The first iron(III) complexes with a chelating diamido ligand, \( \text{[FeX} \text{BuN(SiMe}_2\text{)}\text{O}]_2 \) \((X = \text{Cl, Br})\), form halide-bridged dimers in which each iron(III) centre exhibits 3/2, 5/2 quantum spin admixture; the two metals show weak antiferromagnetic coupling.

Iron(III) centres exhibit a remarkably wide range of single-ion magnetic behaviour. Many octahedral high \((S = 5/2)\) or low \((S = 1/2)\) spin complexes of this \(d^6\) centre are known and non-octahedral/tetrahedral geometries can generate intermediate spin \((S = 3/2)\) complexes as well.\(^1\) In addition, a small group of mononuclear iron(III) complexes show a rare form of magnetic behaviour known as quantum mechanical spin-admixture, in which there is a mixing of \(S = 5/2\) and \(S = 3/2\) states through spin–orbit coupling, generating a new discrete spin-state.\(^2\) The history of these spin-admixed Fe(III) complexes has been dominated by macrocyclic-based systems\(^3\) as a result of modeling studies of the bacterial heme proteins known as ferri cytochrome c,\(^4\) which show spin-admixtures.\(^5\) Fe(II)ClO\(_4\), \(\text{Fe}(_2\text{TPP})\text{ClO}_4\), and \((\text{Fe})\text{FeCl}_4\) are among the few iron(III) complexes exhibiting spin-admixture. However, the observation of this interesting magnetic phenomenon beyond macrocyclic systems has not been widely reported; the spin-admixed complex \(\text{FeBr}_2\text{[}\text{Ni(SiMe}_2\text{CH}_2\text{PPh}_3]\text{]}\) is one of the only examples known to date.\(^6\) We herein report, to the best of our knowledge, the first multinuclear, non-macroyclic Fe(III) complexes to exhibit quantum mechanical spin-admixture.

Reaction of the diamido ligand \(\text{Li}(_2\text{BuN(SiMe}_2\text{)}\text{O})\) with \(\text{FeCl}_3\) in benzene produces a centrosymmetric, dimeric complex in the solid state.\(^7\) The single crystal X-ray structure (Fig. 1) of the first multinuclear iron(III) complex utilizing chelating diamido donors.

The single crystal X-ray structure (Fig. 1) of the first multinuclear iron(III) complex utilizing chelating diamido donors. The Fe–N bond lengths of \(1.951(6)\) Å in trigonal bipyramidal FeBr\(_6\) differ from those of \(1.896(5)\) and \(1.900(5)\) Å in the classic trigonal planar Fe\(_2\)\(\text{N(SiMe}_2\text{)}\_2\text{Cl}_2\) complex.\(^8\) One can be explained by the interaction between the metal centres. Each iron centre is coordinated to two amido donors, two bridging halides, and an amido bridge with the metal–metal interaction between the metal centres. Each iron centre is coordinated to two amido donors, two bridging halides, and an amido bridge with the metal–metal interaction. The asymmetry of the bridging chlorides is exemplified by the diffuse Fe–Cl bond lengths of \(1.987(5)\) Å and \(1.984(4)\) Å which are shorter than the \(1.917(4)\) Å found in the classic trigonal planar Fe\(_2\)\(\text{N(SiMe}_2\text{)}\_2\text{Cl}_2\) complex.\(^8\) Other relevant comparisons include the Fe–N bond lengths of \(1.951(6)\) Å in trigonal bipyramidal FeBr\(_6\) and \(1.896(5)\) and \(1.900(5)\) Å in tetrahedral, high-spin Fe\(_2\)\(\text{pyridine-d}_4\)\(\text{NR}_{3}\) ( \(R = \text{C(CD}_2\text{)}\text{CH}_2\), \(\text{ArF} = 2.5\text{-C}_6\text{H}_4\text{FMe}\)). Note that I is the first structurally characterized iron(III) complex utilizing chelating diamido donors.

The temperature \((T)\) dependence of the magnetic susceptibility \((\chi_M)\) of 1 and 2 were measured from 2 to 300 K.\(^9\) The plot of \(\chi_M\) vs. \(T\) for iron atom \(I\) is shown in Fig. 2; no maximum in \(\chi_M\) is observed at any temperature. The bromoanalogue 2 shows similar behaviour. The \(\mu_{\text{eff}}\) values of 4.5 and 4.4 \(\mu_B\) for 1 and 2 respectively at 300 K are much lower than the expected spin-only value for a pure \(S = 5/2\) high spin state (\(\mu_{\text{eff}} = 5.92\) \(\mu_B\); 5 unpaired electrons) and significantly higher than the spin-only value for a pure \(S = 3/2\) intermediate spin state (\(\mu_{\text{eff}} = 3.87\) \(\mu_B\); 3 unpaired electrons). In addition, the data above 50 K could not be fit at all to the equation describing two antiferromagnetically coupled high-spin Fe(III) metal centres.\(^1\) The profile of the \(\mu_{\text{eff}}\) vs. \(T\) curve is also not consistent with that of a thermal spin-equilibrium between either a \(S = 3/2\) to \(S = 5/2\) spin state or \(S = 1/2\) to \(S = 5/2\) spin state.\(^1\) However, the data is readily explained if the Fe(III) metal centres exist in a \(3/2, 5/2\) spin-admixed state. The \(\mu_{\text{eff}}\) value for 1 at 300 K corresponds to a 24% high-spin (\(S = 5/2\)) admixture into an \(S = 3/2\) state according to the simple Maltempo model.\(^1\)

**Fig. 1** Molecular structure of I (50% probability ellipsoids are shown; tert-butyl groups simplified for clarity). Selected bond lengths (Å) and angles (°): Fe1–Fe1* 3.4784(20), Fe1–O1 2.597(4), Fe1–Cl1 2.342(4), Fe1–Cl1* 2.4652(17), Fe1–N1 1.887(5), Fe1–N2 1.894(4), Si1–N1 1.718(5), Si2–N2 1.723(5), Si1–O1 1.63(5), Si2–O1 1.637(4), N1–Cl1 1.466(6), N2–C20 1.471(8), Cl1–Fe1–Cl1* 86.75(6), Cl1–Fe1–N1 115.36(15), Cl1–Fe1–N2 117.63(17), Cl1*–Fe1–N1 107.90(12), Cl1*–Fe1–N2 108.34(13), N1–Fe1–N2 115.99(21), O1–Fe1–Cl1* 166.43(9), O1–Fe1–N1 68.39(17), O1–Fe1–N2 68.39(17), Si1–O1–Si2 141.18(23).

**Fig. 2** Graph of magnetic moment \((\mu_{\text{eff}})\) vs. temperature \((T)\) for I.
The drop in the $\mu_{eff}$ of I from 4.5 $\mu_B$ at 300 K to 3.0 $\mu_B$ at 50 K is indicative of weak antiferromagnetic coupling between the spin-admixed positions that have nearly temperature independent magnetic moments above 20 K—no magnetic coupling can occur in these cases. Below 20 K, both of these mononuclear systems show zero-field splitting effects which cause a drop in dropwise to anhydrous FeCl$_2$ (0.85 mL, 1.28 mmol) were added dropwise at 0.93 mL, 4.36 mmol), and the solvent was removed in vacuo, the product was extracted with hexanes and filtered through Celite®. Structure solution and refinement was performed using CRYSTALS (D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and D. Pett). Structural analyses were conducted at a higher temperature (1080 C) than is routinely used. Combustion at 1000 °C, even with the addition of $\text{V}_2\text{O}_5$, resulted in a consistently low N-analysis for these compounds, probably due to metal nitride formation.

13 Crystal data for I: $\text{Ca}_3\text{H}_3\text{Cl}_3\text{Fe}_2\text{O}_7\text{Si}_3\text{O}_3\text{FeSiO}_3\text{Mg}_2\text{Si}_2\text{O}_7\times 3\text{H}_2\text{O}$, monoclinic, space group $P2_1/n$, a = 10.73(3) Å, b = 15.74(4) Å, c = 12.53(3) Å, $\beta = 111.96(17)$ °, $V = 1603.2(2)$ Å$^3$, $Z = 4$, $\mu$ (Mo-Kα) = 1.0 mm$^{-1}$; $T = 293 K$, 3025 unique reflections, 1310 observed ($I > 2 \sigma (I)$). The final $R_1 = 0.038$ and $wR_2 = 0.030$ (observed data). Structure solution and refinement was performed using CRYSTALS (D. J. Watkin, K. L. Prout, J. R. Carruthers, P. W. Betteridge and R. L. Cooper). CRYSTALS Issue 11, Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1999). CCDC reference number 175266. See http://www.rsc.org/suppdata/dt/b1/b106621h/ for crystallographic data in CIF or other electronic format.


16 Magnetic susceptibilities were measured on powdered samples at 10000 G using a Quantum Design MPMS-SS SQUID magnetometer. The data were corrected for background and for the diamagnetism of all atoms.


