Spin crossover in iron(III) Schiff-base 1-D chain complexes[†]

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Received 3rd July 2009, Accepted 10th September 2009 First published as an Advance Article on the web 8th October 2009 DOI: 10.1039/b913234a

A series of iron(III) 1-D polymeric materials of the general formula [Fe(III)(Schiff-base)(L)]-(BPh₄).n(CH₃OH) (Schiff base = N,N'-ethylenebis(salicylaldimine) (H₂salen), N,N'-o-phenylenebis(salicylaldimine) (H₂salophen) and N,N'-ethylenebis(acetylacetone)-2,2'-imine (H₂ acen); L = bridging di-pyridyl or di-imidazole ligand, n = 0-4) and analogues therein, have been synthesised and structurally and magnetically characterised. In this series, a range of structural motifs are observed including linear 1-D chains, hydrogen-bonded chains, a 'hybrid' 1-D chain-and -dimer compound and a hydrogen-bonded dinuclear material; all exhibit extensive intermolecular interactions. The magnetic consequences of varying both the equatorial Schiff-base ligands and axial bridging ligands have been investigated. Overall, we find that, independent of the axial bridging ligand employed, the salen equatorial ligand results in a high spin character and the acen ligand results in spin crossover character, generally with a spin transition of a gradual nature. Variations in magnetic behaviour can be rationalized, in part, in terms of the C₂N₂ backbone conformation of the equatorial Schiff base ligand, which may either inhibit or allow a spin transition.

Introduction

Research in spin crossover (SCO) molecular materials continues to gather pace from the points of view of possible technological applications,^{1,2} nanoparticles³ and fundamental aspects.¹ Polynuclear SCO systems are receiving much interest, no doubt spurred on by the work of Kahn et al.4 on 1-D Fe(II) coordination polymers of the type [Fe(II)(R-1,2,4-triazole)₃]²⁺ that were tested commercially as memory devices and displays.⁵ Fundamental and mechanistic work covers a range of areas and, in the case of polynuclear systems, for example, it covers such aspects as determining the relationship between structure and spin transition mechanism, and identifying the spin state on metal centres at intermediate temperature plateaus in 2-step transitions.⁶⁻⁹ An ongoing challenge is to develop ways of predicting the electronic and memory (hysteretic) behaviour of metal compounds of Fe and Co that display spin switching, while realising that many intermolecular effects can influence spin transitions in crystalline species.1,10

Fe(II) containing SCO systems continue to be the most studied because of their bistability features, their abrupt spin transitions and the tendency to often display high degrees of cooperativity in the solid state. Comparatively fewer studies have been devoted to Fe(III) compounds as they commonly show low cooperativity, with the majority of such systems displaying a gradual SCO transition.¹¹ Nevertheless, successful attempts have

been made to engineer a high degree of cooperativity in Fe(III) compounds, such as, for example, exploiting tridentate Schiff base ligands suitably disposed to participate in supramolecular interactions (*i.e.* hydrogen-bonding and π -stacking). For example, the mononuclear compound $[Fe(III)(pap)_2](ClO_4) \cdot H_2O$ (pap = bis-2-hydroxyphenyl-(2-pyridyl)-methaneimine) displays an abrupt SCO with a 15 K wide thermal hysteresis loop ($T_{\frac{1}{2}}\uparrow = 165$ K and $T_{\downarrow}\downarrow = 180$ K).¹² Further highlighting the importance of supramolecular interactions, the mononuclear Fe(III) compounds $[Fe(qsal)_2]NCSe \cdot MeOH$ and $[Fe(qsal)_2]NCSe \cdot CH_2Cl_2$ (qsal = N-(8-quinolyl)-salicylaldiminate) were reported to show cooperative spin transitions with wide thermal hysteresis loops, attributed to extensive π -stacking in the crystal lattice.¹³ Another tridentate hydrazone ligand has recently been shown to yield an abrupt, 2-step spin transition in the complex [Fe(mph)₂](ClO₄)(MeOH)_{0.5}(H₂O)_{0.5} (Hmph = 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenoland hydrogen-bonding between adjacent mph ligands was felt to be involved in the cooperativity mechanism.¹⁴

Schiff base ligands of the pap, qsal and mph types, and others involving N₄O₂ donor sets, have proven to be very effective at inducing SCO with Fe(III) and, more recently, for Fe(II)¹⁵⁻¹⁸ for which higher cooperativity and thermal hysteresis features were noted.11,15-18 Fe(III) Schiff base compounds generally include two tridentate N_2O donor ligands, a single hexadentate N_4O_2 donor ligand, a pentadentate N₃O₂ plus a monodentate N-donor, or, as in the present study, a tetradentate N₂O₂ ligand supplemented by two N-donor heterocyclic bases. Extensive studies on mononuclear systems of the type [Fe(III)(Schiff-base)(L)_n]⁺ (where the ligands are salen, salophen, acen or the Jäger¹⁷ type; n = 1 or 2) have been devoted towards gaining a fundamental understanding of the factors governing their structure-magnetism relations.11 More recently, photomagnetic (LIESST; 'light induced excited spin state trapping') investigations have been reported¹² and multifunctional (SCO/electrical conductivity) materials of

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[†] Electronic supplementary information (ESI) available: Single crystal X-ray diffraction, Fig. S1 to S12 and refinement details, magnetic susceptibility measurements on compounds **1a-e** and **2a-c**, Fig. S13 to S16. CCDC reference numbers 738866–738874 and 739042–739044. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b913234a

type $[Fe(sal_2-trien)][Ni(dmit)_2]_x$ (x = 1 or 3; sal_2-trien²⁻ = N,N'bis(triethylenetetramine)salicylaldiminato; dmit²⁻ = 2-thioxo-1,3dithiole-4,5-dithiolato) have received attention including the effects of polymorphism, in the x = 1 phases, and the effects that ligand conformations and intermolecular contacts have upon SCO.^{19,20}

As in the sal₂-trien/dmit work, above, and in other [Fe(sal₂-trien)]⁺ salts,²¹ it was found earlier, that the magnetic and SCO behaviour of [Fe(III)(Schiff-base)(L)_n]⁺ systems appeared to be largely dependent on ligand orientation, specifically the conformation of the C₂N₂ ethylene backbone of the equatorial Schiffbase ligand, together with the orientation of the axial ligands and the presence of supramolecular interactions between axial and equatorial ligands (particularly for salen complexes).^{11,22} There has been an occasional, early report of salen-Fe(III) polynuclear materials such as the 1-D chain [Fe(III)(salen)(tmid)]ClO₄ (where tmid = 1,1'-tetramethylenediimidazole).²³

Another focus of the current study is to vary the in-plane ligand as early work on the $[Fe(III)(acen)(L)_n]^+$ mononuclear system often led to spin transitions being observed.^{11,24} While the present study was in progress, reports emerged on 1-D chain compounds $[Fe(III)(acen)(bpp)]BPh_4$ and $[Fe(III)(acen)(tmid)]BPh_4$ that displayed spin transitions at high temperatures.^{23,25,26} Since variation in anion is also known to influence SCO properties, it is notable that the incomplete LS \leftrightarrow HS spin transition in $[Fe(III)(acen)(tmid)]BPh_4$ was found to begin at ~240 K, while in the earlier studied perchlorate salt, $[Fe(III)(acen)(tmid)]ClO_4$, it began at ~275 K.^{23,26} $[Fe(III)(salen)L_2]^+$ systems were also similarly influenced by anion variation.²²

Following our recent, and ongoing, studies of 1-D SCO iron(II) compounds,^{6,27} we have made a thorough study of 1-D iron(III) materials, of the Schiff base type, [Fe(III)(Schiffbase)(L)](BPh₄)·n(CH₃OH), and report our findings here. We have carried out a study of the effect of (1) variation of the equatorial tetradentate Schiffbase ligand using salen, salophen and acen, with (2) a concurrent variation of the axial pyridyl- or imidazolyl-bridging ligand, L (see Fig. 1). The Fe \cdots Fe distance across these L bridges are large and thus no intra-chain magnetic exchange is anticipated between Fe(III) centres but mechanical

herein for this series, including a dependence on the conformation of the C_2N_2 backbone of the Schiff-base ligand. Importantly, the SCO character in the acen-containing compounds is quite varied within that series. Comparisons are made to the few early reports, cited above, on related 1-D Fe(III) Schiff base compounds.²³⁻²⁶

and other geometric and Van der Waal effects (H-bonding,

 π - π) may engender chain-chain interactions and thus influence the

SCO features. Clear structure-magnetic correlations are described

Experimental

Physical measurements

Infrared spectra were recorded on a Bruker Equinox 55 series FTIR spectrometer (equipped with a Specac Golden Gate diamond ATR sample) in the range of 4000-500 cm⁻¹, with samples mounted in a diamond anvil (resolution 4.0 cm⁻¹). CHN analyses were performed by Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand.

Magnetic susceptibility

Data were collected using a Quantum Design MPMS 5 SQUID magnetometer under an applied field of 1 T over the temperature range 350–4 K. The powdered or polycrystalline samples were placed in gel capsules and care was taken to allow long thermal equilibration times at each temperature point.

General synthesis

All the reagents and solvents were commercially available and used as received. Methanol was dried by distillation over I_2 and magnesium turnings.

Ligand synthesis

The ligands 4,4'-azopyridine (azpy), *N*-(4-pyridyl)-isonicotinamide (pin), 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (bpdh), 1,4-bis(imidazole-1-yl-methyl)benzene (bix), 4,4'-dipyridylsulfide (dps), salen, salophen, acen were prepared by literature methods.³²⁻³⁶ The ligands bpp, tvp, bpe were purchased from Sigma Aldrich Inc (Fig. 1). The metal complexes [Fe(salen)Cl]₂, [Fe(salophen)Cl]₂ and [Fe(acen)Cl]₂ were prepared by literature methods.³⁷

Metal-complex synthesis

[Fe(salen)(L)](BPh₄)·*n*(CH₃OH) (1a-e). Each of these complexes was prepared by the same general method. To a 10 ml solution of [Fe(salen)Cl]₂ (50 mg, 0.14 mmol) in methanol was added L (0.14 mmol). This solution was heated and stirred for 10 minutes and then filtered into a freshly prepared solution of NaBPh₄ (47.9 mg, 0.14 mmol) in 5 ml of methanol. Within hours large crystals formed. **1a**: [Fe(salen)(azpy)](BPh₄)·2(CH₃OH). Orange-brown needle shaped crystals. Yield: 72 mg, 58%. IR (cm⁻¹): 3458(br), 3052(w), 1602(s), 1598(s), 1544(s), 1013(s). Calcd. for $C_{52}H_{50}BFeN_6O_4$: C, 70.20; H, 5.66; N, 9.45; found C, 69.40; H, 5.36; N, 9.32. **1b**: [Fe(salen)(tvp)](BPh₄)·2(CH₃OH). Orange-brown needle shaped crystals. Yield: 69.6 mg, 56%. IR: 3490(br), 3094(w), 1598(s), 1543(s), 1014(s). Calcd. for $C_{54}H_{52}BFeN_4O_4$:

Fig. 1 Equatorial Schiff base and axial, 2-connecting, bridging ligands used in this study.



C, 73.07; H, 5.90; N, 6.31; found C, 72.09; H, 5.45; N, 6.29. **1c**: [Fe(salen)(bpe)](BPh₄)·2(CH₃OH). Orange-brown needle shaped crystals. Yield: 64.7 mg, 52%. IR: 3570(br), 3052(w), 1614(s), 1545(s), 1154(s), 1019(s). Calcd. for $C_{54}H_{54}BFeN_4O_4$: C, 72.90; H, 6.12; N, 6.30; found C, 72.23; H, 5.79; N, 6.23. **1d**: [Fe(salen)(pin)](BPh₄)·2(CH₃OH). Orange-brown needle shaped crystals. Yield: 54.5 mg, 43%. IR: 3462(br), 2903(w), 1617(s), 1594(s), 1537(s), 1092(s). Calcd. for $C_{53}H_{51}BFeN_5O_5$: C, 70.36; H, 5.68; N, 7.74; found C, 71.32; H, 5.29; N, 8.09. **1e**: [Fe(salen)(bpdh)](BPh₄). Orange-brown needle shaped crystals. Yield: 69 mg, 56%. IR: 3050(w), 1599(s), 1544(s), 11148(s), 1016(s). Calcd. for $C_{54}H_{48}BFeN_6O_2$: C, 73.73; H, 5.50; N, 9.56; found C, 73.55; H, 5.49; N, 9.52.

[Fe(salen)(L)(CH₃OH)](BPh₄)·n(CH₃OH) (2a-c). Each of these complexes was prepared by the same general method. To a 10 ml solution of [Fe(salen)Cl]₂ (50 mg, 0.14 mmol) in methanol was added L (0.14 mmol). This solution was heated and stirred for 10 minutes and then filtered into a freshly prepared solution of NaBPh₄ (0.14 mmol) in 5 ml of methanol. Within hours large crystals formed. 2a: [Fe(salen)(bpp)(CH₃OH)](BPh₄). Orangebrown needle shaped crystals. Yield: 64.7 mg, 53%. IR: 3410(br), 3050(w), 1617(s), 1599(s), 1544(s), 1128(s), 1013(s). Calcd. for C₅₄H₅₂BFeN₄O₃: C, 74.40; H, 6.01; N, 6.43; found C, 74.24; H, 6.01; N, 6.46. **2b**: [Fe(salen)(dps)(CH₃OH)](BPh₄). $\frac{1}{2}$ (CH₃OH). Orange-brown needle shaped crystals. Yield 140.8 mg, 58%. IR: 3458(br), 3052(w), 1602(s), 1598(s), 1544(s), 1013(s). Calcd. for C_{51.5}H₄₈BFeN₄O_{3.5}S: C, 70.48; H, 5.51; N, 6.38; found C, 70.68; H, 5.55; N, 6.44. 2c: [Fe(salen)(bpy)(CH₃OH)](BPh₄). Orangebrown needle shaped crystals formed. Yield 67.4 mg, 58%. IR: 3458(br), 3052(w), 1602(s), 1598(s), 1544(s), 1013(s). Calcd. for C₅₁H₄₆BFeN₄O₃: C, 73.84; H, 5.59; N, 6.75; found C, 73.25; H, 5.71; N, 6.63.

[Fe(salen)(bpdh)](BPh₄)-[Fe(salen)Cl]₂(PF₆).CH₃OH (3a). bpdh (33 mg, 0.14 mol) was added to a 10 ml solution of [Fe(salen)Cl]₂ (100 mg, 0.28 mmol). This solution was filtered into a freshly prepared solution of KPF₆ (50 mg, 0.28 mmol) in 5 ml of methanol. The solvent was slowly evaporated off under a stream of dinitrogen gas and over one week dark red crystals formed. Yield 10.2 mg, 10%. IR: 1612(s), 1543(s), 1016(s), 927(w), 824(m). Calcd. for $C_{47}H_{46}ClBF_6Fe_2N_8O_5P$: C, 51.55; H, 4.23; N, 10.20; found C, 51.34; H, 4.22; N 10.19.

[Fe(salophen)(bpdh)](BPh₄)·2CH₃CH₂OH (4a). Bpdh (30 mg, 0.12 mmol) was added to a 10 ml solution of [Fe(salophen)Cl]₂ (100 mg, 0.25 mmol) in ethanol. This mixture was heated to aid dissolution and then filtered into a freshly prepared solution of NaBPh₄ (85 mg, 0.25 mmol) in 5 ml of ethanol. Within hours large orange-brown needle shaped crystals formed. Yield 87.7 mg, 35%. IR: 3051(w), 1598(s), 1543(s), 1015(s), 829(s). Calcd. for $C_{62}H_{60}BFeN_6O_4$: C, 73.02, H, 5.93, N, 8.24; found C, 73.40; H, 5.57; N, 9.49.

[Fe(acen)(L)](BPh₄)·n(CH₃OH) (5a-f). Each of these complexes was prepared by the same general method. L (0.31 mmol) was added to a 10 ml solution of [Fe(acen)Cl]₂ (100 mg, 0.31 mmol) in methanol. This mixture was then heated to aid dissolution and filtered into a freshly prepared solution of NaBPh₄ (109 mg, 0.31 mmol) in 5 ml of methanol. The solution was stirred

overnight and filtered to leave a powder. Single crystals of **5a** were grown by the slow diffusion of a solution of $[Fe(acen)Cl]_2$ (100 mg, 0.31 mmol) in 2 ml of methanol into a solution of tvp (56.5 mg, 0.31 mmol) and NaBPh₄ (109 mg, 0.31 mmol) in 2 ml of methanol, in a H-shaped tube. X-ray quality crystals of **5a** formed over 3-4 weeks. These were found to co-crystallise with [tvpH](BPh₄), **5a1**. Sufficient **5a1** could not be collected for independent characterisation, but a crystal structure was obtained. (see ESI Fig. S12[†]).

5a. $[(Fe(acen))_2(\mu-tvp)(tvp)(tvpH)](tvpH)(BPh_4)_4 \cdot 1.5(CH_3OH).$ Green powder. Yield 118 mg, 58%. IR: 3053(m), 2999(m), 1610(w), 1503(s), 1388(m), 1066(w), 732(m), 702(w). Calcd. for C_{169.5}H₁₆₄B₄Fe₂N₁₂O_{5.5}: C, 77.89; H, 6.37; N, 6.40; found C, 79.34; H, 6.38; N, 6.06. Calcd. for no CH₃OH, C₁₆₈H₁₅₈B₄Fe₂N₁₂O₄: C, 78.73: H, 6.17; N, 6.56. Calcd. for a 1:1 mixture of 5a and 5a1: C_{205.5}H₁₉₄B₅Fe₂N₁₄O_{5.5}: C, 79.27; H, 6.28; N, 6.30. 5b: [Fe(acen)(bpe)](BPh₄). Green powder. Yield 171 mg, 68%. IR: 3053(m), 2993(m), 1615(w), 1501(s), 1394(m), 1064(w), 732(m), 703(w). Calcd. for C₄₈H₅₀BFeN₄O₂: C 73.76, H 6.45, N 7.17; found C, 74.24; H, 6.01; N 6.46. 5c: [Fe(acen)(bpdh)](BPh₄)·(CH₃OH). Green powder. Yield 156.3 mg (58%). IR: 3055(m), 2999(m), 1611(w), 1501(s), 1392(m), 1030(w), 732(m), 703(w). Calcd. for C₅₁H₅₆BFeN₆O₃: C, 70.60; H, 6.51; N, 9.69; found C, 70.59; H, 6.35; N, 9.68. 5d: [Fe(acen)(bix)](BPh₄).CH₃OH. Blue-green powder. Yield 147.9 mg, 55%. IR: 3118(sh), 3052(m), 2993(m), 1580(w), 1503(s), 1400(m), 1032(w), 732(m), 706(w). Calcd. for C₅₁H₅₆BFeN₆O₃: C, 70.60; H, 6.51; N, 9.69; found C, 70.71; H, 6.23; N, 9.58. 5e: [Fe(acen)(bpp)](BPh₄).²⁴⁻²⁶ Blue powder. Yield 143 mg (58%). IR: 3053(m), 2989(m), 1610(w), 1500(s), 1388(m), 1066(w), 731(w), 703(m). Calcd. for C₄₉H₅₂BFeN₄O₂: C, 73.97; H, 6.59; N, 7.04; found C, 74.09; H, 6.77; N, 6.72. 5f: [Fe(acen)(pin)](BPh₄)·3(CH₃OH). Blue powder. Yield 185.9 mg (65%). IR: 3341(sh), 3055(m), 3000(m), 1702(m), 1580(w), 1498(s), 1389(m), 1062(w), 736(m), 706(w). Calcd. for C₅₀H₅₉BFeN₅O₆: C, 67.27; H, 6.66; N, 7.85; found C, 66.84; H, 5.84; N 7.99.

Crystallographic data collection and refinement

Crystal diffraction data for all structures were collected on a Bruker APEX X8 diffractometer using Mo-K α ($\lambda = 0.71073$ Å) radiation and equipped with an Oxford Instruments nitrogen gas cryostream. Crystals were mounted on a MiTeGen MicroMounts fibre in a small amount of oil. Crystals were quench cooled to 123(2) K for all data sets.

Diffraction data analysis was performed using SAINT+ within the APEX2 software package.²⁷ Empirical absorption corrections were applied to all data using SADABS or TWINABS within the APEX software package for twinned structures.²⁷⁻²⁸ The structures were solved using SHELXS and refined against F² using SHELXL-97 within X-SEED.²⁹⁻³¹ All non–hydrogen atoms in the structures were refined anisotropically and hydrogen atoms were generated using the riding model. Special refinement details are included in the ESI.[†]

Crystal data and refinement parameters are summarised in Table 1. CCDC reference numbers 738866–738874 and 739042–739044 contain the supplementary crystallographic data for this paper.†

Table 1 Crys	tal data and refi	nement paramet	ters									
Compound	la	1b	1c	1d	1e	2 a	2b	2c	3a	4a	5a	5a1
Formula	$C_{52}H_{50}$ - BFeN ₆ O ₄	C ₅₄ H ₅₂ - BFeN ₄ O ₄	C ₅₄ H ₅₄ - BFeN4O4	C ₅₃ H ₅₁ - BFeN,05	C ₅₄ H ₄₈ - BFeN ₆ O ₂	C ₅₄ H ₅₂ - BFeN ₄ O ₃	${ m C}_{103}{ m H}_{96}$ - B ₂ Fe ₂ N ₈ O ₇ S ₂	C ₅₁ H ₄₆ - BFeN ₄ O ₃	C ₄₇ H ₄₆ ClF ₆ - Fe ₂ N ₈ O ₅ P	C ₆₂ H ₅₅ - BFeN ₆ O4	$C_{169.50}H_{164}B_{4-}F_{e_2}N_{12}O_{5.50}$	$\mathrm{C}_{36}\mathrm{H}_{31}\mathrm{BN}_2$
$FW/g mol^{-1}$	889.64 173	887.66	889.67	904.65 173	879.64 173	871.66 173	1755.32 173	829.58 173	1095.04 123	1019.82 173	2612.07	502.44 123
Crystal Svetam	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
Space Group Z	$P2_1/n$	P2 ₁ /n 4	$P2_{1}/n$	$P2_1/n$	$P\overline{1}$	P2 ₁ /n 4	$P\overline{1}$	Pbca 8	$\frac{P\bar{1}}{2}$	C_{C} 4	$P\overline{1}$	$\frac{P2_1}{4}$
	13.48980(10)	13.7711(4)	13.7528(5)	13.7092(10)	$\frac{1}{11.9331(3)}$	17.7548(7)	10.0871(2)	13.2122(7)	12.0126(5)	24.2992(12)	$\frac{1}{16.2950(6)}$	11.3875(10)
$b/\text{\AA}$	14.70170(10)	14.6168(4)	14.7010(7)	14.5012(10)	14.1303(3)	10.4792(4)	17.0283(3)	25.5531(13)	13.9365(6)	11.8936(6)	19.6279(7)	10.4827(8)
<i>د</i> /Å	22.7228(9) on	22.6560(5) 90	22.6381(11) on	22.9555(11) on	14.6055(4) 106.6760(10)	24.2709(10)	27.1416(7)	25.6679(14) on	15.7137(7) 03.666(2)	18.1891(6) on	22.6273(6) 79.6020(10)	23.361(2) on
ω, β/°	97.265(4)	97.0780(10)	96.594(2)	96.135(3)	94.1480(10)	96.0470(10)	90.9760(10)	00	107.727(2)	93.565(2)	80.3540(10)	101.464(3)
√/₀	90	60	60	60	106.6390(10)	60	105.7480(10)	90	107.489(2)	60	79.952(2)	60
V/Å ³	4470.27(18)	4525.7(2)	4546.7(4)	4537.4(5)	2228.14(10)	4490.6(3)	4362.53(16)	8665.8(8)	2354.70(18)	5246.6(4)	6939.5(4)	2733.0(4)
$\delta_{calc}/Mg m^{-3}$	1.322	1.303	1.300	1.324	1.311	1.289	1.336	1.272	1.544	1.291	1.250	1.221
Data/	0.391 17992/0/580	7714/0/581	0.304 7250/0/581	0.200 8819/0/591	0.209 13213/0/577	7682/0/572	0.444 16346/0/1123	0.390 4018/18/542	0./0/ 14108/0/634	0.343 6942/4/646	0.273 19827/2/1801	4063/1/373
Restraints/ Parameters												
R(int) Flack	0.0588 0.55938	0.0511	0.0650	0.0539 0.32843	0.0512	0.0506	0.0441	0.0588	0.0776	0.0308	0.1103	0.1226
parameter $R(F)/\%$	0.0732(0.0778)	0.0603(0.0924)	0.0743(0.0947)	0.1175(0.1361)	0.0546(0.0971)	0.0596(0.0687)	0.0685(0.0956)	0.0725(0.0912)	0.1645(0.1771)	0.0803(0.0931)	0.0902(0.1109)	0.0771(0.1058)
(I > 20(I), am) $R_w(F^2)/\%$	0.1881(0.1919)	0.1076(0.1224)	0.1319(0.1387)	0.2249(0.2365)	0.1139(0.1314)	0.0998(0.1034)	0.1262(0.1440)	0.1395(0.1475)	0.2944(0.2986)	0.1712(0.1833)	0.1841(0.1971)	0.2023(0.2338)
(1>20(1), all) GoF	1.191	1.050	1.214	1.220	1.023	1.218	1.108	1.198	1.505	1.106	1.139	1.111

Crvstal data and refinement parar

Table 2 Selected bond lengths, angles and structural parameters



				1								
Bonds (Å)	1a	1b	1c	1d	1e	2a	2b	2c	3a	4 a	5a (Fe1)	5a (Fe2)
Fe-N(sal)	2.106(3)	2.104(3)	2.103(4)	2.095(4)	2.1121(19)	2.116(3)	2.123(3), 2.096(3)	2.107(5)	2.096(7)	2.108(6)	1.900(4)	1.891(4)
Fe-N(sal)	2.107(2)	2.104(3)	2.109(3)	2.110(4)	2.121(2)	2.123(3)	2.101(3), 2.115(3)	2.110(5)	2.120(6)	2.105(6)	1.913(4)	1.907 (4)
Fe-O(sal)	1.8855(19)	1.887(2)	1.886(3)	1.872(3)	1.8906(15)	1.905(2)	1.890(2), 1.909(2)	1.902(4)	1.894(5)	1.881(6)	1.904(3)	1.898 (3)
Fe-O(sal)	1.907(2)	1.911(2)	1.918(3)	1.905(3)	1.9077(16)	1.906(2)	1.902(2), 1.897(2)	1.902(4)	1.901(5)	1.910(6)	1.910(3)	1.900(3)
Fe-N(py)	2.225(2)	2.193(3)	2.196(4)	2.197(3)	2.2001(18)	2.212(2)	2.190(3)	2.190(5)	2.171(6)	2.181(7)	2.037(4)	2.011(4)
Fe-N(py)/Fe-OMe	2.242(2)	2.203(3)	2.203(4)	2.221(3)	2.2206(17)	2.066(2)	2.117(3), 2.091(3)	2.113(4)	2.214(6)	2.214(6)	2.036(4)	2.029(4)
Angles (°)	1a	1b	1c	1d	1e	2a	2b	2c	3a	4a	5a (Fe1)	5a (Fe2)
A	106.02(9)	106.51(10)	106.26(12)	105.54(13)	109.06(7)	108.67(9)	107.88(10), 107.59(10)	107.36(19)	108.1(2)	103.4(3)	86.00(14)	86.02(15)
В	88.65(9)	88.41(10)	88.45(13)	88.16(13)	87.84(8)	87.98(9)	87.60(10), 87.38(11)	87.67(19)	86.5(3)	88.8(3)	93.39(15)	93.57(16)
С	87.95(9)	87.81(10)	87.81(13)	88.92(13)	87.22(7)	86.57(9)	87.20(10), 88.19(10)	87.5(2)	88.4(2)	90.7(3)	93.70(16)	94.07(16)
D	78.28(9)	78.13(11)	78.33(13)	78.32(14)	76.82(8)	77.22(9)	77.55(11), 77.27(11)	77.9(2)	77.1(2)	77.0(3)	87.04(16)	86.56(16)
py-Fe-py dihedral ^a	11.7	15.1	24.0	21.2	48.5	_		_	52.0	83.6	14.8	28.2
Structural Parameters	1a	1b	1c	1d	1e	2a	2b	2c	3a	4 a	5a (Fe1)	5a (Fe2)
C ₂ N ₂ conformation	Meso	meso	meso	meso	meso	meso	meso	meso	envelope	umbrella	meso	meso
Inter-chain Fe ··· Fe Intra-chain Fe ··· Fe	13.476(2) 7.792(2)	13.736(3) 7.775(5)	13.753(2) 7.811(9)	13.709(3) 7.648(7)	15.668(2) 5.957(5)	8.840(1)	7.629(9), 7.819(9)	6.940(2)	15.424(4) 7.296(3)	15.656(6) 10.341(1)	16.295(1) 37.445(1), 13.462(1)	10.689(1) —

" Dihedral angle between Fe-py planes.

Results

Structural analysis

A summary of relevant bond lengths, angles and structural parameters is provided in Table 2.

1a-e. The five compounds **1a-e** are of the general formula $[Fe(III)(salen)(L)](BPh_4)\cdot n(MeOH)$ (L = 4,4'-azpy, tvp, bpe, pin and bpdh, Fig. 2). Compounds **1a-d** all crystallize in the monoclinic space group: $P2_1/n$, and **1e** crystallizes in the lower symmetry triclinic space group $P\overline{1}$. Each structure consists of distorted octahedral Fe(III) centres coordinated equatorially by the tetradentate Schiff base ligand salen which provides a N_2O_2 donor set (Table 2). These $[Fe(III)(salen)]^+$ moieties are then bridged by the two-connecting pyridyl-donor ligands, completing the octahedral coordination geometry around each Fe(III) centre. Infinite cationic 1-D linear chains are thus formed (Fig. 2(a)). The intra- and inter-chain Fe \cdots Fe separations within each chain vary depending on the ligand length (Table 2).

The main distinction between **1a-d** and **1e** is the packing arrangement of the chains and the resultant intermolecular interactions. For **1a-d** the chains are arranged in alternating rows of pairs which are close packed. The charge balance for the cationic chains is provided by tetraphenylborate anions which are located between the pairs of chains. These anions are involved in four-fold edge-to-face phenyl embraces comprised of $-CH \cdots \pi$ interactions as illustrated in Fig. 2(b). Solvent methanol molecules are also present in these materials and are involved in hydrogen-bonding interactions with the salen phenolate oxygen, and are also involved



Fig. 2 Representative example of 1-D chain materials of the type $[Fe(salen)(L)](BPh_4) \cdot n(MeOH)$, showing (a) the structure of the infinite 1D chain $[Fe(salen)(L)]^+$ moiety of **1a** where L = azpy; and (b) the four fold phenyl embrace which occurs between chains and BPh_4^- anions.

in $-OH \cdots \pi$ interactions with the tetraphenylborate rings. For **1e** the parallel packed cationic chains show a staggering of the salen ligand in alternate chains such that maximum pack efficiency is achieved (Table 2). In this compound the efficient chain packing arrangement results in the absence of solvent molecules in the crystal lattice. The packing also comprises of pairs of chains, where the C₂N₂ backbone of the salen ligands face outwards, and these

pairs of chains are separated by tetraphenyl borate anions. Each tetraphenylborate anion is involved in three -CH $\cdots \pi$ interactions.

2a-c. The compounds 2a-c have the general formula [Fe(III)salen(L)(MeOH)](BPh₄) (Fig. 3) where distorted octahedral Fe(III) centres are equatorially coordinated by salen to form [Fe(III)(salen)]+ units. These units are axially coordinated by one pyridyl nitrogen atom from either L = bpp, dps or bpy, and the octahedral coordination is completed by one oxygen atom of a methanol molecule to give a N₃O₃ donor set. While each of these compounds is of the same general formula, they crystallise in different symmetries and show subtly different intermolecular interactions. For 2a and 2c, each mononuclear moiety interacts with adjacent molecules via hydrogen bonding interactions between the methanol -OH and the non-bonded pyridyl nitrogen of L; thus producing an overall structural motif of zig-zag hydrogen bonded 1-D chains (Fig. 3(2a) and (2c)). The chains in 2a are packed in pairs similar to that seen in 1e, whereas there is no pairing in 2c. The remaining crystal volume is occupied by tetraphenylborate anions which for 2a are involved in one -CH $\cdots \pi$ interaction with a pyridyl group on bpp ligand. In contrast, while 2b also consists of hydrogen-bonded zig-zag chains, the [Fe(III)salen(L)(MeOH)]⁺ moieties show two different, alternating, hydrogen-bonding arrangements along each chain. Firstly, interactions exist between the methanol -OH and the non-bonded pyridyl nitrogen of the bpp ligand as seen for 2a and secondly, there is one interaction from bound methanol -OH to solvent -OH which then further hydrogen-bonds to the non-bonded pyridyl nitrogen of the bpp (Fig. 3(2b)). The Fe(III) centres are colinear in 2a and 2c but not in 2b.



Fig. 3 1-D hydrogen bonded compounds of the type [Fe(III)salen(L)-(MeOH)](BPh₄). L = bpp (2a), L = dps (2b) and, L = bpy (2c).

3a. The atypical structure of **3a** may be considered to consist of two distinct portions comprised of linear 1-D chains of $[Fe(III)(salen)(bpdh)]^+$ and the starting material $[Fe(III)(salen)CI]_2$ (Fig. 4). The 1-D chains are configured as seen in **1e**, where $[Fe(III)(salen)]^+$ moieties are bridged by bpdh ligands, thus completing the distorted octahedral Fe(III) N₄O₂ donor set (Table 1). The second portion of **3a**, consisting of the



Fig. 4 Representation of the structure of the 'hybrid' material **3a**, which shows pairs of 1-D chains of [Fe(III)(salen)(bpdh)]⁺ separated by [Fe(III)(salen)Cl]₂ dimers.

dimer starting material, occurs in alternating layers throughout the crystal lattice, where one layer consists of a single array of $[Fe(III)(salen)Cl]_2$ dimers, and the other consists of one 'pair' of $[Fe(III)(salen)(bpdh)]^+$ chains. Notably, the salen ligands in the 'paired' rows of $[Fe(III)(salen)(bpdh)]^+$ are staggered, as described for **1e**, although the intra-chain separation suggests the chains are not closely packed (Table 2). The area between chains is filled with methanol molecules and hexafluorophosphate anions which pack between 1D chain and $[Fe(III)(salen)Cl]_2$ dimer layers.

4a. The compound **4a**, $[Fe(III)(salophen)(bpdh)](BPh_4)$. 2EtOH, contains the salen analogue ligand salophen. The structure consists of 1-D chains of distorted octahedral Fe(III) centres coordinated equatorially by the bulky salophen (Table 2). The [Fe(III)(salophen)]⁺ moieties are then bridged by the twoconnecting pyridyl ligand bpdh, to form infinite 1-D chains (Fig. 5). In contrast to 1a-e, the salophen ligands are in a staggered conformation along the chains. Close packing of these chains is likely inhibited by the bulky phenyl groups of the salophen ligand and as such there is a much larger intra-chain Fe ... Fe separation than for the salen analogues (Table 2). Tetraphenylborate anions are located throughout the crystal lattice and, unlike the salen analogues, they are not involved in -CH $\cdots \pi$ interactions with the 1-D chains. Furthermore, there is no pairing of chains as seen in 1a-e. Solvent ethanol is present in the crystal lattice and is involved in a hydrogen-bonding interaction with a phenolate oxygen atom of the salophen ligand.



Fig. 5 Representation of the structure of $[Fe(III)(salophen)-(bpdh)]BPh_4.2EtOH (4a).$

5a. The compound **5a** consists of infinite linear hydrogen bonded chains comprised of $[(Fe^{III}(acen))_2(\mu-tvp)(tvp)(tvpH)]^{2+}$ units and a protonated non-coordinating tvp molecule (Fig. 6(a)). The $[(Fe^{III}(acen))_2(\mu-tvp)(tvp)(tvpH)]^{2+}$ portion contains two Fe(III) centres both with equatorial N₂O₂ donor sets provided by the acen ligand. The two Fe(III)



Fig. 6 Representation of the structure of the hydrogen bonded dinuclear **5a** which (a) contains two Fe(III)(acen) centres joined by a μ -tvp ligand and capped by either tvp or Htvp. (b) These units are hydrogen-bonded through unbound Htvp ligands into infinite 1-D chains.

centres are bridged by one tvp ligand. The remaining axial donor set is then provided by two typ molecules which 'cap' the ends of the dimer to complete the N₄O₂ overall donor set (Table 2). The non-coordinating pyridyl group of one 'capping' tvp ligand is protonated and engages in a hydrogen bond with the single protonated non-coordinating tvp molecule, thus forming hydrogen-bonded 1-D chains of Fe(III) dimers (Fig. 6(b)). The closely packed chains (Table 2) are surrounded by tetraphenylborate anions, although there is sufficient room to accommodate two methanol molecules. The tetraphenylborate anions are closely associated with the protonated pyridyl groups such that two tetraphenylborate anions form an 'enclosure' around the protonated pyridyl ring, and the aromatic hydrogens on either side of the protonated pyridyl nitrogen atom engage in -CH \cdots π bonds with these enclosing tetraphenylborate anions. Each tetraphenylborate anion participates in only one -CH $\cdots \pi$ bond, implying that there are no inter-chain interactions.

5b-f. Single crystals of the compounds **5b-f** were not obtained, hence their constitutions and structures were deduced from IR spectroscopic and microanalytical measurements on the powders and by comparison to the reported analogue [Fe^{III}(acen)(bpp)](BPh₄), **5e** (Fig. 7 (bottom)). This previously reported coordination polymer consists of 1-D zig-zag chains of [Fe(III)acen]⁺ units linked *via* bpp ligands.²⁵ There are no interchain or intermolecular interactions reported in the papers.²⁴⁻²⁶ Likely, the materials **5b-d** and **5f** also consist of 1-D chains but the linear or zig-zag conformation of these chains is unknown



Fig. 7 (top) Schematic representation of **5b-f** where Fe(III)(acen) units are linked by L = bpe, bpdh, bix, bpp or pin into 1-D chains. (bottom) The structure of [Fe(III)(acen)(bpp)](BPh₄), **5e**, as reported by Imatomi *et al.*^{25,26}

and would probably vary significantly over the series owing to the difference in ligand lengths and flexibilities (Fig. 7 (top)).

Magnetic susceptibility measurements

1a-e. Magnetic susceptibility measurements on each of the salen-containing 1-D chain materials **1a-e** revealed a high spin d⁵ character over all temperatures (ESI; Fig. S13†) The μ_{eff} values remained constant at *ca.* 5.5-5.9 μ_{B} over the temperature range 4-300 K consistent with that expected for Fe(III) in the high spin, S = 5/2, state.

2a-c. The data on each of the hydrogen-bonded salen containing 1-D chain materials **2a-c** revealed a high spin character over all temperatures (ESI; Figs. S14-16†). The μ_{eff} values remained constant at *ca*. 5.8-5.9 μ_{B} over the temperature range 4-300 K consistent with that expected for Fe(III) in the high spin state.

3a. Susceptibility measurements on the 'hybrid' 1-D chain/chloro-dimer revealed μ_{eff} values at 300 K of *ca.* 8.36 μ_B (5.91 μ_B per Fe(III)) consistent with two high spin Fe(III) ions. Between 300 and 4 K the μ_{eff} values decreased gradually to a final value of 3.7 μ_B , per Fe, as expected owing to the presence of weakly antiferromagnetically coupled [Fe^{III}(salen)Cl]₂ units that have a *J* value of -7 cm⁻¹ (Fig. 8).³⁷ The decrease in μ_{eff} is not due to SCO.



Fig. 8 Magnetic moment, per 2Fe, *versus* temperature over the temperature range 4-350 K for the mixed 1-D chain and dimer compound **3a**.

5a. A spin transition was observed that was not quite complete even at high temperatures (Fig. 9). At 350 K the μ_{eff} value of 4.70 μ_{B} is less than the high spin value for the Fe(III) centres. Between 350 and 175 K the μ_{eff} values decreased to a value of *ca*. 2.12 μ_{B} . Below 175 K the μ_{eff} values again decreased, but gradually, to reach a value of *ca*. 1.8 μ_{B} at 4 K, consistent with that expected for Fe(III) in the t_{2g}^{5} low spin state.

5b-f. Each of these acen containing 1-D Fe(III) chain complexes undergo spin transitions, but with varying degrees of completeness and occurring over different temperature ranges (Fig. 9). For **5b** the μ_{eff} value at 350 K of 3.5 μ_B decreased gradually over the whole temperature range to reach a lowest value of 2.08 μ_B at 4 K, consistent with the majority of Fe(III) sites being in the low spin state. The μ_{eff} value for **5c** at 350 K of 3.45 μ_B decreased gradually over the whole temperature range to reach a minimum value of 1.85 μ_B at 4 K, consistent with a low spin Fe(III) character. For **5d** the μ_{eff} value at 350 K of 5.0 μ_B is again



Fig. 9 Magnetic moment, per Fe, *versus* temperature over the temperature range 4-350 K for the acen containing hydrogen bonded chain material 5a (this powder sample has constitution 1:1 5a:5a1) and the 1-D chain materials 5b-f.

consistent with an intermediate high spin-low spin character for the Fe(III) centres. Between 315 and 165 K the μ_{eff} values decreased to a value of ca. 2.75 $\mu_{\rm B}$. Below 165 K the $\mu_{\rm eff}$ values again decrease, but more gradually, to reach a minimum value of ca. 2.21 $\mu_{\rm B}$ at 4 K, consistent with that expected for the majority of the Fe(III) sites being in the low spin state. For **5e** the μ_{eff} value at 350 K of 5.7 μ_{B} is consistent with an essentially complete high spin character for the Fe(III) centres. Between 300 and 100 K the μ_{eff} values decreased, with $T_{1/2}$ ~180 K, to a value of *ca*. 2.77 $\mu_{\rm B}$. Below 100 K the $\mu_{\rm eff}$ values decreased again but more gradually, to reach a minimum value of ca. 2.34 $\mu_{\rm B}$ at 4 K, consistent with that expected for the majority of the Fe(III) centres being in the low spin state. For 5f the μ_{eff} value at 300 K of *ca*. 6.06 μ_{B} is consistent with high spin Fe(III). Between 300 and 155 K the $\mu_{\rm eff}$ values decreased gradually and then more rapidly to 90 K, to reach ca. 2.96 $\mu_{\rm B}$. The $T_{1/2}$ is 135 K. Below 90 K the μ_{eff} values decreased again, but more gradually, to reach a minimum value of 2.16 μ_B at 4 K, consistent with low spin Fe(III) sites.

Discussion

Synthesis

The aim of producing a range of 1-D chain Fe(III) complexes containing the Schiff base ligand salen was achieved here, together with the synthesis of a number of other, unexpected, materials. Interestingly, all the salen-containing compounds were obtained under the same reaction conditions, but different products resulted, in a somewhat unpredictable manner. Importantly, the complexes **1a-e** were readily obtained as single crystals, often in a matter of hours and usually within 24 h, through a one-pot mixing of all the reactants. This suggests that the 1-D chain arrangement, which is efficiently interlocked *via* -CH $\cdots \pi$ interactions with the tetraphenylborate anions, is a thermodynamically stable product. Notably, if the 1-D chain materials were left standing in solution after formation, rather than being removed from the mother-liquor, large red crystals of the well known μ -oxo bridged

[Fe(III)(salen)]₂O dimer formed.³⁸ However, synthesis under an inert atmosphere was not deemed necessary, as removal of the products from the mother-liquor shortly after formation avoided μ-oxo dimer contamination. Further to this, while the complexes **2a-c** were synthesised using the same method and stoichiometry to those used for **1a-e**, hydrogen-bonded 1-D chains which contain coordinated methanol molecules formed, instead of the target 1-D chains. Since the ligands that resulted in this hydrogen-bonded 1-D chains structure are, in general, shorter than those used to form **1a-e**, they may not sterically favour the formation of 1-D chains of type [Fe(III)(salen)(L)]_n.

Further highlighting the unpredictable nature of the 1-D chain formation, the 'hybrid' compound 3a, containing both the starting material [Fe(III)(salen)Cl]₂ and the 1-D chain target molecule cocrystallised, was obtained when the hexafluorophosphate anion was used in place of tetraphenylborate. Notably, this compound took 1 week to crystallise whereas the analogue **1e** crystallised within 24 h.

Also, within this study, attempts were made to synthesise a range of 1-D chain materials using the Schiff-base ligand salophen; however, only that with bpdh, the longest of all the pyridyl donor ligands, was successful. It is likely that the bulky nature of the salophen ligand requires a larger intra-chain Fe... Fe separation and thus a longer pyridyl linker ligand for formation of the chain species. Presumably the L ligands provide weakly basic conditions as well as coordinating properties. It proved difficult to re-synthesise **4a** after the first attempt, suggesting that subtle factors influence its formation and isolation.

From the relative scarcity of acen-containing crystal structures obtained in the present study, it is obvious that crystallised products for [Fe(III)(acen)(L)]⁺ systems are not as readily formed with the pyridyl/imidazolyl donor ligands as they are for [Fe(III)(salen)(L)]⁺ systems. Attention may be drawn here to the less bulky aromatic nature of the acen ligand, compared to salen and salophen, that results in less intermolecular crystal packing effects involving the bulky tetraphenylborate anion, and it is thus less likely to yield crystalline products. In all cases, except 5a with tvp, only powdered samples were obtained for acen systems and their structures have been proposed from a range of physical techniques (see Fig. 7 (top)). Also included in this series is the previously reported material [Fe(acen)(bpp)](BPh₄)^{25,26} that helped in our proposed structural analysis of the remainder of this series (Fig. 7 (bottom)). As just mentioned, 5a was the only [Fe(III)(acen)(L)]+ compound where structural analysis could be carried out, and crystals suitable for crystallographic study were formed over a period of seven days under atmospheric conditions by slow diffusion in an H-shaped tube. Structural analysis revealed not a single molecule 1-D chain, as expected, but a hydrogen-bonded 'chain of dimers'; the bulk powdered sample was confirmed to be the same by microanalysis and powder X-ray diffraction analysis. The production of a tvpH⁺ unit in this material implies an effective acidic solution is present in the synthesis and we note that 5a co-crystallised with yellowplate crystals of tvpH⁺BPh₄⁻, **5a1**. Crystals of **5a** could not be adequately purified by hand-separation, so magnetism studies were carried out on the powdered sample. Elemental analysis on the powder gave good agreement between, either, a 1:1 mixture of 5a:5a1 and the non-methanolate of 5a, with the former being favoured.

Structural and magnetic analysis

Salen-containing complexes. Despite all changes made to L, with the tetradentate Schiff-base salen, a temperature dependence in μ_{eff} was not observed (**1a-e**). These compounds display typical high spin d⁵ behaviour in which the μ_{eff} values remain constant at *ca*. 5.9 μ_{B} between 300 K and 4 K, with χ_{m} values correspondingly Curie-like. The high spin behaviour was further confirmed in the crystal structure data at 123 K of these materials where the Fe-N and Fe-O bond lengths are typical of high spin Fe(III) values (Table 2), ^{11,14,20-22,26}

It has previously been observed that for a spin transition to occur in mononuclear [Fe(III)(salX)(L)₂]⁺ systems, the C_2N_2 backbone must adopt the envelope conformation; the other possible conformations include *meso* and planar (or umbrella) (Fig. 10). It has been suggested that the envelope conformation allows a spin transition to occur with minimal geometrical change, whereas the *meso* and planar conformations constrain the salen ligand such that is it not able to adapt to the incipient spin transition.²² The *meso* and planar conformations essentially 'lock' the complex in the high spin form. In the compounds **1a-e** described here, the *meso* conformation has been adopted whereby aromatic moieties deviate slightly, by approximately equal distances and in opposite directions to each other, from the FeN₂O₂ mean plane (Fig. 10(b)).



Fig. 10 Possible salen C_2N_2 backbone conformations (a) envelope (*e.g.* **3a**), (b) *meso* (*e.g.* **1a**) and (c) planar (umbrella, *e.g.* **4a**).



Fig. 11 Observed acen ligand conformations in (a) $[Fe(III)(acen)-(Him)_2](BPh_4)^{39}$ (b) $[Fe(III)(acen)(bpp)](BPh_4)^{25,26}$ and (c) 5a.

It is worth noting that it is not solely the configuration of the equatorial Schiff base ligand that may dictate whether or not a spin transition is possible. In the previously reported compound $[Fe(III)(salen)(tmid)](ClO_4)$, an incomplete spin transition is observed below 100 K; crystallographic study shows that for each

In the compound 4a, contrasting to 1a-e, the salophen ligand has adopted the umbrella conformation, where the aromatic moieties deviate from the FeN₂O₂ mean plane in the same direction, while the carbon atoms comprising the C₂N₂ backbone deviate from it very little (Fig. 10(c)). This conformation has been observed in [Fe(III)(5-CH₃O-salen)(Him)₂]Cl, and is known to produce high spin Fe(III) compounds.³⁹ This suggests that 4a is also a high spin compound but insufficient sample precluded magnetic studies being made

In the hydrogen-bonded chain materials **2a-c**, the N₃O₃ donor set that they contain is not conducive to SCO behaviour in [Fe(III)(salen)]⁺ systems. Thus they remain high spin and show high spin Fe(III) Fe-N and Fe-O bond lengths. [(Fe(III)(salen))₂(μ azpy)(H₂O)₂](ClO₄)₂·(azpy)·(H₂O) contains a similar coordination environment to **2a-c**, and was found to remain high spin over all temperatures.⁴⁰

The 'hybrid' salen material **3a** displays a superposition of the magnetic susceptibility of the antiferromagnetically spin-coupled [Fe(III)(salen)Cl]₂ dimer, and that due to the [Fe(III)(salen)(bpdh)]⁺ chains. The corresponding μ_{eff} values decrease markedly with temperature as expected for [Fe(III)(salen)Cl]₂ units being present. The chains are then high spin d⁵, since the calculated μ_{eff} for two high spin d⁵ ions is 8.36 μ_B (5.92 μ_B per Fe(III)) at 300 K and the observed value is of this magnitude. Typical high spin Fe(III) Fe-N and Fe-O distances are observed for the 1-D chains 123 K (Table 2). Interestingly, the salen ligand in the 1-D chain portion of **3a** has adopted the envelope conformation (Fig. 10(a)), suggesting that a spin transition could have occurred but, presumably the ligand field around each Fe is not strong enough.

Acen containing complexes

In the present study, SCO behaviour has been observed for the compounds 5a-f (Fig. 9) and these contain a range of bridging L ligands. This, along with the previous literature examples of SCO [Fe(III)(acen)]+ compounds, suggests that acen provides a versatile platform for the synthesis of SCO materials. Furthermore, the range of $T_{1/2}$ temperatures observed over this 1-D series suggests that altering the character of the axial bridging ligand provides an effective means to tune the properties of the spin transition. Already reported are the three SCO 1-D chain materials [Fe(III)(acen)(bpp)](BPh₄), [Fe(III)(acen)(tmid)](BPh₄) and [Fe(III)(acen)(tdim)](ClO₄),²³⁻²⁶ all of which undergo gradual spin transitions that are incomplete at high temperatures. The first of these has recently been shown, at temperatures midway between where the HS and LS states are stabilised, to consist of alternating HS and LS chains while the second consists of HS-LS-HS-LS units within the chains,^{25,26} a situation akin to our observations on some Fe(II) 1-D systems.6,27

Within the present series of compounds, a range of ligand lengths, flexibilities, hydrogen-bonding and π - π stacking capabilities has been included. However, as structural analysis was usually not possible, only general structural-magnetic correlations can be

drawn. Compound 5f, containing the ligand pin, displays a spin transition with the lowest transition temperature and the most abrupt transition. This ligand is possibly the least flexible in the current series and also contains central functional groups capable of hydrogen-bonding. Compounds 5d-e display the next highest transition temperatures and contain the flexible ligands bix and bpp, where bix probably confers a zig-zag motif as seen for bpp (Fig. 7).^{25,26} Lastly, **5b-c** undergo spin transitions at the highest transition temperatures and contain ligands (tvp and bpe) which are more rigid and less likely to adopt the zig-zag motif, but, unlike pin, are not likely to engage in intermolecular interactions. The ligand field strength of the particular bridging ligand N-donor will play a role in the observed transition temperature; however, the only compound of this series to contain a stronger field imidazole donor group, 5d, shows a spin transition with an intermediate $T_{1/2}$ temperature in relation to this series. This suggests that it is a combination of crystal packing and ligand field effects that contribute to the observed magnetic behaviour.

Complex 5a provides a novel example of a dinuclear Fe(III) SCO complex where the only previous examples reported are $[(Fe_2(salen)_2(\mu-azpy)(H_2O)_2](ClO_4)_2 \cdot (azpy) \cdot (H_2O)_4^{40}$ and pentadentate (N₃O₂) Schiff base Fe(III) complexes such as [Fe₂((3-MeO-sal)₂-trien)₂(μ -tmid)](BPh₄)₂⁴¹and others that have 4,4'-bipy, tvp and azpy bridges axially bound.^{6,40} Structural analysis on 5a revealed no obvious inter-chain interactions. The Fe(III) centres are connected directly by a rigid, linear bridging ligand. 5a undergoes a gradual and incomplete transition which suggests that in this case, the use of a rigid bridging ligand has not resulted in a highly cooperative system. Whether the gradual nature of this transition is, in part, due to a staggering of spin transition temperatures of the two distinct Fe(III) centres, similar to that thought to occur between independent 1D chains in [Fe(III)(acen)(bpp)]BPh₄ (vide supra), and at alternating Fe(III) centres within 1D chains of [Fe(III)(acen)(tmid)]BPh₄ is unclear.^{25,26}

The poor cooperativity in [Fe(III)(acen)(L)](BPh₄); L = bpp, tmid, was attributed to the lack of inter-chain/intermolecular interactions and the flexible nature of the bridging ligand which confers a zig-zag packing motif.^{25,26} Since related monomeric systems [Fe(III)(acen)(4-methylpyridine)₂](BPh₄) and [Fe(III)(acen)(3,4dimethylpyridine)₂](BPh₄) undergo complete, more abrupt spin transitions,²⁴ this suggests that better cooperativity is occurring in these systems than in the polymeric systems mentioned above, but structural details were lacking. Furthermore, a comparison between the above 1-D chain acen systems and the hysteretic monomeric compound [Fe(III)(pap)₂](ClO₄).H₂O,¹² that displayed extensive π -stacking in the crystal lattice, suggests that covalent linkages between heterocyclic axial donors are unsuited to the transmission of cooperative interactions in these 1D systems.

Finally, a detailed categorisation of equatorial Schiff-base ligand conformation, as described for the salen analogues, has not been attempted previously for acen and derivatives. There are some subtle structural aspects of interest that are apparent here. The pertinent acen-containing compounds are the low spin complex [Fe(III)(acen)(Him)₂](BPh₄)⁴² and the SCO complexes [Fe(III)(acen)(bpp)](BPh₄),^{25,26} [Fe(III)(acen)(tmid)](BPh₄)²⁶ and **5a**. In comparing the relative acen ligand geometries in each it can be seen that, as for salen, different conformations of the C₂ backbone (C₁ and C₂ in Fig. 11(d)) are observed. [Fe(III)(acen)(Him)₂](BPh₄) shows the envelope conformation and

 $[Fe(III)(acen)(bpp)](BPh_4)$, $[Fe(III)(acen)(tmid)](BPh_4)$ and **5a** all show the *meso* conformation. As suggested by the classification of the acen conformation in each compound, there are notable differences in the deviations of the imine carbon atoms (C₃ and C₄, Fig. 11(d)) from the FeN₂O₂ mean planes in each compound.

In $[Fe(III)(acen)(Him)_2](BPh_4)$ one imine carbon deviates above the FeN_2O_2 mean plane and the other lies approximately within the plane. In contrast, for [Fe(III)(acen)(bpp)](BPh₄), $[Fe(III)(acen)(tmid)](BPh_4)$ and 5a, the imine carbon atoms deviate above and below the plane by equal amounts. From this it appears that the acen ligand conformation may have an opposite trend to that observed for the salen materials, where the envelope conformation, rather than the meso conformation, is usually prohibitive to a spin transition. For [Fe(III)(acen)L]⁺ systems, the greater the degree of distortion around the Fe(III) centre (generated by the ligand geometry) the more a LS character is attained. Furthermore, the dihedral angle formed by imidazole ligands on opposing sides of the Fe(III) centre in the compound [Fe(III)(acen)(Him)₂](BPh₄) is significantly greater than it is for 5a, and for [Fe(III)(acen)(bpp)](BPh₄) at 108K, and this might contribute to the observed spin state. Further data are required on [Fe(III)(acen)]+ systems.

We have shown that there is demonstrable dependence of the C₂N₂ backbone configuration on magnetic behaviour in [Fe(III)(salX)]⁺ compounds, noted recently also in Fe(III)-sal₂trien compounds,^{20,21} and the present work tends to suggest the same for [Fe(III)(acen)]⁺ compounds. Interestingly, for comparable $[Fe(II)(O_2N_2)(L)_2]$ iron(II) compounds of the Jäger type, differences in magnetic behaviour have also been linked to the magnitude of the bond lengths in the five-membered ring comprising the Fe(II) centre and C₂N₂ backbone of the Schiff base ligand.^{17,18} The recently reported SCO compound [FeL1b(py)₂] was compared with the HS [FeL2b(py)₂] compound,^{17,18} the tetradentate ligand L1b having an en-linked backbone while L2b a o-phen-linked one. Comparison of bonds lengths within the five-membered ring Fe-N-C-C-N for each of **1a-e** to [Fe(III)(salen)(tmid)](ClO₄) in the HS state,²³ and for **5a** to [Fe(III)(acen)(bpp)](BPh₄) and Fe(III)(acen)(tmid)](BPh₄) in the LS state^{25,26} and also [Fe(III)(acen)(Him)₂](BPh₄),⁴² suggests that this interpretation may not apply to [Fe(III)(Schiff-base)]+ compounds. Significant bond length differences for compounds displaying different magnetic behaviour are not observed. It should be noted, however, that for Fe-N_{axial} bond lengths there appears to be a considerable difference between HS and SCO compounds; values are given for 1a-e, 3a and 5a in Table 2, while for [Fe(III)(salen)(tmid)](ClO₄) in the HS form the average Fe-N_{axial} = 2.157(4) Å.

Conclusions

This new series of 1-D chain Schiff base-containing materials underscores a number of key points about how magnetic behaviour correlates to ligand conformation. Magneto-structural characterisation of new [Fe(III)(salX)(L)]⁺ compounds is supplied that is supportive of the previously held notion that a spin transition cannot occur when the C_2N_2 backbone of the equatorial ligand adopts the *meso* conformation. For example, varying the length and character of the bridging pyridyl ligand does not appear to have any magnetic consequences for [Fe(III)(salen)(L)]⁺ systems where the *meso* conformation has been adopted. Further to this,

the compound 3a, in which salen has adopted the envelope conformation, suggests that the total ligand field strength may be too weak to induce a spin transition in [Fe(III)(salen)(L)]⁺ systems when L is a pyridyl donor ligand. For [Fe(III)(salen)(L)]⁺ systems, variation of the length and character of the bridging pyridyl ligand does have structural consequences - the shorter and more flexible ligands tend to form hydrogen bonded 1-D chain motifs in which one of the axial positions of the Fe(III) coordination environment is occupied by a methanol molecule. A series of new examples of SCO 1-D chain materials of the type [Fe(III)(acen)(L)]⁺ are presented, wherein axial ligand variation has resulted in a range of magnetic behaviours. Comparison of the structural conformation of the acen ligand in 5a to previously reported analogues is suggestive of a correlation between structure and magnetism as observed for [Fe(III)(salen)(L)]+ systems. Aims in future studies include the expansion of the current [Fe(III)(acen)(L)]⁺ series using a range of other N-donor ligands, and counter ion variation. Also, compounds in which L is a three- or four-connecting ligand may be investigated, in order to see the effect of introducing [Fe(III)(acen)(L)]+ SCO centres into higher dimensional materials.

Acknowledgements

Mr. Jarry Abbas kindly contributed to preliminary syntheses. The Australian Research Council provided a Discovery Grant for this work.

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