes, despite the substantial acidity of trifluoroacetic acid [Equation (1)].

\[
\text{[Fe}^{II}\text{H}^3\text{M}^3(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{3+}\text{H}_2\text{O} + 6 \text{CF}_3\text{COOH} \rightarrow \text{[Fe}^{II}\text{H}^3\text{M}^3(\mu_3\text{-O})(\text{CF}_3\text{COO})_6(\text{H}_2\text{O})_3]^{3+}\text{H}_2\text{O} + 6 \text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \quad (1)
\]

Similar metathesis reactions have also been applied successfully to higher-nuclearity carboxylates. All the trifluoroacetate compounds are readily soluble in water and a variety of organic solvents, so that growing single crystals of 1–3 by concentration, vapour diffusion or liquid diffusion was limited to certain solvent combinations, as reflected by the compositions of the crystals described below.

**Description of Structures**

Molecular structures of [Fe₂Mn(μ₃-O)(CF₃COO)₆(H₂O)₃]·2MeNO₂·H₂O (1’) and [Fe₂Co(μ₃-O)(CF₃COO)₆(H₂O)₃]·3Me₂CO·1/2Mes (2’) were examined under cryogenic conditions (100 K). An ORTEP diagram of [Fe₂Co(μ₃-O)(CF₃COO)₆(H₂O)₃] is presented in Figure 1. The principal lattice matrices of the complexes are listed in Table 6, while bond lengths and angles of 2’ are presented in Table 1.

\[
\text{[Fe}_2\text{Co(μ}_3\text{-O})(\text{CF}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot3\text{Me}_2\text{CO}\cdot1/2\text{Mes (Mes = 1,3,5-trimethylbenzene) (2’)}
\]

The monoclinic unit cell of the complex contains 4 molecules of the trinuclear complex, 12 molecules of acetone, and 2 molecules of mesitylene. In the crystal structure of 2’, all the trinuclear molecules are located in parallel layers of sequence ABAB. Hence the molecules of the third layer occupy positions precisely above those of the first layer. The absence of interlayer trimer–trimer cohesion forces (e.g. through the lack of any intertrimer hydrogen bonds) allows the solvent molecules to readily penetrate and occupy the interlayer volume. The interstices between trinuclear species are occupied by molecules of acetone and mesitylene, the aromatic ring planes of mesitylene being perpendicular to the trinuclear skeleton: in each case the carboxylate groups have a planarity of the µ₁-oxygen atom made up by two iron(III) atoms and a cobalt(III) atom. Six µ-trifluoroacetate anions also join the metal atoms through carboxylate trimers. The reactions proceeded without any destruction of the oxo-bridged trinuclear skeleton of the Mn, Co, or Ni complexes, despite the substantial acidity of trifluoroacetic acid [Equation (1)].

![Figure 1. ORTEP plot of the structure of the skeleton of complex 1'. Thermal ellipsoids are shown at the 20% level for clarity; H and F atoms are omitted for clarity of presentation](image)

**Table 1. Selected distances and angles in [Fe₂Co(μ₃-O)(CF₃COO)₆(H₂O)₃]·3Me₂CO·1/2Mes**

<table>
<thead>
<tr>
<th>Distances [Å]</th>
<th>Angles [°]</th>
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<tr>
<td>Fe₁–Fe₂</td>
<td>3.26(1)</td>
</tr>
<tr>
<td>Fe₁–Co</td>
<td>3.33(1)</td>
</tr>
<tr>
<td>Fe₂–Co</td>
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<tr>
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</tr>
<tr>
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<td>2.076(6)</td>
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<tr>
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<tr>
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<tr>
<td>O₆–Fe₂–O⁷</td>
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<tr>
<td>O₆–Fe₂–O⁹</td>
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</tr>
<tr>
<td>O₄–Fe₂–O₄*</td>
<td>91.3(3)</td>
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</tbody>
</table>

[a] The positions of the atoms with an asterisk are defined by the appropriate symmetry operations. The standard deviations are reported in parentheses.
metal ions shows that it is an sp²-hybridised oxide ion, removing the ambiguity associated with a possible µ₂-OH⁻ bridge. The average µ₁-O-Fe distance of 1.870(5) Å is typical for Fe³⁺-O⁻⁻⁻ bonds in trinuclear (carboxylato)(µ₂-oxo) complexes.[18] Comparison of this value with corresponding distances in [Fe²⁺Fe⁴⁺(µ₃-O)(CH₃COO)₆(4-Et-py)]₄ (µ₃-O-Fe²⁺ 2.01 Å, µ₃-O-Fe⁺⁺ 1.86 Å at 163 K)[19] favours the assumption that the oxidation state of the iron atoms in 2 remains +3. If the µ₁-O²⁻⁻⁻ radius is taken as 1.22 Å,[20] the ionic radius of Fe²⁺ can be estimated to be 0.64 Å, somewhat smaller than the value reported at room temperature (0.78 Å).[20] The µ₁-O-Co distance [1.993(5) Å] is greater than µ₁-O-Fe, due to the larger ionic radius of Co²⁺.[20] For each Fe²⁺ ion, three sets of values of the Fe-O bond lengths are found: short µ₁-O-Fe distances (1.87 Å), two intermediate Fe-O distances (2.03 Å for Fe₁-O₁ and Fe₁-O¹⁹), and three longer Fe-O and Fe-OH₂ bonds (ranging from 2.05 Å for Fe₂-O₅ and Fe₂-O⁵⁺, to 2.08 Å for Fe₁-O⁷ and Fe₂-O⁹, where O is oxygen atoms of the carboxylate bridges). For the Co²⁺ ion, the differences between the Co-O bond lengths [2.069(4) and 2.078(4) Å] are less significant than the corresponding bond lengths in analogous trinuclear acetato complexes. This can be rationalised by a weaker donor power of the trifluoroacetate ion (due to the inductive effect of the CF₃ group) in comparison with the acetate group. All the M-OH₂ bond lengths are 2.08 Å.

In the acetato complex [Fe₂Co(µ₃-O)(CH₃COO)₆(H₂O)₃]₂H₂O, which crystallises in a monoclinic system (Z = 8),[21] disorder causes the metal atoms to appear to be arranged at the corners of an equilateral triangle, hence concealing the identities of the individual Fe³⁺ and Co²⁺ ions. In the present trifluoroacetate case, the observed C₂ᵥ symmetry of the trinuclear unit allows the distinction between Fe³⁺ and Co²⁺ to be made.

[Fe₂Mn(µ₃-O)(CF₃COO)₆(H₂O)₃]₂MeNO₂·H₂O (1')

This complex also crystallises in a monoclinic space group. The parallel layers of trinuclear species are arranged in an ABCDEABCDE sequence. The overall R factor for the structure is quite large because of the disorder of the tris(trifluoroacetyl) group and solvent molecules. However, the trinuclear skeleton is confirmed and certain details are clearly apparent. The structure of 1' is not identical to that of 2', the trinuclear moiety forms a slightly distorted isoceles triangle: [Fe₁-Mn 3.328(2) Å; Fe₂-Mn 3.368(2) Å; Fe₁-Fe 2.373(2) Å]. The coordination spheres of the metal ions are essentially octahedral, with the Fe-µ₃-O distances in the typical range for these systems: the µ₃-O-Fe bond lengths (1.86 and 1.87 Å for atoms Fe₁ and Fe₂, respectively) differ slightly from the corresponding values in 2', while a similar effect is seen for the Fe-OH₂ bond (2.10 and 2.06 Å for Fe₁ and Fe₂, respectively). The Fe-O distances vary from 2.01 to 2.07 Å, similar Fe-O distances have been found in analogous compounds.[22] Meanwhile, the µ₃-O-Mn (2.02 Å), Mn-Oc and Mn-OH₂ distances (2.11–2.15 Å) are in a range consistent with the persistence of Mn²⁺ under the conditions of synthesis. In consonance with this, the Mössbauer spectrum of this compound (vide infra) testifies to the presence of iron(III) rather than iron(II) in 1'.

**Mass Spectra**

FAB mass spectra clearly indicate the trinuclear nature of complexes 1–3, as well as the persistence of the Fe₂M³⁺(µ₃-O) skeletons. Although ions such as [Fe₂M³⁺(µ₃-O)(CF₃COO)₉(H₂O)]⁺ or [Fe₂M³⁺(µ₃-O)(CF₃COO)]⁻ are not immediately apparent, intense peaks associated with partially solvated [Fe₂M³⁺(µ₃-O)(CF₃COO)₂(H₂O)]⁺ cations are present in each case (Table 2). The spectra also display fragmentation patterns corresponding to consecutive loss of trifluoroacetate groups and water molecules. The relative intensities suggest a greater lability for trifluoroacetate than for water.

**Table 2.** FAB-MS data for the complexes [Fe₂M(µ₃-O)(CF₃COO)₆(H₂O)]·H₂O (M = Mn, Co, Ni)

<table>
<thead>
<tr>
<th>Ion composition</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
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<tr>
<td>[Fe₂M(µ₃-O)(CF₃COO)₆(H₂O)]⁺</td>
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<td>790</td>
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<td>752</td>
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<tr>
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<td>674</td>
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<tr>
<td>[Fe₂M(µ₃-O)(CF₃COO)]⁻</td>
<td>635</td>
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<td>[Fe₂M(µ₃-O)(CF₃COO)₂(H₂O)]⁺</td>
<td>447</td>
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<tr>
<td>[Fe₂M(µ₃-O)(CF₃COO)]⁻</td>
<td>432</td>
<td>432</td>
<td>431</td>
</tr>
<tr>
<td>[Fe₂M(µ₃-O)(CF₃COO)]⁻</td>
<td>334</td>
<td>338</td>
<td>337</td>
</tr>
</tbody>
</table>

**IR Spectra**

The IR absorption bands for 1–3 (Table 3) are consistent with those reported in the literature for the acetate analogues[22,23] and are similarly assigned: ν(COO⁻)_, ν(COO⁻)as in 1–3 are shifted to a lower energy by 40–50 cm⁻¹ relative to the trinuclear basic acetates,[23] indicating
that the replacement of the CH₃ radical by the more powerfully electron-accepting CF₃ moiety weakens the metal–Oₐc force constant.

The splitting of the symmetric and asymmetric valence vibrations (Av, Table 3) signals bidentate bridging carboxylate groups around the Fe₂M(µ₃-O) fragment,[23] while the bands at 600–650 cm⁻¹ are assigned to vibrations of the Fe₂M(µ₃-O) skeleton.

Electronic Spectra

The electronic spectra of 1–3 (Table 4) are similar to those reported for other trinuclear basic carboxylates containing iron(III),[23] and are useful in revealing the spin states of the metal ions. At longer wavelengths, absorbance bands are observed which are characteristic of d–d transitions from the 6A₁g ground state of a distorted octahedral high-spin Fe₃⁺ ion. For instance, the band at 17500 cm⁻¹ is assigned to the 6A₁g→4A₂g d–d transition, the intensity of which is enhanced due to the influence of exchange interactions[24] inside the trinuclear moiety. The remaining Fe₃⁺ d–d transitions are obscured by intense absorbance bands near 29000 and 22000 cm⁻¹ (ε = 1500–3000 dm⁻³ mol⁻¹ cm⁻¹) associated with the ligand-to-metal charge-transfer transitions which are characteristic of such iron(III) systems.[25,26] The electronic spectrum of [Fe₂Ni(µ₃-O)(CF₃COO)₆(H₂O)₃]H₂O (3) exhibits an absorbance band at 13580 cm⁻¹ (Table 4). The position and intensity of this band are consistent with a 3A₂g d transition, the intensity of which is slightly enhanced relative to similar bands of the metal ions. For instance, the band at 17500 cm⁻¹ is ascribed to the 6A₁g→3T₁g electronic transition of this trinuclear complex, even at room temperature, is significantly lower than the expected spin-only χₘT value (13.125 cm⁻¹·K⁻¹ mol⁻¹) for a non-interacting g = 2 high-spin set of one manganese(II) and two iron(III) ions. This clearly indicates strong antiferromagnetic coupling within the Fe₂Mn framework. In general, two high-spin iron(III) ions with S = 5/2 and one manganese(II) ion with S = 5/2 can couple to give a total molecular spin (Sₜ) ranging from 1/2 to 15/2. Magnetic data were analysed according to the exchange Hamiltonian [Equation (2)], and the coupling pathways are presented in Scheme 1.

\[ H = -2J_{FeM}[S_{Fe}/S_M + S_M S_{Fe}]/2 - 2J_{FeFe}[S_{Fe}/S_Fe] \]  

Figure 2. Temperature dependence of the magnetic susceptibility of 1, plotted as χ₁₄ vs. T; the solid line is the least-squares fit

Scheme 1. Magnetic exchange pathways in the trinuclear core

The zero-field energy levels for the Fe₂M complexes were calculated according to Equation (3)[25] where Sₜ is Sₜ = S; Sₐ, the spin of Mₐ (5/2 for Mn, 3/2 for Co, and 2/2 for Ni); Sₜ, Sₜ = Sₜ, Sₜ; ST = Sₜ + Sₐ according to Kambe’s notation.[27]

\[ E(Sₜ, Sₜ) = J_{FeM}[S_{Fe}/S_M + S_M S_{Fe}]/2 + J_{FeFe}[S_{Fe}/S_{Fe}] + S_M(S_{Fe} + S_{Fe}) + S_{Fe}/S_{Fe} + S_{Fe}/S_{Fe}/2 \]  

Within this approach, Sₚ ranges integrally from 0 to 5, so that for instance, when Sₚ = 1, Sₜ for the Co₁⁻containing molecule may take values of 1/2, 3/2, or 5/2. Substitution
of the eigenvalues for the spin-states derived from the above exchange Hamiltonian into the van Vleck equation results in an expression for the $\chi_M T$ values for the $\text{Fe}_2\text{Mn}$ complex [Equation (4)], where $a = -25J_{\text{Fe-Mn}} - 12.5J_{\text{Fe-Co}}$; $b = -10J_{\text{Fe-Mn}} + 12.5J_{\text{Fe-Co}}$; $c = 3J_{\text{Fe-Mn}} - 12.5J_{\text{Fe-Co}}$; $d = 14J_{\text{Fe-Mn}} - 12.5J_{\text{Fe-Co}}$; $e = 23J_{\text{Fe-Mn}} - 12.5J_{\text{Fe-Co}}$; $f = 30J_{\text{Fe-Mn}} - 12.5J_{\text{Fe-Co}}$; $\gamma = -20J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $h = -7J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $\alpha = 4J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $j = 13J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $K = 20J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $l = 25J_{\text{Fe-Mn}} - 2.5J_{\text{Fe-Co}}$; $m = -15J_{\text{Fe-Mn}} + 5.5J_{\text{Fe-Co}}$; $n = -4J_{\text{Fe-Mn}} + 5.5J_{\text{Fe-Co}}$; $p = 12J_{\text{Fe-Mn}} + 5.5J_{\text{Fe-Co}}$; $q = 17J_{\text{Fe-Mn}} + 5.5J_{\text{Fe-Co}}$; $r = 20J_{\text{Fe-Mn}} + 5.5J_{\text{Fe-Co}}$; $s = -10J_{\text{Fe-Mn}} + 11.5J_{\text{Fe-Co}}$; $u = 6J_{\text{Fe-Mn}} + 11.5J_{\text{Fe-Co}}$; $v = 11J_{\text{Fe-Mn}} + 11.5J_{\text{Fe-Co}}$; $w = 14J_{\text{Fe-Mn}} + 11.5J_{\text{Fe-Co}}$; $x = -5J_{\text{Fe-Mn}} + 15.5J_{\text{Fe-Co}}$; $y = 2J_{\text{Fe-Mn}} + 15.5J_{\text{Fe-Co}}$; $z = -7J_{\text{Fe-Mn}} + 15.5J_{\text{Fe-Co}}$; $\phi = 17.5J_{\text{Fe-Co}}$.

Despite the deviation of this complex from an exact isoceles triangle, a satisfactory fit was achieved using two $J$ parameters. The best fit was obtained with fixed values of $g_{\text{Fe}} = g_{\text{Mn}} = 2.00$, giving $J_{\text{Fe-Co}} = -56.50(7)$ and $J_{\text{Fe-Mn}} = -16.23(4)$ cm$^{-1}$ [$R^2 = 1.85 	imes 10^{-3}$] where $R^2 = \Sigma (\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \Sigma \chi_{\text{obs}}^2$. An energy diagram (Figure 3) for the spin states of 1 reveals that the ground state is a quadruplet ($S_T, S^z = (3/2, 1)$, with a low-lying sextuplet ($5/2, 0$) 0.61 cm$^{-1}$ above it. The experimental $\chi_M T$ value at 5 K (3.19) is intermediate between the calculated values for these two spin-states: 1.88 cm$^{-1}$K-mol$^{-1}$ for a quadruplet and 4.38 cm$^{-1}$K-mol$^{-1}$ for a sextuplet ground state, and the $\chi_M T$ data thus betoken Boltzmann distribution over these two states. Previously, Blake et al. reported that $S_T/3$ is the ground state for [Fe$_2$Mn($\mu_3$O)(CH$_3$COO)$_2$](py)$_3$ $\cdot 0.7$py.[24]

**Complex [Fe$_2$Co($\mu_3$O)(CF$_3$COO)$_2$(H$_2$O)$_3$]$\cdot$H$_2$O (2)**

In general, the magnetic properties of 2 resembled those of the manganese analogue (Figure 4). On cooling, $\chi_M T$ for this complex decreased from 4.76 cm$^{-1}$K-mol$^{-1}$ at 300 K to 2.00 at 5 K (Figure 4). The observed $\chi_M T$ value at room temperature is less than one half of the spin-only $\chi_M T$ value (10.61 cm$^{-1}$K-mol$^{-1}$) for a non-interacting FeCoFe ion set. Again, this directly testifies for the existence of strong antiferromagnetic coupling within the FeCo framework. Two high-spin iron(II) ions and one high-spin (S = 3/2) cobalt(II) ion can couple to give spins ranging from $S_T = 1/2$ to $S_T = 13/2$. The experimental data were fitted according to the isotropic spin-Hamiltonian [Equation (2)] to give Equation (5), where $a = -15J_{\text{Fe-Co}} - 12.5J_{\text{Fe-Co}}$; $b = -12J_{\text{Fe-Co}} - 12.5J_{\text{Fe-Co}}$; $c = 9J_{\text{Fe-Co}} - 12.5J_{\text{Fe-Co}}$; $d = 18J_{\text{Fe-Co}} - 12.5J_{\text{Fe-Co}}$; $e = -12J_{\text{Fe-Co}} - 2.5J_{\text{Fe-Co}}$; $f = -J_{\text{Fe-Co}} - 2.5J_{\text{Fe-Co}}$; $\gamma = 8J_{\text{Fe-Co}} - 2.5J_{\text{Fe-Co}}$; $h = 15J_{\text{Fe-Co}} - 2.5J_{\text{Fe-Co}}$; $\omega = -9J_{\text{Fe-Co}} + 5.5J_{\text{Fe-Co}}$; $j = 5.5J_{\text{Fe-Co}}$; $K = 7J_{\text{Fe-Co}} + 5.5J_{\text{Fe-Co}}$; $l = 12J_{\text{Fe-Co}} + 5.5J_{\text{Fe-Co}}$; $m = -6J_{\text{Fe-Co}} + 11.5J_{\text{Fe-Co}}$; $n = 6J_{\text{Fe-Co}} + 11.5J_{\text{Fe-Co}}$; $\rho = 9J_{\text{Fe-Co}} + 11.5J_{\text{Fe-Co}}$; $q = -3J_{\text{Fe-Co}} + 15.5J_{\text{Fe-Co}}$; $r = 2J_{\text{Fe-Co}} + 15.5J_{\text{Fe-Co}}$; $s = 5J_{\text{Fe-Co}} + 15.5J_{\text{Fe-Co}}$; $\tau = 17.5J_{\text{Fe-Co}}$.

Here, $p$ is the fraction of a nonmononuclear ferric paramagnetic (S = 5/2) impurity, and $g_{\text{mol}}$ is for the trinuclear complex.

The best fit was obtained with $g_{\text{mol}} = 2.09(1)$; $J_{\text{Fe-Co}} = -42.8(3.5)$ cm$^{-1}$; $J_{\text{Fe-Co}} = -17.8(1.4)$ cm$^{-1}$; $p = 0.031(5)$ and $TIP = 0$ ($R^2 = 6.17 	imes 10^{-6}$). Fixing $g_{\text{Fe}}$ at 2.00 gave $g_{\text{Co}} = 2.27$ according to $3g_{\text{mol}} = (2g_{\text{Fe}} + g_{\text{Co}})$. The associated spin ladder energy diagram reveals a (1/2, 1) ground state with a (3/2, 0) state 3.2 cm$^{-1}$ above it (Figure 5). These states are well-separated from the second excited state (3/2, 1), which is 50 cm$^{-1}$ above them.

**Complex [Fe$_2$Ni($\mu_3$O)(CF$_3$COO)$_2$(H$_2$O)$_3$]$\cdot$H$_2$O (3)**

For this complex, the $\chi_M T$ value monotonically decreased from 3.03 cm$^{-1}$K-mol$^{-1}$ at 300 K to about 1.15
The best fit was obtained with a fixed $g_F$ value of 2.00 and $g_{Ni} = 2.215(2)$; $J_{Fe-Fe} = -45.60(1)$ and $J_{Fe-Ni} = -16.96(2)$ cm$^{-1}$ ($R^2 = 8.54 \times 10^{-5}$). The unexpected shape of the $\chi_M T$ vs. $T$ curve can be clarified from the associated energy diagram for the spin-states (Figure 7). This reveals a (1, 0) ground state, succeeded by the first two excited states (0, 1) and (1, 1), so that there is a diamagnetic state between the two lowest-lying triplet states. When the temperature is decreased, the singlet first excited state becomes populated and the higher states with $S_T \geq 1$ become less populated, reducing $\chi_M T$. However, a further decrease in temperature depopulates this singlet level, in favour of the triplet ground state, so that the reduction in the $\chi_M T$ value with decreasing temperature is thus arrested and reversed.

\[
\chi_M T = (N g_m^2 \beta^2 / 3k) (546 e^{-a_T kT} + 330 e^{-b_T kT} + 180 e^{-c_T kT} + 30 e^{-d_T kT} + 6 e^{-e_T kT} + 30 e^{-f_T kT} + 6 e^{-g_T kT} + 9 e^{-h_T kT} + 7 e^{-i_T kT} + 11 e^{-j_T kT} + 2 e^{-k_T kT} + 5 e^{-l_T kT} + 3 e^{-m_T kT} + 7 e^{-n_T kT} + 5 e^{-o_T kT} + 3 e^{-p_T kT} + 6 e^{-q_T kT})
\]
When comparing the magnetochemical characteristics of 1–3, one notes that $J_{Fe-M}$ ($M = M^{II}$) is insensitive to the identity of $M^{II}$, whereas the $J_{Fe-Fe}$ values are affected by the nature of the third metal ion in the triangular skeleton. These results are in agreement with observations by Blake et al.[24] that $J_{Fe-Fe}$ increases significantly in $Fe_2M^{II}$ relative to that in similar trinuclear (carboxylato)(oxo)iron(III) complexes. It is noteworthy that trinuclear pivalate complexes[28] also show significant antiferromagnetic exchange.

Mössbauer Spectra

The electronic properties of complexes 1–3 were examined by $^{57}$Fe Mössbauer spectroscopy at 80 and 300 K (Figure 8, Table 5). Each of the spectra display one quadrupole-split doublet. The values of the isomer shifts (IS, $\delta$) and quadrupole splittings (QS) for 1–3 are close to those reported previously for similar heterometallic trinuclear complexes, and correspond to a high-spin iron(III) ion. Second-order Doppler effects (an increase in the isomer shift at cryogenic temperatures[30]) and Goldanskii–Karyagin anisotropy[30] (manifested by the different relative intensities of the two peaks of the doublet at higher temperatures) are minor, but detectable in the spectra. The data indicate that there is no occurrence of any intermetallic redox process during or subsequent to the synthesis – i.e. there is no electron transfer from $M^{3+}$ (especially from the more readily oxidizable Co$^{3+}$ and Mn$^{2+}$) to $Fe^{3+}$. However, the isomer shifts in 1–3 are smaller than in some other[31] heterotrinuclear complexes (Table 5), which may be accounted for by the electron-withdrawing nature of the CF$_3$ group; the decreased donor ability of the carboxylate group thus reduces the electron density in the 3d subshell.[30] Similar effects have been reported for other homopolynuclear iron(III) species.[32,33] The relatively high quadrupole splitting in 1–3 also reflects the significant electron-density transfer from the iron(III) centre to the trifluoroacetate anion. Previous work indicates that quadrupole splitting increases with $Fe^{III}$–carboxylate bond ionicity.

The Mössbauer results reveal no spin-spin interactions which would be indicative of the exchange coupling that is so compellingly suggested by the magnetic susceptometry.

Table 5. Mössbauer spectroscopic parameters of complexes 1–3

<table>
<thead>
<tr>
<th>Complex</th>
<th>$T$ [K]</th>
<th>IS [Mm/s]</th>
<th>QS [mm/s]</th>
<th>$I_1/I_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Fe_2Mn(\mu_3-O)(CF_3COO)_6(H_2O)_3]H_2O$</td>
<td>80</td>
<td>0.55</td>
<td>1.38</td>
<td>1.02(6)</td>
</tr>
<tr>
<td>$[Fe_2Co(\mu_3-O)(CF_3COO)_6(H_2O)_3]H_2O$</td>
<td>300</td>
<td>0.39</td>
<td>0.90</td>
<td>0.91(6)</td>
</tr>
<tr>
<td>$[Fe_2Ni(\mu_3-O)(CF_3COO)_6(H_2O)_3]H_2O$</td>
<td>300</td>
<td>0.43</td>
<td>1.15</td>
<td>1.05(6)</td>
</tr>
<tr>
<td>$[Fe_2Fe(\mu_3-O)(CF_3COO)_6(H_2O)_3]CF_3COOH$[a]</td>
<td>80</td>
<td>0.53</td>
<td>1.23</td>
<td>1.01(6)</td>
</tr>
<tr>
<td>$[Fe_3(\mu_3-O)(CH_2COO)_6(H_2O)_3]Cl$·$5H_2O$[b]</td>
<td>300</td>
<td>0.58</td>
<td>0.55</td>
<td>–</td>
</tr>
</tbody>
</table>


Figure 8. $^{57}$Fe Mössbauer spectrum of 1; the solid line is the least-squares fit; isomer shifts are referred to $\alpha$-iron at room temperature.

The relatively high $J$ values alone lead to the expectation that a “coupled” spectrum might be observed at 80 K. However, similar apparently paradoxical results have been reported by Rentschler and co-workers,[28] who pointed out that they are a consequence of the difference in the experimental time scales of the phenomena on which the two types of measurements are based; the magnetic exchange occurs on a timescale that is too fast to be detected by $^{57}$Fe Mössbauer spectroscopy.

Conclusion

Three new heterometallic trinuclear basic trifluoroacetates [$Fe_2M^{II}($μ$_2$-O)($CF_3COO$)$_6($H$_2$O)$_3$]$H_2O$ (M = Mn, Co, Ni) have been prepared. The crystal structures of two complexes were obtained at 100 K. FAB-MS data, IR and UV/
Vis spectra, along with magnetochemical and Mössbauer studies were interpreted in terms of the trinuclear nature of the compounds. The complexes exhibit substantial intramolecular antiferromagnetic exchange. The absence of any iron(II) centre, as proved by the Mössbauer investigation, showed that no electron transfer from MnII or CoII to FeIII occurred in these complexes. Increased values of quadrupole splittings are a result of the electron-withdrawing abilities of the CF3– group in the trifluoroacetate anions.

Experimental Section

General: Reagents and solvents (UkrReaKhim and Merck) were generally used as received. The precursory acetate complexes [FeIII(MII(µ3-O)(CH3COO)6(H2O)3)]3H2O (M = Mn, Co, Ni) were prepared as described elsewhere.[24]

[FeIII2MII(µ3-O)(CF3COO)6(H2O)3]3H2O (M = Mn, Co, Ni): The initial acetato complex [FeIII2MII(µ3-O)(CH3COO)6(H2O)3]3H2O (1.3 g, ca. 2 mmol) was dissolved in aqueous trifluoroacetic acid (15 mL of a 60% solution), and the resulting solution was refluxed for 1 h. After cooling, the reaction mixture was diluted with an equal volume of acetone. Slow concentration of the reaction mixture over several days resulted in the formation of a dark red single crystal of Z2. Magnetic susceptibility measurements were performed at 5 and 300 K. Mössbauer spectra were measured in the transmission mode on conventional spectrometers, a temperature-controlled Leybold cryostat was used for low-temperature spectra. A 3·105 Bq 57Co(Rh) sample was used as the γ-ray source, while isomer shifts were referred to α-iron at room temperature. Spectra were deconvoluted using the MossWin program.[34]

X-ray Crystallographic Study: Crystals suitable for crystallography were grown from CH3NO2/mesitylene (for the Mn complex) or from CH3NO2/(CH3)2CO/mesitylene layering (for the cobalt complex). A dark red single crystal of Z2 was coated with perfluoropolyether, picked up with a glass fibre and immediately mounted in the cold nitrogen stream to prevent loss of solvent. Intensity data were collected with a Siemens SMART diffractometer at 100 K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Final cell constants were obtained from a least-squares fit of 4419 reflections. Data collection was performed by hemisphere runs taking frames at 0.3°. A semiempirical absorption correction using the program SADABS[35] was performed on the data set of Z2. Crystallographic data are listed in Table 6. The Siemens SHELXTL software package was used for solution, refinement and artwork of the structure. The structure was readily solved by direct methods and difference Fourier techniques. All non-hydrogen atoms except atoms in disordered parts were refined anisotropically and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Split atom models were used to account for the disorder of the CF3COO groups and a mesitylene solvent molecule lying on the crystallographic mirror plane. The C–F and F–F distances of the CF3 groups were re-

Table 6. Crystal data and structure refinement details

<table>
<thead>
<tr>
<th></th>
<th>1'</th>
<th>2'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C12H8N2O22Fe2Co</td>
<td>C12H8N2O22Fe2Mn</td>
</tr>
<tr>
<td>Formula mass</td>
<td>1078.89</td>
<td>1153.13</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/m</td>
</tr>
<tr>
<td>a [Å]</td>
<td>22.002(5)</td>
<td>21.426(4)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>13.647(3)</td>
<td>14.185(3)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>98.23(3)</td>
<td>117.99(2)</td>
</tr>
<tr>
<td>β [°]</td>
<td>7359.9(2)</td>
<td>4232.50(13)</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ρcalcld. [g cm⁻³]</td>
<td>1.241</td>
<td>1.810</td>
</tr>
<tr>
<td>T [K]</td>
<td>100(2)</td>
<td>100</td>
</tr>
<tr>
<td>μ [mm⁻¹] (Mo-Kα)</td>
<td>1.16</td>
<td>1.214</td>
</tr>
<tr>
<td>Number of reflections collected</td>
<td>11349</td>
<td>8847</td>
</tr>
<tr>
<td>Number of independent reflections</td>
<td>6424</td>
<td>3622</td>
</tr>
<tr>
<td>Number of parameters</td>
<td>457</td>
<td>346</td>
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<tr>
<td>Rint</td>
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<td>0.0541</td>
</tr>
<tr>
<td>R1 (all data)</td>
<td>0.1316</td>
<td>0.0874</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.3665</td>
<td>0.1822</td>
</tr>
</tbody>
</table>

The standard deviations are reported in parentheses.
Acknowledgments

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