Pentanuclear complexes with unusual structural topologies from the initial use of two aliphatic amino-alcohol ligands in Fe chemistry†

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Five novel pentanuclear Fe3+ clusters with the aliphatic amino-alcohol ligands 3-amino-1-propanol (Hap) and 2-(hydroxymethyl)piperidine (Hhmp) [Fe5(µ3-O)(µ4-O)(O2CR)11+ core which consists of two vertex-sharing [Fe3(µ3-O)(µ4-O)]7+ triangles. The structure of 5 is based on the [Fe5(µ3-O)(µ4-O)]11+ core, in which the five Fe3+ ions adopt a monocapped trigonal topology. Variable-temperature magnetic susceptibility measurements on powdered microcrystalline samples of 1 and 5 revealed the existence of antiferromagnetic interactions which led to an S = 5/2 ground state. Mössbauer spectroscopy studies on powdered microcrystalline samples of 1 and 5 confirmed that all iron ions of both complexes are in the Fe3+ (S = 5/2) state. The variation of the ligand environment in the various iron sites was reflected in their different quadruple splitting parameters. At T < 50 K the Mössbauer spectra indicated the onset of spin relaxation effects in the time scale of the technique (10−7−10−4 s).

Introduction

The chemistry of polynuclear Fe compounds is a topic of great scientific interest due to its relevance to many areas, including bioinorganic chemistry and materials science. In the bioinorganic area, for example, there is a great desire to model the structure and function of the ferric oxyhydroxide core of the iron storage protein ferritin, which contains up to 4500 Fe centers.12 In addition, the Fe3S4 cubane clusters are famous examples of biologically relevant polynuclear Fe compounds with remarkable electron transfer and biocatalytic properties.5 In the field of materials science, high-nuclearity iron compounds often exhibit interesting magnetic properties. For example, a number of such compounds exhibit large ground-state spin values because of spin frustration, with some of them displaying enhanced magnetocaloric effect4 or single-molecule magnetism (SMM) behaviour.5–11

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It is thus not surprising that considerable effort has been expended in order to develop new synthetic strategies for the isolation of novel polynuclear Fe compounds. One of the most successful methods towards this direction involves the use of chelating alcohol-containing ligands because alkoxides are good bridging groups and thus facilitate the assembly of polynuclear compounds.12 As a result, several such ligands were successfully employed in Fe cluster chemistry including various 2-(hydroxyalkyl)pyridine derivatives,14 benzotriazolyl alcohols,16 aliphatic amino-polycarboxylates (e.g. diethanolamine, triethanolamine, etc),18,21 salicylidene-alcoholamines,16,17 di-2-pyridylketone derivatives,18 etc. These investigations have resulted in a plethora of polynuclear Fe compounds with large nuclearities, up to 64,18 a variety of structural topologies and sometimes interesting magnetism.

As part of our ongoing search for new synthetic routes to high nuclearity species,13a,19,22 we turned our attention towards the employment of aliphatic amino-alcohols in Fe carboxylate chemistry. Among the organic species that have been successfully employed for the synthesis of high nuclearity metal clusters are 1,3-propanediol (H2pd)19,21 and 2-(hydroxymethyl)pyridine (Hhmp).13a,24,25 We have been investigating the use of ligands that present some similarity to the above-mentioned examples but have not been used widely in metal cluster chemistry. Thus, we have been
recently exploring the use of 3-amino-1-propanol (Hap), which is related to H₃pd, and also 2-(hydroxymethyl)piperidine (Hhmpip), which can be considered as the aliphatic analogue of Hhmp, in Fe carboxylate chemistry. To the best of our knowledge there are no Fe complexes reported with these ligands and only a handful of M₅ (x > 2) clusters with any metal ion in general.²⁶

We report herein the synthesis and structural, magnetic and spectroscopic characterization of five new pentanuclear Fe₅⁺ clusters with the ligands Hap and Hhmpip: [Fe₅(m₄-O)(L₃)(O₂CC(CH₃)₃)₇] [L = ap, R = Ph (1); L = ap, R = C(CH₃)₃ (2); L = hmpip, R = Ph (3); L = hmpip, R = C(CH₃)₃ (4)] and [Fe₅(m₄-O)(μ₄-O)(OC(CH₃)₃)(H₂O)₃] [L(O₂CC(CH₃)₃)] (5). These clusters possess the [Fe₅(μ₄-O)]₃⁻ (1–4) and [Fe₅(μ₄-O)(μ₃-O)]₃⁻ (5) structural cores which display topologies rarely found in metal cluster chemistry. Magnetic susceptibility studies on powdered microcrystalline samples of 1 and 5 revealed the existence of dominant antiferromagnetic exchange interactions that result in a spin ground state S₅ = 5/2 for both complexes. Mössbauer spectroscopic studies for complexes 1 and 5 confirmed that all Fe ions of both complexes are in the oxidation state 3⁺ (S = 5/2) and provided information about their coordination environment. Moreover, Mössbauer spectroscopy was also used to monitor the spin relaxation behaviour of 1 and 5.

Experimental section

Materials

All reactions were performed under aerobic conditions. Solvents and reagents were obtained from commercial sources and used as received. [Fe₂O(O₂CC(CH₃)₃)₆(H₂O)₃(NO₃)] (0.1 g, 0.097 mmol) and [Fe₂O-(O₂CC(CH₃)₃)₆(H₂O)₃(OH)]H₂O. [Fe₂O(O₂CC(H₃)₃)₆(H₂O)₃(NO₃)] and [Fe₂O(O₂CC(H₃)₃)₆(H₂O)₃][O₂CC] were prepared as described elsewhere.²⁷,²⁸

Syntheses

[Fe₅O₃(μ₄-O)(O₂CC)-MeCN (1-MeCN)]. To a stirred solution of [Fe₅O₃(O₂CC)₃(H₂O)₃(NO₃)] (0.1 g, 0.097 mmol) in 15 mL of MeCN was added Hap (0.041 mL, 0.536 mmol) and the resulting brown solution was refluxed for 30 min and then cooled to room temperature. The resulting mixture was filtered off and the filtrate was allowed to stand undisturbed in closed vials at room temperature. After a week, brown, X-ray quality crystals of 1 were formed, collected by filtration, washed with MeCN and dried under vacuum (yield: 4%). Elemental analysis (%) calcd for C₇₃H₈₃Fe₅N₄O₂₀: C 61.07, H 4.68, N 3.86. Found: C 60.69, H 4.76, N 3.77. Selected IR data (KBr): ν (cm⁻¹) 3429 (m, br), 3134 (m), 2934 (m), 2925 (m), 2926 (m), 2876 (m), 1601 (s), 1500 (s), 1491 (m), 1458 (m), 1445 (m), 1406 (s), 1346 (s), 1302 (m), 1175 (m), 1125 (s), 1069 (s), 1059 (s), 1026 (s), 932 (m), 719 (s), 689 (s), 673 (s), 655 (m), 542 (m), 505 (m), 469 (s).

[Fe₅O₃(μ₄-O)(O₂CC(CH₃)₃)] (2). Method A. To a solution of [Fe₅O(O₂CC(CH₃)₃)₆(H₂O)₃][NO₃] (0.1 g, 0.110 mmol) in 15 mL of N,N-dimethylformamide (DMF) was added Hap (0.042 mL, 0.55 mmol) and left under magnetic stirring for ~15 min. Then it was filtered off and the filtrate was layered with MeCN (15 mL). After a week, a few yellow-brown, X-ray quality crystals of 2 were formed, collected by filtration, washed with MeCN and dried under vacuum (yield: 4%). Elemental analysis (%) calcd for C₆₀H₇₀Fe₅N₅O₂₀: C 35.67, H 4.06, N 3.75. Found: C 35.63, H 4.01, N 3.39. Selected IR data (KBr): ν (cm⁻¹) 3429 (m, br), 3154 (m), 2925 (m), 2924 (m), 2872 (m), 1580 (s), 1502 (s), 1483 (s), 1396 (m), 1375 (m), 1360 (m), 1342 (m), 1227 (m), 1211 (m), 1063 (m), 708 (m), 606 (m), 584 (m), 546 (m), 507 (m), 420 (m).

[Fe₅O₃(hmpip)(O₂CC)] (3). Method A. To a solution of [Fe₅O(O₂CC)₆(H₂O)₃][NO₃] (0.1 g, 0.097 mmol) in 15 mL of MeCN was added Hhampp (0.055 g, 0.478 mmol) and the resulting brown solution stirred for 45 min. Then it was filtered off and the filtrate was left undisturbed at room temperature. A few brown crystals of 3.1 MeCN·H₂O were formed after two weeks, collected by filtration, washed with MeCN, and dried under vacuum (yield: 3%). Elemental analysis (%) calcd for C₇₃H₈₃Fe₅N₄O₂₀·MeCN: C 61.07, H 4.68, N 3.86. Found: C 60.99, H 4.72, N 3.80. Selected IR data (KBr): ν (cm⁻¹) 3429 (m, br), 3134 (m), 2934 (m), 2925 (m), 2924 (m), 2876 (m), 1601 (s), 1500 (s), 1491 (m), 1458 (m), 1445 (m), 1406 (s), 1346 (s), 1302 (m), 1175 (m), 1125 (s), 1069 (s), 1059 (s), 1026 (s), 932 (m), 719 (s), 689 (s), 673 (s), 655 (m), 542 (m), 505 (m), 469 (s).
1360 (m), 1331 (m), 1263 (w), 1227 (m), 1215 (m), 1092 (m), 1067 (m), 1045 (m), 1032 (m), 991 (m), 789 (m), 708 (m), 619 (m), 606 (m), 588 (m), 536 (m), 521 (m), 496 (m), 467 (m), 426 (m).

Method B. Solid Hmpip (0.067 g, 0.58 mmol) was added to a solution of [Fe\(_3\)O\(_2\)(O\(_2\)CC(CH\(_3\))\(_3\))(H\(_2\)O)\(_2\)(OH)]\(_4\) in 15 mL of MeCN and the resulting, brown solution stirred for 1 h, filtered off and the filtrate was left undisturbed in a sealed flask at room temperature. Brown crystals of 4.03 H\(_2\)O were slowly formed over 5 days, isolated by filtration, washed with MeCN, and dried under vacuum (yield: 41%). The product was identified by IR spectral comparison with authentic material and from unit cell determination.

\[ \text{[Fe}_3\text{O}_2\text{(O}_2\text{CC(CH}_3\text{))}_6\text{(H}_2\text{O)O(H)}\text{H}_2\text{O}]_{\text{4}} \]

To a solution of FeCl\(_3\) \((1.0 \text{ g, 6.17 mmol) and H}_2\text{O}_2\text{CC(CH}_3\text{)}\text{3}(1.26 \text{, 12.34 mmol) in MeCN (150 mL) was added Hap (1.41 mL, 18.43 mmol) and the resulting mixture was stirred for 1.5 h, filtered off and the filtrate was left undisturbed at room temperature in a sealed flask. After a few weeks brown crystals of 5.0H\(_2\)OCC(CH\(_3\))\(_3\))\(_3\) were formed, collected by filtration, washed with MeCN, and dried under vacuum (yield 33%).

Elemental analysis (%) calcd for Cs\(_6\)H\(_{10}\text{Fe}_2\text{N}_3\text{O}_3\text{ (5.0H}_2\text{OCC(CH}_3\text{))}_3\): C 44.60, H 7.22, N 1.86. Found: C 44.50, H 6.98, N 1.76. Selected IR data (KBr): \(\text{3429 (m, br), 2963 (m), 2937 (m), 2870 (m), 2855 (m), 2375 (s), 2243 (s), 1625 (s), 1544–1552 (s).}\)

X-ray crystallography

Data were collected on an Oxford Diffraction Xcalibur diffractometer, equipped with a CCD area detector and a graphite monochromator using Mo-K\(_\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software. The structures were solved by direct methods using SIR92\(^\text{38}\) and refined on \(F^2\) using full-matrix least squares using SHELXL97.\(^{39}\) Software packages used: CrysAlis CCD for data collection,\(^{29}\) CrysAlis RED for cell refinement and data reduction,\(^{39}\) WINGX for geometric calculations,\(^{32}\) and DIAMOND\(^{40}\) for molecular graphics. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. The H atoms of water molecules could not be located. Unit cell data and structure refinement details are listed in Table 1. Full details can be found in the CIF files provided in the ESI.\(^{41}\)

Physical measurements

Elemental analyses (C, H, N) were performed by the in-house facilities at the University of Cyprus, Chemistry Department. IR spectra were recorded on KBr pellets in the 4000–400 cm\(^{-1}\) range using a Shimadzu Prestige–21 spectrometer. Variable-temperature magnetic susceptibility measurements were carried out on powdered microcrystalline samples of 1-MeCN and 5-HO\(_2\)OCC(CH\(_3\))\(_3\))\(_3\) in the 2–300 K temperature range using a Quantum Design MPMS SQUID susceptometer. Diamagnetic corrections for the complexes were estimated from Pascal’s constants. Alternating current (ac) magnetic susceptibility experiments were carried out on a Quantum Design PPMS magnetometer. \(^{57}\)Fe Mössbauer spectra were recorded in the constant acceleration mode at temperatures controlled with a Janis cryostat. Isomer shifts are reported relative to iron metal at room temperature. Simulations of the Mössbauer spectra were obtained with the program WMOSS (See Co., Edina, Minnesota) or with locally written routines.

Results and discussion

Syntheses

A synthetic method that has been extensively used by us\(^{5a,29}\) and also by others\(^{5a,12a,13b,14}\) for the synthesis of new high
nuclearity Mn and Fe clusters involved the reaction of trinuclear [Mn3O(O2CR)6]11+/12+ compounds with a bidentate chelate. For example their reaction with Hhmp and H2pd ligands, which are related to the Hhmpip and Hap employed in the present study, under a variety of different conditions has resulted in several polynuclear Mn and Fe clusters.12a,20,23b In such reactions the [Mn3O11+/12+] triangular core serves as a useful building block for higher nuclearity metal clusters.12 Thus, the reaction of [Fe3O(O2CPh)6(H2O)3(NO3)] with Hap in 1:5 molar ratio in MeCN afforded compound 1 in 64% yield. Similar reactions of [Fe3O(O2CC(CH3)3)6(H2O)3(NO3)] with Hhmpip and Fe3O(O2CC(CH3)3)6(H2O)3(NO3) with Hap and Hhmpip were also performed and resulted in the isolation of single crystals of complexes 2–4 in very low yields (<5%).

$$\text{5[Fe}_3\text{O(O2CR)}_6\text{(H}_2\text{O)}_3\text{(NO}_3\text{)] + 12HL \rightarrow 3[Fe}_3\text{O}_2\text{(L)l(O2CC(CH}_3\text{))}_3\text{]} + 9\text{HO}_2\text{CR} + 5\text{HNO}_3 + 14\text{H}_2\text{O}$$

(1) $\text{R} = \text{Ph}, \text{HL} = \text{Hap, 1; R} = \text{C(CH}_3\text{)}_3, \text{HL} = \text{Hap, 2; R} = \text{Ph,}$

$\text{HL} = \text{Hhmpip, 3; R} = \text{C(CH}_3\text{)}_3, \text{HL} = \text{Hhmpip, 4}$

In order to achieve higher yield synthetic procedures for 2–4 several modifications were applied in the reaction conditions. Some of the reaction modifications involved the use of a variety of different Fe3+ precursors including a few other trinuclear Fe3+ species. Thus, the reaction of [Fe3O(O2CPh)6(H2O)3(NO3)] with Hap or Hhmpip in 1:5 molar ratio in DMF or MeCN resulted in complexes 2 and 4, respectively, in 40–45% yield, whereas the reaction of [Fe3O(O2CC(CH3)3)6(H2O)3(NO3)] with Hhmpip in 1:5 molar ratio in MeCN led to complex 3 in 66% yield. When, however, FeCl3 was used as a starting material in a reaction with Hap, a different product was isolated. Thus, the reaction of FeCl3 with Hap in the presence of HO2CC(CH3)3 in 1:3:2 molar ratio in MeCN afforded compound 5. The formation of 5 is summarized in eqn (2).

$$\text{5FeCl}_3 + 2\text{Hap} + 9\text{HO}_2\text{CC(CH}_3\text{)}_3\text{)} + 2\text{H}_2\text{O} \rightarrow$$

$$[\text{Fe}_5(\mu_3-O)(\mu_2-O)\text{(O2CC(CH}_3\text{))}_3\text{(ap)}_2\text{Cl}(\text{HO}_2\text{CC(CH}_3\text{)})] + 14\text{HCl}$$

(2) Reactions of i) FeCl3 with Hhmpip and ii) various Fe3+ salts (e.g. Fe(NO3)3) with both ligands under various conditions were also performed and resulted in the formation of microcrystalline materials that we were unable to characterize further.

Structures

Representations of the molecular structure, the structural core and the topological motif that was derived using an approach reported recently14 of compound 1 are presented in Fig. 1 and selected interatomic distances are listed in Table 2. Compounds 1–4 display related structures since they all contain the same [Fe5(\mu3-O)11+] structural core. Their main differences are the type of carboxylate and amino-alcohol ligands and thus, only the structure of compound 1 will be discussed in detail and will be compared to those of 2–4. Structural figures and tables with selected interatomic distances for complexes 2–4 are provided in the ESL.† Compound 1-MeCN crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit of 1-MeCN consists of the [Fe5(\mu3-O)11+] cluster and one MeCN molecule of crystallization. All Fe atoms of 1 adopt a distorted octahedral coordination geometry and are in the oxidation state 3+. The structure of 1 is based on the [Fe5(\mu3-O)11+] core which consists of two vertex-sharing [Fe5(\mu3-O)11+] triangles. This core adopts a quasi-planar configuration with a mean deviation from the best fit plane of ~0.22 Å and the maximum deviation from this plane being observed for Fe5 and O20 (~0.44–0.46 Å). The two [Fe5(\mu3-O)11+] triangles apart from sharing a Fe3+ ion (atom Fe2) are also connected through two alkoxide arms of two ap3 ligands. The peripheral ligation of the Fe atoms is accomplished by seven benzoate groups and four amino-alcohol
ligands, which are all in their monoanionic forms (ap\(^-\)) and (O\(_2\)CPh), respectively, as confirmed by BVS calculations,\(^{15}\) charge considerations and inspection of metric parameters. The four ap\(^-\) ligands are coordinated in \(\eta^1: \eta^1: \mu_1\) fashion, with the alkoxo group acting as a \(\mu_1\) ligand and the amino-group ligated to one Fe center. In addition, five of the benzoate ligands bridge in the common \(\text{syn-syn-} \eta^1: \eta^1: \mu_2\) fashion, whereas the remaining two act as terminal ligands. A close examination of the packing of 1 revealed the existence of both intra- and intermolecular hydrogen bonding interactions involving carboxylate oxygen and amine N atoms (O...N ~3.0 Å within the same molecule and O...N ~2.9 Å between adjacent molecules of 1). The molecules of 1 are thus in close proximity, with the shortest Fe...Fe separation between adjacent Fe units being ~6.258 Å.

Alternatively the topology of the Fe\(_5\) cluster of 1 can be described based on an elegant approach reported recently.\(^{16}\) According to this approach the topological motif of the Fe\(_5\) cluster can be represented as consisting of three Fe\(_3\) triangles, with the central triangle sharing an edge with each of the two peripheral ones (Fig. 1, bottom, right). Thus, complex 1 is trinodal (2,3,4) (with Fe1 and Fe3 being the 2-connected nodes, Fe4 and Fe5 being 3-connected nodes and Fe2 representing the 4-connecting node) and the cluster’s vertex symbol (v.s.) is \((3)(3^2,4)\)(3^3,4^2,5).

The structure of compound 2 is very similar to that of 1, with the main differences between them being the presence of pivalate groups in 2 (instead of benzoates in 1) and the absence of lattice solvent molecules in its crystal structure. The structures of 3 and 4 are also related to those of 1 and 2 with their main differences being the presence of hmpip\(^-\) in the former complexes instead of the ap\(^-\) ligand. Note that the hmpip\(^-\) groups are coordinated in a \(\eta^1: \eta^1: \mu_2\) fashion (as exactly the ap\(^-\) ones in 1 and 2) with the piperidine N atom acting as terminal ligand for a Fe center and the methoxy-group bridging a pair of Fe atoms.

The only other known examples of pentanuclear clusters with an \([\text{Fe}(\mu_3-O)]^{11+}\) core are compounds \([\text{Fe}_5\text{O}_6\text{(OH)}\text{(O\(_2\)CMe)}\text{(hmbp)}\text{]}\text{(ClO}_4\text{)}_2\text{]}\ (\text{Hhmbp} = 6\text{-hydroxymethyl-2,2'-bipyridine}),\[^{34}\] [Fe\(_5\)O\(_6\)C\(_6\)Ph\(_2\)]\text{(edte)}\text{H}_2\text{O}\text{]}\ (edteH\(_2\text{I} = N,N',N''\text{-tetraakis(2-hydroxyethyl)ethylendiamine})\[^{14}\] and \([\text{Fe}_5\text{O}_6\text{(OMe)}\text{(Bta)}\text{]}\text{(BtaH)}\text{(MeOH)}\text{Cl}\text{]}\ (\text{Bta} = \text{benzotriazole}).\[^{16}\] However, the \([\text{Fe}(\mu_2-O)]^{11+}\) core of 1 has a significantly different topology than those of the above mentioned clusters. In particular, the former two clusters consist of an \([\text{Fe}(\mu_3-O)]^{11+}\) butterfly-like subunit on the top of which is attached a fifth Fe atom through alkoxide bridges, whereas the latter one is better described as an elongated 'ferric tetrahedron'. The core topology of 1 not only appears for the first time in Fe chemistry but is also uncommon for any metal ion in general.\[^{37}\] In addition, compounds 1, 2 and 3, 4 represent the initial examples of Fe complexes with the ligands Hap and Hhmpip, respectively. In fact, there are only a few metal complexes in general reported with both ligands\[^{36}\] and especially with Hhmpip the only known complexes are some dinuclear In, Al and Ga compounds.\[^{26-28}\] Thus, complexes 3 and 4 represent the initial examples of M\(_1\)-Hhmpip (\(x > 2\)) metal clusters.

Compound \(\text{5HO}_2\text{CC(CH}_3\text{)}_3\), crystallizes in the monoclinic space group \(P2_1/c\). Representations of the molecular structure, the structural core and the topological motif that was derived using an approach reported recently\(^{14}\) of compound 5 are presented in Fig. 2 and selected interatomic distances are listed in Table 3.

The asymmetric unit of \(\text{5HO}_2\text{CC(CH}_3\text{)}_3\), contains the cluster \([\text{Fe}(\mu_3-O)(\mu_3-O\text{(O}_2\text{CCH}_3\text{)}}\text{(Hhmbp)}\text{]}\text{(ClO}_4\text{)}\text{]}\) (Fig. 2) and one lattice pivalic acid molecule. All Fe atoms of 1 adopt a distorted octahedral coordination geometry and are in the oxidation state 3+. The structure of 5 is based on the \([\text{Fe}(\mu_3-O)(\mu_3-O)]^{11+}\) unit, which displays a monocapped trigonal pyramidal
topology. The four Fe centers that are located at the vertices of the trigonal pyramid are bridged through the \( \mu_2\)-O\(^{2-} \) group whereas the fifth, capping Fe atom is linked to two Fe atoms of the pyramid base via the \( \mu_2\)-O\(^{2-} \) ligand. The peripheral ligation of \( \mathbf{5} \) is completed by eight \( \mathrm{O}^{2-}, \mathrm{piv} \), one \( \mathrm{HO}_2\mathrm{CC}(\mathrm{CH}_3) \), two \( \mathrm{ap}^- \) and one \( \mathrm{Cl}^- \) ligands. The protonation levels of \( \mathrm{O}^{2-}, \mathrm{ap}^-, \mathrm{O}_2\mathrm{CC}(\mathrm{CH}_3) \), and \( \mathrm{HO}_2\mathrm{CC}(\mathrm{CH}_3) \) were determined by BVS calculations,\(^{38} \) inspection of metric parameters and charge balance considerations. Seven of the pivalate groups bridge in the common \( \mathrm{syn}_2\mathrm{syn}_2-\eta^1: \eta^1: \mu_2 \) fashion, while the remaining \( \mathrm{O}_2\mathrm{CC}(\mathrm{CH}_3) \) acts as a chelate ligand coordinating to one Fe atom. The pivalic acid coordinates as monodentate ligand to Fe3. One of the \( \mathrm{ap}^- \) ligands coordinates in a \( \eta^1: \eta^1: \mu_2 \) fashion, with the alkoxo group bridging a pair of Fe centers and the amine N acting as terminal ligand for one Fe atom, whereas the second one bridges two Fe\(^{3+} \) ions through its alkoxo group with its amine group remaining uncoordinated. Finally, the \( \mathrm{Cl}^- \) ion coordinates as a terminal ligand to the capping Fe atom. A close examination of the packing of \( \mathbf{5} \) shows the existence of both intra- and intermolecular hydrogen bonding interactions. Specifically, intramolecular hydrogen bonding interactions involve the O atoms of lattice and bound pivalic acid molecules and pivalate ligands, the N atom of one \( \mathrm{ap}^- \) ligand and one \( \mathrm{Cl}^- \) anion. Neighboring molecules of \( \mathbf{5} \) are linked through intermolecular hydrogen bonding interactions between an amine N atom of an \( \mathrm{ap}^- \) ligand and a carboxylic oxygen atom and \( \mathrm{Cl}^- \) ion (N--\( \cdot\cdot\cdot\)Cl \( ~3.3 \) Å, N--\( \cdot\cdot\cdot\)O \( ~3.0 \) Å). The molecules of \( \mathbf{5} \) are thus in very close proximity, with the shortest Fe--Fe separation between adjacent Fe\(_5\) units being \( ~6.121 \) Å.

Alternatively, the topology of compound \( \mathbf{5} \) can be described based on the approach recently reported.\(^{34} \) According to this approach, compound \( \mathbf{5} \) is a trinodal (2,3,4) cluster (Fig. 2). Fe5 is the 2-connected node, Fe2 and Fe3 are 3-connected nodes, whereas Fe1 and Fe4 represent the 4-connecting nodes. The vertex symbol for this topology is \( (3)(3^3)(4^2) \). Although the monocapped trigonal pyramidal topology has appeared in other Fe\(_5\) clusters,\(^{44} \) to the best of our knowledge, there is no known Fe compound with the structural core \([\mathrm{Fe}_5(\mu_2-O)(\mu_2-O)]^+\). In addition, a Cambridge database search showed that the \([\mathrm{M}_5(\mu_2-O)(\mu_2-O)]^+\) monocapped trigonal pyramidal core of \( \mathbf{5} \) not only appears for the first time in Fe chemistry but is also uncommon in metal cluster chemistry, in general.\(^{38},^{39} \)

**Magnetic properties**

The \( \chi_M T \) value at 300 K is similar for complexes \( \mathbf{1} \) and \( \mathbf{5} \) (7.74, and 7.97 cm\(^3\) mol\(^{-1}\) K\(^{-1}\)), well below the theoretically expected value of five non-interacting \( S = 5/2 \) spins (21.88 cm\(^3\) mol\(^{-1}\) K\(^{-1}\)), indicating significant antiferromagnetic interactions. This is corroborated by the decrease of \( \chi_M T \) upon cooling, reaching a value around 20 K (\( \mathbf{1}: 4.22; \mathbf{5}: 4.34 \) cm\(^3\) mol\(^{-1}\) K) indicative of an \( S = 5/2 \) ground state (4.37 cm\(^3\) mol\(^{-1}\) K). In particular, \( \mathbf{5} \) shows a well defined plateau below 45 K. For complex \( \mathbf{1} \) the lack of such a plateau suggests the presence of low-lying excited states. As is shown in Fig. 3 (top) the \( \chi_M T \) vs \( T \) curves for complexes \( \mathbf{1} \) and \( \mathbf{5} \) in the 300–25 K temperature range have distinctly different shapes. This is consistent with the different structural and magnetic topologies of \( \mathbf{1} \) and \( \mathbf{5} \) which result in different magnetic exchange coupling schemes. However, \( \mathbf{1} \) and \( \mathbf{5} \) exhibit similar low temperature \( \chi_M T \) values, suggesting common ground state spin values.

![Graph showing \( \chi_M T \) vs \( T \) for complexes \( \mathbf{1} \) and \( \mathbf{5} \)](image)

**Fig. 3** (Top) Temperature dependence of the susceptibility data, plotted as \( \chi_M T \) vs \( T \) for compounds \( \mathbf{1} \) and \( \mathbf{5} \) and (bottom) magnetization data at 2.0 K for compounds \( \mathbf{1} \) and \( \mathbf{5} \). The dashed and solid lines in the bottom figure correspond to the Brillouin curves for an \( S = 5/2 \) \((g = 2.0) \) system in the absence of zero field splitting and an \( S = 5/2 \) with \( D = 0.7 \) cm\(^3\) \((g = 2.0) \) system, respectively.

Isothermal magnetization studies at 2 K for the two complexes revealed the onset of saturation near 5 T, at magnetization values (\( 1: 4.68; \mathbf{5}: 5.19 \) \( N_A \mu_B \); \( N_A \) is Avogadro's number and \( \mu_B \) is the Bohr magneton) corresponding to \( S = 5/2 \) ground states. However, none of the complexes exhibited an ideal Brillouin behavior. It was only possible to simulate the \( M \) vs. \( H \) variation of \( \mathbf{5} \) with an \( S = 5/2 \) spin value exhibiting an axial zero-field splitting value of \( |D| = 0.7 \) cm\(^3\) in general.\(^{38},^{39} \)

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A dc magnetic field disrupts quantum tunneling of magnetization within the ground state spin manifold and the observed relaxation involves excited states. Prompted by these studies, we performed ac susceptibility measurements on powdered microcrystalline samples of 1 and 5. No out-of-phase ac signals were observed for 1 in the presence of a dc magnetic field of a few kOe for temperatures down to 2.0 K. Note that the static magnetic susceptibility measurements of 1 suggest the presence of low lying excited states. These might provide efficient pathways for fast relaxation with characteristic times shorter than $\sim 10^{-7}$ s (the limit of our instrument). In addition, incomplete cancellation of quantum tunneling of magnetization may occur. Fig. 4 shows the temperature dependence of the real $\chi'$ and imaginary $\chi''$ parts of susceptibility from a powdered sample of 5 in the presence of a dc field of 6 kOe at four different frequencies. A theoretical curve corresponding to the expected temperature dependence of $\chi'$ (calculated from the equation $\chi' = d\chi_{\text{static}}/dH_d$) for an $S = 5/2$ system with $D = 0.7$ cm$^{-1}$ in the absence of relaxation effects is superimposed on the data of Fig. 4. Below 7 K a decrease of $\chi'$ is observed, suggesting the onset of relaxation effects. Indeed, out-of-phase ac signals have been observed in the past for another polynuclear Fe$^{3+}$ (S = 5/2) cluster and can be explained assuming that the non-zero $\chi''$ corresponds to a minority fraction of molecules that exhibit slow relaxation, with the majority of molecules relaxing fast.

Mössbauer studies

Mössbauer spectra from powder samples of 1 and 5 recorded at 295 K are shown in Fig. 5. The variation of the iron environment in 1, which contains four FeON$_5$ and one FeO$_6$ chromophores, is reflected in the 295 K Mössbauer spectrum, which consists of at least two different quadrupe doublets (Fig. 5). This spectrum may be deconvoluted with two quadrupe doublets at a 4 : 1 ratio. The majority doublet, 1A, is characterized by $\Delta E_{Q,1A} = 1.13(2)$ mm s$^{-1}$ and $\delta_{1A} = 0.41(1)$ mm s$^{-1}$, whereas for the minority doublet, 1B, $\Delta E_{Q,1B} = 0.44(2)$ mm s$^{-1}$ and $\delta_{1B} = 0.42(2)$ mm s$^{-1}$. The isomer shift values are consistent with high spin ferric ions in O/N environment. The FeON$_5$ environments are more asymmetric than the FeO$_6$ ones suggesting that the former should exhibit larger $\Delta E_0$ values. On the basis of the stoichiometry and the relationship between the values of $\Delta E_0$, the two sites we may assign doublet 1A to the FeON$_5$ and 1B to the FeO$_6$ environments.

An examination of the molecular structure of complex 5 reveals that it contains three different types of coordination environments. Thus, three Fe centers display a FeO$_{6}$, one a FeO$_{5}$Cl and one a FeO$_{5}$N coordination environments. As in the case of cluster 1, the differentiation of the iron sites is evidenced in the spectrum, which consists of at least two different doublets. The resolution of the spectrum however does not allow us to distinguish three distinct doublets at the anticipated 3 : 1 : 1 ratio. For the deconvolution of the spectrum we used two different doublets at a 4 : 1 ratio. The majority doublet, 5A, is characterized by $\Delta E_{Q,5A} = 0.52(2)$ mm s$^{-1}$ and $\delta_{5A} = 0.43(1)$ mm s$^{-1}$ and for the minority doublet 5B, $\Delta E_{Q,5B} = 1.06(2)$ mm s$^{-1}$ and $\delta_{5B} = 0.41(2)$ mm s$^{-1}$. The isomer shift values are consistent with high spin ferric ions in O/N environment. Doublet 5B accounting for one iron site per molecule exhibits the largest value $\Delta E_0$. It can be assigned either to the FeO$_{5}$Cl or to the FeO$_{5}$N environment. Doublet 5A, which accounts for roughly four iron sites per cluster, should correspond to the other coordination environments.

Representative Mössbauer spectra collected at low temperatures are shown in Fig. 6. The spectra do not exhibit significant

**Fig. 4** Alternating current magnetic susceptibility measurements from a microcrystalline powder sample of 5 in the presence of a dc magnetic field of 6 kOe conducted at 94 ($\times$), 1814 ( ), 5631 ( ) and 9111 (+) Hz; (H$_d$ = 5 Oe). The solid line corresponds to the expected temperature dependence of $\chi'$ in the absence of relaxation effects for an $S = 5/2$ system with $D = 0.7$ cm$^{-1}$.

**Fig. 5** Mössbauer spectra from powder samples of 1 and 5 at 295 K. Solid lines are theoretical simulations as discussed in the text. Doublets 1A, 1B, 5A, and 5B have been shifted for clarity.
modifications upon lowering the temperature down to 80 K, apart from an increase of the average isomer shift due to second order Doppler shift. Below 50 K, however, a gradual broadening of the spectra occurs. This behaviour suggests that the rate for spin inversion compares with the characteristic time of the Mössbauer spectroscopy ($t \sim 10^{-4} - 10^{-3}$ s). For 1, a magnetically split spectrum is observed at 4.2 K, while for 5 broad spectra are observed even at 1.5 K. Magnetically split spectra from oligo- or polynuclear iron clusters are often correlated with slow paramagnetic relaxation. Mössbauer spectra depend on both spin–lattice and spin–spin relaxation mechanisms. The crystal packing for both 1 and 5 indicate relatively short inter-molecular distances (shortest Fe···Fe separation between adjacent Fe units being ~ 6.1–6.3 Å). As a result, spin–spin relaxation should have a significant contribution and may partially account for the behaviour of the Mössbauer spectra in addition, in the present case spin–spin relaxation is expected to be temperature dependent due to thermal population of different spin manifolds as a function of temperature. Therefore it is not possible to distinguish the contribution of each mechanism in the observed spectra.

Conclusions

The initial use of the aliphatic amino-alcohol ligands Hap and Hmpip in Fe cluster chemistry has provided access to two new families of pentanuclear clusters. Complexes 1–4 possess the quasi-planar $[\text{Fe}_5(\mu_1-O)]^{11+}$ core consisting of two vertex-sharing $[\text{Fe}_{6}(\mu_3-O)]^{12+}$ units, whereas complex 5 possesses the $[\text{Fe}_{5}(\mu_1-O)(\mu_1-O)]^{11+}$ core, in which the five Fe$^{2+}$ ions adopt a monocapped trigonal pyramidal topology. These core topologies are unusual not only for Fe cluster chemistry but for any metal ion in general. Dc magnetic susceptibility studies on powdered microcrystalline samples of 1 and 5 revealed the existence of dominant antiferromagnetic exchange interactions resulting in an $S = 5/2$ spin ground state. Ac magnetic susceptibility measurements in powdered microcrystalline samples of 5 revealed out-of-phase signals only in the presence of external magnetic fields that were attributed to a small fraction of molecules exhibiting slow spin–lattice relaxation. Mössbauer spectroscopy confirmed that the iron sites in 1 and 5 are in the Fe$^{3+}$ ($S = 3/2$) oxidation state. The temperature dependence of the Mössbauer spectra for complexes 1 and 5 indicated intermediate relaxation with the contribution of both spin–lattice and spin–spin relaxation mechanisms for $T < 50$ K. Further studies involving reactions of salts or preformed clusters of Fe and also other paramagnetic metal ions with the Hap and Hmpip ligands are in progress and will be reported in due course.

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Notes and references
