$\{\text{FeCl}[{}^t\text{BuN}(\text{SiMe}_2)]_2\text{O}\}_2$: The first multinuclear iron(III) complex exhibiting spin-admixture

Garry Mund, Raymond J. Batchelor, Rajendra D. Sharma, Colin H. W. Jones and Daniel B. Leznoff*

Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C. V5A 1S6 Canada. E-mail: dleznoff@sfu.ca

Received 23rd July 2001, Accepted 12th November 2001
First published as an Advance Article on the web 12th December 2001

The first iron(III) complexes with a chelating diamido ligand, $\{\text{FeX}[{}^t\text{BuN}(\text{SiMe}_2)]_2\text{O}\}_2$ (X = 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^5 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 the S = 5/2 and S = 3/2 spin states through spin–orbit coupling, generating a new discrete spin-state.[2–4] The history of these spin-admixed Fe(III) complexes has been dominated by macrocyclic-based systems[5] as a result of modeling studies of the bacterial heme proteins known as ferricytochrome c′, which show spin-admixture.[6] Fe(TPP)ClO$_4$,[7] Fe(Me$_8$TPP)ClO$_4$[8] and (Pc)FeCl[9] 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 $\text{FeBr}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ is one of the only examples known to date.[10] We herein report, to the best of our knowledge, the first *multinuclear*, non-macrocyclic Fe(III) complexes to exhibit quantum mechanical spin-admixture.

Reaction of the diamido ligand $\text{Li}_2[{}^t\text{BuN}(\text{SiMe}_2)]_2\text{O}$[11] with FeX$_3$ (X = Cl, Br) in Et$_2$O at −30 °C resulted in an immediate colour change to dark purple. From this solution, the air-sensitive $\{\text{FeX}[{}^t\text{BuN}(\text{SiMe}_2)]_2\text{O}\}_2$ (**1**, X = Cl; **2**, X = Br) complexes were isolated in moderate yield.[12] The ^{1}H NMR spectra of **1** and **2** have broad, shifted peaks consistent with their paramagnetism (see below). Single crystals of **1** were obtained by slow evaporation of a hexanes solution.

The single crystal X-ray structure (Fig. 1) of **1** clearly reveals a centrosymmetric, dimeric complex in the solid state.[13] The Fe1–Fe1* distance of 3.4784(20) Å precludes any bonding interaction between the metal centres. Each iron centre is coordinated to two amido donors, two bridging halides and also weakly to the oxygen atom in the ligand backbone (Fe1–O1: 2.597(4) Å). Hence, each iron(III) centre is roughly five-coordinate, with a distorted trigonal bipyramidal geometry. The asymmetric nature of the bridging chlorides is exemplified by the different Fe–Cl bond lengths of 2.3181(19) (Fe1–Cl1) and 2.4652(17) Å (Fe1–Cl1*). The Fe–N distances of 1.887(5) Å, and 1.894(4) Å are shorter than the 1.917(4) Å found in the classic trigonal planar $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$ complex.[14] Other relevant comparisons include the Fe–N bond lengths of 1.951(6) Å in trigonal bipyramidal $\text{FeBr}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$[10] and 1.896(5) and 1.900(5) Å in tetrahedral, high-spin Fe(pyridine-d$_5$)(NRAr$_\text{F}$)$_2$ (R = C(CD$_3$)$_2$CH$_3$, Ar$_\text{F}$ = 2,5-C$_6$H$_3$FMe).[15] Note that **1** is the first structurally characterized iron(III) complex utilizing chelating diamido donors.

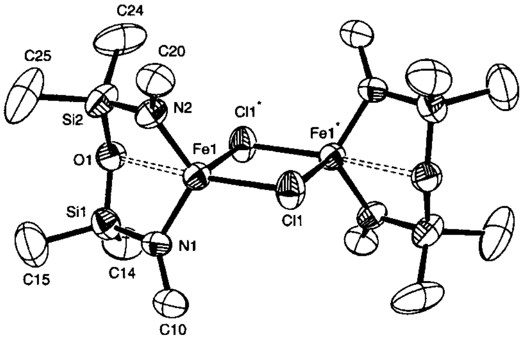

Fig. 1 Molecular structure of **1** (50% probability ellipsoids are shown; *tert*-butyl groups simplified for clarity). Selected bond lengths (Å) and angles (°): Fe1–Fe1* 3.4784(20), Fe1–O1 2.597(4), Fe1–Cl1 2.3181(19), Fe1–Cl1* 2.4652(17), Fe1–N1 1.887(5), Fe1–N2 1.894(4), Si1–N1 1.718(5), Si2–N2 1.723(5), Si1–O1 1.635(4), Si2–O1 1.637(4), N1–C10 1.466(8), 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* 79.74(9), O1–Fe1–Cl1 166.43(9), O1–Fe1–N1 68.39(17), O1–Fe1–N2 68.55(17), Si1–O1–Si2 141.18(23). * = 1 − x, −y, 2 − z.

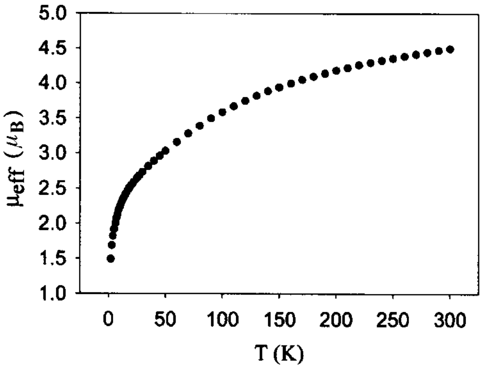

Fig. 2 Graph of magnetic moment (μ_B) *vs.* temperature (K) for **1**.

The temperature (T) dependence of the magnetic susceptibility (χ_M) of **1** and **2** were measured from 2 to 300 K.[16] The plot of μ_eff *vs.* T per iron atom for **1** is shown in Fig. 2; no maximum in χ_M is observed at any temperature. The bromo-analogue **2** shows similar behaviour. The μ_eff values of 4.5 and 4.4 μ_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 (μ_eff = 5.92 μ_B; 5 unpaired electrons) and significantly higher than the spin-only value for a pure S = 3/2 intermediate spin state (μ_eff = 3.87 μ_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 μ_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 μ_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.[3]

DOI: 10.1039/b106621h

The drop in the μ_{eff} of **1** from 4.5 μ_B at 300 K to 3.0 μ_B at 50 K is indicative of weak antiferromagnetic coupling between the spin-admixed iron atoms of the dimer. Qualitative support for this comes from the μ_{eff} *vs.* T data for mononuclear $FeBr_2[N(SiMe_2CH_2PPh_2)_2]$[10] and intermediate-spin Fe(4,4′-bipy)$_2$(NCS)$_3$,[17] both of which, unlike for **1**, 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 μ_{eff} to 3.5 and 3.8 μ_B respectively; this also occurs in **1** but its μ_{eff} at 2 K is much lower, at 1.5 μ_B. Detailed modeling of the magnetic data for **1** may not yield meaningful results given the simultaneous presence of weak antiferromagnetic coupling, zero-field splitting (at low T) and a spin-admixed system, for which a comprehensive model beyond the oversimplified Maltempo one is not accessible.[1,4]

Additional evidence discounting a pure $S = 5/2$ spin state comes from the UV-vis spectra of **1** and **2**. A high-spin state would lack any spin-allowed d–d transitions. However, a spin state incorporating either $S = 3/2$ or spin-admixed character could have spin-allowed transitions. Both **1** (484 nm; $\varepsilon = 4877$ M^{-1} cm^{-1}) and **2** (458 nm; $\varepsilon = 5017$ M^{-1} cm^{-1}) have absorbances in the visible region that could be assigned as d–d transitions, as have been described for intermediate-spin $FeCl_3 \cdot 2PMe_3$.[18] However, the possibility that these transitions could be due to a charge-transfer process cannot be completely discounted.

The Mössbauer spectrum (Fig. 3) of **1** at 4.2 K provides convincing supporting evidence for spin-admixture in these systems. The isomer shift (δ) of **1** is +0.25 ± 0.02 mm s^{-1} (*vs.* α-Fe foil). Iron(III) spin-admixture is characterized by an extremely wide quadrupole doublet,[2,9] compared with a much smaller (or zero) splitting for high-spin iron(III) systems.[19] The large $\Delta E_Q = 3.52 \pm 0.02$ mm s^{-1} for **1** can be compared with the 2.94 and 3.5 mm s^{-1} reported for (Pc)FeCl[9] and Fe(TPP)ClO$_4$,[7] typical macrocyclic spin-admixed iron(III) systems. The bromo-complex **2** has an identical spectrum. Importantly, the Mössbauer spectra of **1** and **2** remain unchanged at 77 K and at room temperature, confirming the lack of spin-equilibrium behaviour.

In conclusion, compounds of the type $\{FeX[{}^tBuN(SiMe_2)]_2O\}_2$ (X = Cl, Br) have been shown to exhibit the rare form of magnetic behavior known as quantum mechanical spin-admixture. The effect of altering the electronic and steric properties of the ligand on the spin state and coordination geometry of these unique Fe(III) diamido complexes is under investigation.

We are grateful to Professor Robert C. Thompson (Univ. British Columbia) and Victor Sanchez for magnetometer access and assistance with magnetic susceptibility data collection and to NSERC of Canada (D. B. L.) and Simon Fraser University for financial support.

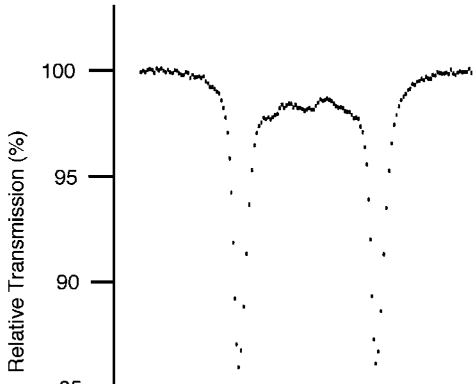

Fig. 3 Mössbauer spectrum of **1** at 4.2 K.

Notes and references

1 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.

2 C. A. Reed and F. Guiset, *J. Am. Chem. Soc.*, 1996, **118**, 3281.

3 M. M. Maltempo, *J. Chem. Phys.*, 1974, **61**, 2540.

4 S. Mitra, V. R. Marathe and R. Birdy, *Chem. Phys. Lett.*, 1983, **96**, 103; F. U. Axe, C. Flowers, G. H. Loew and A. Waleh, *J. Am. Chem. Soc.*, 1989, **111**, 7333; E. L. Bominaar and R. Block, *J. Chem. Phys.*, 1991, **95**, 6712.

5 V. Schünemann, M. Gerden, A. X. Trautwein, J. Fischer, R. Weiss, A. Tabard and R. Guilard, *Angew. Chem., Int. Ed.*, 1999, **38**, 3181; T. Ikeue, T. Saitoh, T. Yamaguchi, Y. Ohgo, M. Nakamura, M. Takahashi and M. Takeda, *Chem. Commun.*, 2000, 1989; S. Mitra, in *Iron Porphyrins. Part II*, eds. A. B. P. Lever and H. B. Gray, Addison Wesley, Reading, 1983 .

6 M. Maltempo, T. H. Moss and M. A. Cusanovich, *Biochim. Biophys. Acta*, 1974, **342**, 290; H. Ogoshi, H. Sugimoto, E. Watanabe, Z. Yoshida, Y. Maeda and H. Sakai, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3414; W. R. Scheidt, D. K. Geiger, R. G. Hayes and G. Lang, *J. Am. Chem. Soc.*, 1983, **105**, 2625.

7 C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalian and G. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2949; R. Cheng and P. Chen, *Chem. Eur. J.*, 1999, **5**, 1708.

8 R. Cheng, P. Chen, P. Gau, C. Chen and S. Peng, *J. Am. Chem. Soc.*, 1997, **119**, 2563.

9 B. J. Kennedy, K. S. Murray, P. R. Zwack, H. Homborg and W. Kalz, *Inorg. Chem.*, 1986, **25**, 2539; M. Hanack, U. Keppeler, A. Lange, A. Hirsch and R. Dieing, in *Phthalocyanines: Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, vol. 2.

10 M. D. Fryzuk, D. B. Leznoff, E. S. F. Ma, S. J. Rettig and V. G. Young, Jr., *Organometallics*, 1998, **17**, 2313.

11 A. J. Elias, H. W. Roesky, W. T. Robinson and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1993, 495; N. A. H. Male, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487.

12 Synthesis of **1**: The oil $[{}^tBuNH(SiMe_2)]_2O$ (0.16 g, 0.62 mmol) was dissolved in 10 mL of Et_2O and two equivalents of 1.6 M ^{n}BuLi (0.85 mL, 1.28 mmol) were added dropwise at −78 °C. After stirring for one hour at room temperature, the resulting solution was added dropwise to anhydrous $FeCl_3$ (0.1 g, 0.62 mmol) in 30 mL of Et_2O at −30 °C, yielding a dark purple solution. After an hour, the solvent was removed *in vacuo*, the product was extracted with hexanes and filtered through Celite®. Removal of the hexanes *in vacuo* gave dark purple $\{FeCl[{}^tBuN(SiMe_2)]_2O\}_2$ (**1**). Yield: 0.15 g (66%). Anal. calcd. for $C_{12}H_{30}N_2ClFeOSi_2$: C: 39.40, H: 8.27, N: 7.66. Found: C: 39.56, H: 8.48, N: 7.22%. ^{1}H NMR (C_6D_6): δ 41 (v br), 34 (v br). UV-Vis (C_6H_{14}): 484 nm ($\varepsilon = 4877$ M^{-1} cm^{-1}). MS: *m*/*e* 365 (M$^+$), 350 (M$^+$ − CH$_3$).

For **2** a similar procedure, starting with $FeBr_3$ (0.4 g, 1.36 mmol), was used. Yield: 0.46 g (82%). Anal. calcd. for $C_{12}H_{30}N_2BrFeOSi_2$: C: 35.13, H: 7.37, N: 6.83. Found: C: 35.21, H: 7.42, N: 6.71%. ^{1}H NMR (C_6D_6): δ 41 (v br), 32 (v br). UV-Vis (C_6H_{14}): 458 nm ($\varepsilon = 5017$ M^{-1} cm^{-1}). MS: *m*/*e* 411 (M$^+$), 331 (M$^+$ − Br). Elemental analyses were conducted at a higher temperature (1080 °C) than is routinely used. Combustion at 1000 °C, even with the addition of V_2O_5, resulted in a consistently low N-analysis for these compounds, probably due to metal nitride formation.

13 Crystal data for **1**: $C_{12}H_{30}ClFeN_2OSi_2$, $M = 365.85$, monoclinic, space group $P2_1/n$, $a = 10.737(3)$, $b = 15.744(3)$, $c = 12.523(3)$ Å, $\beta = 111.967(19)°$, $V = 1963.2(8)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.0 mm^{-1}, $T = 293$ K, 3025 unique reflections, 1310 observed ($I_0 > 2.5\sigma(I_0)$). The final $R_F = 0.038$ and $R_{WF} = 0.030$ (observed data). Structure solution and refinement was performed using CRYSTALS (D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. 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.

14 M. B. Hursthouse and P. F. Rodesiler, *J. Chem. Soc., Dalton Trans.*, 1972, 2100.

15 S. L. Stokes, W. M. Davis, A. L. Odom and C. C. Cummins, *Organometallics*, 1996, **15**, 4521.

16 Magnetic susceptibilities were measured on powdered samples at 10000 G using a Quantum Design MPMS-5S SQUID magnetometer. The data were corrected for background and for the diamagnetism of all atoms.

17 N. Moliner, J. A. Real, M. C. Muñoz, R. Martínez-Mañez and J. M. C. Juan, *J. Chem. Soc., Dalton Trans.*, 1999, 1375.

18 J. D. Walker and R. Poli, *Inorg. Chem.*, 1989, **28**, 1793.

19 P. Gütlich, R. Link and A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer-Verlag, Berlin, 1978.