## FULL PAPER

## Spin crossover of ferric complexes with catecholate derivatives. Single-crystal X-ray structure, Magnetic and Mössbauer investigations<sup>†</sup>

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Complexes of general formula [(TPA)Fe(R-Cat)]X·*n*S were synthesised with different catecholate derivatives and anions (TPA = tris(2-pyridylmethyl)amine, R-Cat<sup>2-</sup> = 4,5-(NO<sub>2</sub>)<sub>2</sub>-Cat<sup>2-</sup> denoted DNC<sup>2-</sup>; 3,4,5,6-Cl<sub>4</sub>-Cat<sup>2-</sup> denoted TCC<sup>2-</sup>; 3-OMe-Cat<sup>2-</sup>; 4-Me-Cat<sup>2-</sup> and X = BPh<sub>4</sub><sup>-</sup>; NO<sub>3</sub><sup>-</sup>; PF<sub>6</sub><sup>-</sup>; ClO<sub>4</sub><sup>-</sup>; S = solvent molecule). Their magnetic behaviours in the solid state show a general feature along the series, *viz.*, the occurrence of a thermally-induced spin crossover process. The transition curves are continuous with transition temperatures ranging from *ca.* 84 to 257 K. The crystal structures of [(TPA)Fe(DNC)]X (X = PF<sub>6</sub><sup>-</sup>; BPh<sub>4</sub><sup>-</sup>) and [(TPA)Fe(TCC)]X·*n*S (X = PF<sub>6</sub><sup>-</sup>; NO<sub>3</sub><sup>-</sup> and *n* = 1, S = H<sub>2</sub>O; ClO<sub>4</sub><sup>-</sup> and *n* = 1, S = H<sub>2</sub>O; BPh<sub>4</sub><sup>-</sup> and *n* = 1, S = C<sub>3</sub>H<sub>6</sub>O) were solved at 100 (or 123 K) and 293 K. For those two systems, the characteristics of the [FeN<sub>4</sub>O<sub>2</sub>] coordination core and those of the dioxolene ligands appear to be consistent with a prevailing Fe<sup>III</sup>–catecholate formulation. This feature is in contrast with the large quantum mixing between Fe<sup>III</sup>–catecholate and Fe<sup>II</sup>–semiquinonate forms recently observed with the more electron donating simple catecholate dianion. The thermal spin crossover process is accompanied by significant changes of the molecular structures as shown by the average variation of the metal–ligand bond distances which can be extrapolated for a complete spin conversion from *ca.* 0.123 to 0.156 Å. The different space groups were retained in the low- and high-temperature phases.

#### Introduction

The properties of ferric catecholate systems were extensively investigated as they provide interesting functional models of the intradiol catechol dioxygenases.<sup>1,2</sup> These enzymes operate in the sequence of chemical reactions necessary for the degradation of aromatic compounds, one key step consisting in the intradiol cleavage of the catecholate groups in the presence of dioxygene. It is well established that the activity for intradiol catechol cleavage depends on the iron–catecholate interaction, *i.e.* increases with the semiquinonato character of the dioxolene ligand and the Lewis acidity of the Fe<sup>III</sup> ion.<sup>2</sup> The dioxygenase reactivity is clearly reinforced in the presence of electron-donating substituents on the catechol group.<sup>3</sup> The most efficient model system consists of [(TPA)Fe(DBC)]BPh<sub>4</sub> (DBC<sup>2–</sup> = 3,5-di-*tert*-butylcatecholate dianion and TPA = tris(2-pyridylmethyl)amine).<sup>2</sup>

In addition to the iron–catecholate interaction, these complexes may exhibit an electronic lability associated to the spin multiplicity of the electronic state of the metal ion. Indeed, the study of the magnetic behaviour of [(TPA)Fe(Cat)]BPh<sub>4</sub> (Cat<sup>2–</sup> = catecholate dianion)<sup>4</sup> has revealed the occurrence of an unexpected thermal high-spin (HS)  $\leftrightarrow$  low-spin (LS) crossover in the solid state.<sup>5,6</sup> Gradual and incomplete spin crossover processes were also reported for [(TPA)Fe(DBC)]BPh<sub>4</sub> and [(TPA)Fe(R-cat)]BPh<sub>4</sub> (R-Cat = 3- and 4-chlorocatecholates).<sup>4,7</sup> Moreover, evidence for an extensive quantum mixing of Fe<sup>III</sup>Cat and Fe<sup>II</sup>SQ forms in both spin states were provided by DFT calculations for [(TPA)Fe(Cat)]BPh<sub>4</sub>.<sup>6</sup>

† Electronic supplementary information (ESI) available: Fig. S1 shows the powder X-ray diffraction patterns recorded at room temperature for the **1a**, **2a**, **3a**, **4a** and **5a** compounds. See http://www.rsc.org/suppdata/ dt/b4/b418294d/

In this paper, we report an experimental investigation of the spin crossover properties of ferric catecholate complexes of the type [(TPA)Fe(R-Cat)]X (see Scheme 1, the different  $H_2$ -R-Cat ligands). Substituents of the catechol group and anions were varied as they allow the internal electron transfer or the ligand field strength to be modulated. The spin interconversion shown by these compounds was investigated through variable-temperature single-crystal X-ray diffraction, magnetic and Mössbauer measurements.



## Experimental

Ferric salts, NaPF<sub>6</sub>, NaBPh<sub>4</sub>, H<sub>2</sub>TCC, H<sub>2</sub>Cat, H<sub>2</sub>-3-OMe-Cat, H<sub>2</sub>-4-CH<sub>3</sub>-Cat and solvents were purchased from Aldrich, Acros

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or Fluka chemicals and used without further purification. TPA and  $H_2DNC$  were prepared according to the procedures described in the literature.<sup>8,9</sup> Complexes [(TPA)Fe(R-Cat)]BPh<sub>4</sub> (R-Cat = Cat, 3-OMe-Cat, 4-CH<sub>3</sub>-Cat) (noted **3a–5a**) were synthesised under an argon atmosphere.

## Preparation of $[(TPA)Fe(R-Cat)]X \cdot S (R-Cat^{2-} = DNC^{2-}, TCC^{2-}, X^- = BPh_4^-, PF_6^-, NO_3^- and S = solvent)$

H2-R-Cat (0.255 mmol) was dissolved in methanol (10 mL) and deprotonated by 0.510 mmol of Et<sub>3</sub>N (71.5  $\mu$ L). This solution was slowly added to a mixture of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (103 mg, 0.255 mmol) and TPA (74 mg, 0.255 mmol) in methanol (10 mL).

**[(TPA)Fe(DNC)]BPh<sub>4</sub> (1a) and [(TPA)Fe(TCC)]BPh<sub>4</sub> (2a).** The solution of  $[(TPA)Fe(R-Cat)]^+$  was stirred at 50 °C for 15 min before the addition of one equivalent of NaBPh<sub>4</sub> in methanol (10 mL). The microcrystalline powder (1a, dark green and 2a acetone, purple) was isolated by filtration, washed with methanol and dried under vacuum. Single crystals suitable for X-ray diffraction were obtained by the evaporation of a (1/1) methanol/acetone solution of complex. Anal. Calcd. for FeC<sub>48</sub>H<sub>40</sub>N<sub>6</sub>O<sub>6</sub>B (1a, 863.52 g.mol<sup>-1</sup>): C 66.76, H 4.67, N 9.73. Found C 66.63, H 4.62, N 9.73. For FeC<sub>48</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>4</sub>B (2a, 911.31 g.mol<sup>-1</sup>): 63.26, H 4.20, N 6.15. Found C 63.23, H 4.57, N 6.21.

**[(TPA)Fe(DNC)]PF<sub>6</sub> (1b) and [(TPA)Fe(TCC)]PF<sub>6</sub> (2b).** The complex salts were prepared at room temperature with an addition of an excess of NaPF<sub>6</sub> (0.3 mmol for **1b**, 3 mmol for **2b**) in 15 mL of (1 : 2) methanol/water. Large single crystals of **1b** were obtained from the mixture upon standing overnight. For **2b**, the crude solid was recrystallised from a filtered methanol solution. Deep purple platelets of **2b** were isolated by filtration, washed with water and dried in air. Anal. Calcd for  $FeC_{24}H_{20}N_6O_6PF_6$  (**1b**, 689.28 g.mol<sup>-1</sup>): C 41.80, H 2.93, N 12.19. Found C 41.73, H 2.96, N 12.09. For  $FeC_{24}H_{18}N_4O_2Cl_4PF_6$  (**2b**, 737.04 g mol<sup>-1</sup>): C 39.11, H 2.46, N 7.60. Found C 38.77, H 2.45, N 7.42.

[(TPA)Fe(DNC)]NO<sub>3</sub>·H<sub>2</sub>O (1d·H<sub>2</sub>O) and [(TPA)Fe(TCC)]-NO<sub>3</sub>·H<sub>2</sub>O (2d·H<sub>2</sub>O). The solution of complex diluted with water (10 mL) was slowly evaporated. Dark green needles of 1d·H<sub>2</sub>O or deep purple crystals of 2d·H<sub>2</sub>O were obtained after several days, filtered, washed with water and dried in air. Anal. Calcd. for FeC<sub>24</sub>H<sub>22</sub>N<sub>7</sub>O<sub>10</sub> (1d·H<sub>2</sub>O, 624.32 g mol<sup>-1</sup>): C 46.17, H 3.55, N 15.70. Found C 46.04, H 3.47, N 15.76. For FeC<sub>24</sub>H<sub>20</sub>N<sub>5</sub>O<sub>6</sub>Cl<sub>4</sub> (2d·H<sub>2</sub>O, 672.10 g mol<sup>-1</sup>): C 42.99, H 2.78, N 10.45. Found C 42.80, H 2.80, N 10.44.

Preparation of [(TPA)Fe(DNC)]ClO<sub>4</sub>·H<sub>2</sub>O (1c·H<sub>2</sub>O) and  $[(TPA)Fe(TCC)]ClO_4 \cdot H_2O$  (2c·H<sub>2</sub>O). CAUTION: Perchlorate salts combined with organic ligands are potentially explosive and should be handled with care. The mixture of Fe(ClO<sub>4</sub>)<sub>3</sub>.10H<sub>2</sub>O (136.3 mg, 0.255 mmol) and TPA (74 mg, 0.255 mmol) in methanol (30 mL) was heated at 60  $^\circ\mathrm{C}$  to prevent the precipitation of [(TPA)Fe(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>. To this solution was added a methanol solution (10 mL) of H2-R-Cat (0.255 mmol) previously deprotonated by 0.510 mmol of Et<sub>3</sub>N (71.5 µL). After stirring for 30 min at 60 °C, the reaction mixture was allowed to cool to room temperature. This solution was diluted with water (10 mL) and allowed to stand at 4 °C overnight. A dark green powder of  $1c \cdot H_2O$  resulted and was isolated by filtration, washed with water and dried in air. Single crystals of 2c·H<sub>2</sub>O suitable for X-ray diffraction were obtained from the dark purple powder dissolved in a methanol/water solution. Anal. Calcd. for  $FeC_{24}H_{22}N_6O_{11}Cl$  (1c·H<sub>2</sub>O, 661.76 g.mol<sup>-1</sup>): C 43.57, H 3.35, N 12.71. Found C 43.83, H 3.15, N 12.92. For FeC<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O<sub>7</sub>Cl<sub>5</sub> (2c·H<sub>2</sub>O, 709.54 g.mol<sup>-1</sup>): C 40.63, H 2.84, N 7.90. Found C 40.37, H 2.58, N 7.82.

 $[(TPA)Fe(R-Cat)]BPh_4$  (R-Cat = Cat: 3a, R-Cat = 3-OMe-Cat: 4a, R-Cat = 4-CH<sub>3</sub>-Cat: 5a). These complexes were syn-

thesised under an argon atmosphere according to the procedure described in ref. 4. The microcrystalline powders were isolated by filtration under an inert atmosphere, washed with methanol and dried under vacuum. Anal. Calcd. for  $FeC_{48}H_{42}N_4O_2B$  (**3a**, 773.52 g mol<sup>-1</sup>): C 74.19, H 5.20, N 7.39, Fe 7.15, B 1.40. Found C 74.49, H 5.47, N 7.24, Fe 7.23, B 1.40. Anal. Calcd. for  $FeC_{49}H_{44}N_4O_3B$  (**4a**, 803.55 g mol<sup>-1</sup>): C 73.24, H 5.52, N 6.97, Fe 6.95, B 1.35. Found C 72.61, H 5.49, N 7.13, Fe 6.95, B 1.40. For  $FeC_{49}H_{44}N_4O_2B$  (**5a**, 787.56 g mol<sup>-1</sup>): C 74.73, H 5.63, N 7.11, Fe 7.10, B 1.37. Found C 74.90, H 5.65, N 7.18, Fe 7.10, B 1.00.

#### Cyclic voltametry measurements

These data were recorded with an EGG PAR potentiostat (M273 model). The counter electrode was an Au wire, the working electrode, a glassy carbon disk, was carefully polished before each voltamogram with a 1  $\mu$ m diamond paste, sonicated in an ethanol bath and then washed carefully with ethanol. The reference electrode was a saturated calomel electrode. The solvent used was distilled acetonitrile where NBu<sub>4</sub>PF<sub>6</sub> was added to obtain a 0.1 M supporting electrolyte. The experiments were carried out at RT.

#### UV-vis measurements

These were performed using a Varian Cary 5E double-beam spectrophotometer at RT. The solutions were prepared under an argon atmosphere.

#### X-Ray measurements

Diffraction data collection was performed on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 2°  $\Phi$  scans and later refined on all data. A 180°  $\Phi$  range was scanned, with  $2^{\circ}$  steps, with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz polarisation. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with anisotropic thermal parameters for all non H-atoms (except in the case of acetone solvent atoms of 2a acetone for which isotropic thermal parameters were chosen), H atoms were introduced (except in the case of H atoms of the water molecule of  $2c \cdot H_2O$  and  $2d \cdot H_2O$ ) at calculated positions and constrained to ride on their parent C atoms. All calculations were performed on an O2 Silicon graphics station with the SHELXTL package.<sup>10</sup> The labelling of the donor atoms is shown in Scheme 2. The temperature values chosen for the measurements ( $T_1 = 293$  K,  $T_2 = 173, 123 \text{ or } 100 \text{ K}$ ) correspond to different fractions of HS species. The fraction of HS iron(III) ions can be estimated from the magnetic data (assuming that  $\chi_{\rm M} T_{\rm HS} = 4.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and  $\chi_{\rm M}T_{\rm LS} \approx 0.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for pure HS and LS species, respectively). At  $T_1(T_2)$ , it is equal to 0.95(0.09) for 1a; 0.83 (0.02) for 1b; (1) for 2a acetone, 0.80 (0.03) for 2b; (0.02) for  $2c \cdot H_2O$  and 0.71 (0.01) for  $2d \cdot H_2O$ .



Scheme 2 Scheme of the coordination sphere and labels.

#### Magnetic measurements

The temperature dependence of the magnetic susceptibility have been carried out on samples of typical weight 15–20 mg using a Quantum Design SQUID magnetometer (MPMS5S model) calibrated against a palladium sample.

#### Mössbauer measurements

A constant-acceleration type Mössbauer spectrometer equipped with a 1024-channel analyser operating in the time scale mode,

and a 25 mCi  ${}^{57}$ Co/Rh source was employed. The isomer shifts reported here are relative to  $\alpha$ -Fe at room temperature. Spectra of the samples (thickness of about 5 mg Fe cm<sup>-2</sup>) were collected between 293 and 30 K by means of a combined He continuous flow/bath cryostat. The Mössbauer spectra were analysed by means of a computer program (RECOIL).<sup>11</sup>

## **Results and discussion**

## **X-Ray diffraction**

All complexes under study exhibit a thermal spin crossover process except **2a**·acetone, which remains in the HS state at any temperature (*vide infra*). Therefore the structures of **1a**, **1b**, **2b** and **2d**·H<sub>2</sub>**O** were determined at two temperatures ( $T_1 = 293$  K,  $T_2 = 123$  or 100 K) whereas the one of **2a**·acetone was solved at 173 K. For **2c**·H<sub>2</sub>**O**, the measurement was carried out in the LS phase (HS fraction = 0.02) at 123 K. Crystal data collection and refinement parameters for all complexes are given in Table 1. Selected bond lengths and angles are listed in Table 2.

**2b** crystallises in the orthorhombic space group Pna2(1) (Z = 4). Both **2c**·H<sub>2</sub>**O** and **2d**·H<sub>2</sub>**O** crystallise as a monoclinic space group P2(1)/c (Z = 4) with similar unit cell volume and parameters. These latter are also very close to those found for **2b**. Finally **1a** and **2a**-acetone are described by *P*-1 triclinic space groups (Z = 2) with different unit cell parameters.

By decreasing the temperature, the space groups of all these complexes are retained and significant variations of the unit cell parameters and volumes are observed. For example, the variation between 293 and 123 (or 100) K of the unit cell volume per formula unit ( $\Delta V$ ) is found to be 30.6 (**1b**); 37.4 (**2d**·H<sub>2</sub>**O**); 38.6 (**2b**) and 40.0 Å<sup>3</sup> (**1a**). Such values are the sum of two contributions: the volume change corresponding to the thermal spin crossover (*vide infra*) and the lattice thermal expansion.

# Molecular structures of 1a, 1b, 2a-acetone, 2b and 2d-H\_2O in the HS form

For this set of complexes, prevailingly in the HS form at 293 K, the FeN<sub>4</sub>O<sub>2</sub> core possesses distorted octahedral geometries (1a, Fig. 1) similar in nature to those previously described for the related HS ferric catecholate compounds.<sup>2</sup> The common structural features are (i) large values of the metal-ligand bond lengths, (ii) bond angles showing marked deviations from the octahedral geometry, (iii) an asymmetry of the metal environment due to the coordination of the tripodal ligand (see the bond lengths and angles in Table 2). The mean values of selected bond lengths are reported in Table 3. From the data collected in Tables 2 and 3, the structural parameters of 1a and 2a acetone are fully consistent with those characterised for HS Fe<sup>III</sup> catecholate systems ( $\langle Fe-N_{amine} \rangle = 2.151-2.246$  Å,  $(\text{Fe}-\text{N}_{\text{pyridine}}) = 2.109-2.227 \text{ Å}, (\text{Fe}-\text{O}) = 1.907-1.979 \text{ Å}).^{2,12}$ The slight discrepancies observed for 1b and  $2b,\ 2d \cdot H_2O$ indicate the presence of some amount of LS species at 293 K that agrees with the results of the magnetic measurements. The characteristics of the dioxolene ligands can be analysed through the values of the C-O bond length and those of the aromatic ring.<sup>12,13</sup> The mean values of the C–O and C–C



Fig. 1 The molecular structure of 1a at 100 K.

	1a		1b		2a-acetone	2b		2c·H2O	2d·H <sub>2</sub>	0
Formula M/g mol <sup>-1</sup>	${ m FeC}_{48}{ m H}_{40}{ m B}$	N <sub>6</sub> O <sub>6</sub>	${ m FeC}_{24}{ m H}_{20}{ m F}$	7 <sub>6</sub> N <sub>6</sub> O <sub>6</sub> P 28	FeC <sub>51</sub> H <sub>44</sub> BCl <sub>4</sub> N <sub>4</sub> O <sub>3</sub> 969.36	$FeC_{24}H_{18}CI_{4}$	$F_6N_4O_2P$	${ m FeC}_{24}{ m H}_{20}{ m Cl}_5{ m N}_4{ m O}_7$	$FeC_{24}H_{20}C$ 672.1	${}^1_4\mathrm{N_5O_6}_0$
T/K Crystal System	100(2) Triclinic	293(2) Triclinic	100(2) Orthorhombic	293(2) Orthorhombic	173(2) Triclinic	123(2) Orthorhombic	293(2) Orthorhombic	123(2) Monoclinic	100(2) Monoclinic	293(2) Monoclinic
Space group a/Å	P-1 11.148(2)	<i>P</i> -1 11.209(2)	Pbca 18.179(4)	Pbca 18.426(4)	<i>P</i> -1 11.325(2)	$Pna2_1$ 8.3300(17)	$Pna2_1$ 8.4640(17)	$P2_1/c$ 9.0280(18)	$P2_1/c$ 9.0550(18)	$P2_1/c$ 9.1690(18)
$b/\AA$	11.581(2)	11.577(2)	16.165(3)	16.268(3)	13.660(3)	36.197(7)	36.992(7)	34.587(7)	33.831(7)	34.833(7)
$a/^{\circ}$	18.302(4) 86.36(3)	18.563(4) 88.17(3)	18.696(4) 90	19.144(4) 90	15.052(3) 80.35(3)	9.2190(18) 90	9.3710(19) 90	8.7080(17) 90	8.5990(17) 90	8.7130(17) 90
β/° /°	74.79(3)	75.81(3)	06	06	84.10(3) 80.20(3)	06	06	94.48(3) 00	92.66(3) 00	91.92(3) 00
$V/A^3$	2044.7(9)	2124.8(9)	5494(2)	5739(2)	2283.4(8)	2779.7(10)	2934.1(10)	2710.8(9)	2631.4(9)	2781.2(10)
$Z D_{ m c}/{ m g~cm^{-3}}$	2 1.403	2 1.350	8 1.667	8 1.596	2 1.410	4 1.761	4 1.669	4 1.739	4 1.697	4 1.605
$\mu/\text{mm}^{-1}$	0.429	0.413	0.700	0.671	0.613	1.058	1.002	1.103	1.031	0.976
Data measured Rint	0.0750	0.0630	0.1350	0.1380	0.0530	0.1220	0.1500	0.0812	0.1590	0.0675
Independant data	6417	6715	4585	4841	7138	3922	4097	4461	2802	4425
$wR_2$	0.1023	0.1266	0.0964	0.1261	0.2283	0.1273	0.1688	0.0974	0.1900	0.1399
$R_1 \left[ I > 2\sigma(I) \right]$	0.0512	0.0603	0.0471	0.0632	0.0914	0.0617	0.0814	0.0432	0.0838	0.0625

**Fable 1** Crystal, data collection and refinement parameters determined for **1a**, **1b**, **2a** acetone, **2b**, **2c**.**H**,**O** and **2d**.**H**,**O**. Wavelength (Mo-Ka) = 0.71073 Å

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Table 2Selection of bond lengths (Å) and bond angles (°) for complexes [(TPA)Fe(R-Cat)]X.S.

	1a		11		2a-acetone	5	<u>م</u>	2c·H <sub>2</sub> O	2d H	ŀ0	
T/K	100(2)	293(2)	100(2)	293(2)	173(2)	123(2)	293(2)	123(2)	100(2)	293(2)	
Fe-O1	1.877(2)	1.922(3)	1.850(2)	1.904(4)	1.921(4)	1.854(5)	1.874(9)	1.857(3)	1.876(7)	1.902(4)	
Fe-02	1.915(2)	1.941(3)	1.923(2)	1.938(3)	1.949(4)	1.920(6)	1.952(10)	1.914(3)	1.911(11)	1.927(4)	
Fe-N1	2.018(3)	2.182(4)	1.995(3)	2.153(4)	2.191(5)	1.993(6)	2.138(13)	1.990(3)	1.992(9)	2.129(5)	
Fe-N2	1.964(3)	2.114(4)	1.940(3)	2.071(4)	2.120(5)	1.904(7)	2.111(12)	1.944(3)	1.945(14)	2.062(5)	
Fe-N3	1.974(3)	2.109(4)	1.963(3)	2.087(5)	2.111(6)	1.936(7)	2.120(14)	1.957(3)	1.980(11)	2.086(5)	
Fe-N4	1.994(3)	2.131(4)	1.967(3)	2.092(5)	2.138(6)	1.964(7)	2.108(12)	1.965(3)	1.959(11)	2.087(5)	
C19-01	1.330(4)	1.329(5)	1.339(4)	1.332(6)	1.325(8)	1.343(10)	1.361(18)	1.332(4)	1.300(19)	1.329(7)	
C24-02	1.339(4)	1.337(5)	1.322(4)	1.316(6)	1.330(8)	1.334(9)	1.350(16)	1.327(4)	1.349(14)	1.330(7)	
C19-C24	1.422(5)	1.422(6)	1.422(5)	1.426(7)	1.430(9)	1.427(12)	1.47(2)	1.422(5)	1.39 (2)	1.405(8)	
01-Fe-O2	86.62(10)	84.81(13)	86.70(10)	84.73(15)	84.40(18)	87.0(3)	85.5(5)	87.01(11)	86.2(4)	85.26(18)	
O1-Fe-N1	177.23(11)	172.05(14)	176.93(11)	172.79(16)	169.2(2)	177.3(3)	172.7(4)	178.23(12)	178.7(6)	174.67(18)	
O1-Fe-N2	92.04(11)	91.12(14)	91.49(12)	91.11(17)	90.50(19)	91.9(3)	92.3(5)	92.43(12)	92.9(5)	92.9(2)	
O1-Fe-N3	99.41(11)	105.27(15)	96.80(12)	101.68(19)	99.9(2)	97.5(3)	104.1(5)	97.78(12)	96.0(4)	99.67(19)	
O1-Fe-N4	96.78(11)	100.80(16)	97.84(12)	103.07(18)	106.5(2)	96.6(3)	100.2(4)	96.42(12)	97.4(4)	103.0(2)	
O2-Fe-N1	95.91(11)	102.84(13)	95.70(11)	102.19(17)	105.6(2)	95.1(3)	101.4(4)	94.46(12)	95.1(5)	99.76(19)	
O2-Fe-N2	176.31(11)	174.07(14)	178.19(12)	175.68(18)	172.1(2)	176.4(3)	175.3(4)	177.03(12)	176.3(4)	175.67(18)	
O2-Fe-N3	94.70(11)	96.07(14)	87.22(11)	89.65(16)	91.6(2)	89.5(3)	89.9(5)	88.60(12)	92.5(5)	93.61(19)	
O2-Fe-N4	90.45(11)	92.39(15)	94.65(11)	95.79(16)	93.6(2)	90.4(3)	93.9(4)	92.48(12)	88.4(5)	89.64(17)	
N1-Fe-N2	85.37(11)	81.09(14)	86.12(12)	82.01(18)	79.9(2)	86.1(3)	81.0(5)	86.16(13)	85.8(5)	82.3(2)	
N1-Fe-N3	81.56(12)	76.35(16)	81.42(13)	76.58(18)	76.4(2)	84.3(3)	78.5(5)	83.27(12)	83.7(4)	78.4(2)	
N1-Fe-N4	82.08(12)	76.96(17)	83.91(13)	78.45(18)	77.2(2)	81.7(3)	77.1(5)	82.54(12)	83.0(4)	78.9(2)	
N2-Fe-N3	88.91(12)	89.15(15)	93.06(12)	92.36(18)	95.3(2)	87.3(3)	86.6(5)	88.59(13)	91.2(5)	90.55(19)	
N2-Fe-N4	86.29(11)	84.12(15)	85.53(12)	83.98(17)	82.1(2)	93.1(3)	90.6(4)	90.48(13)	88.1(5)	86.99(18)	
N3-Fe-N4	163.27(12)	153.18(16)	165.32(13)	155.04(19)	153.5(2)	165.9(3)	155.6(6)	165.80(13)	166.6(4)	157.3(2)	

**Table 3** The average metal–ligand bond lengths (Å) for [(TPA)Fe(R-Cat)]X·S complexes, S1 = H<sub>2</sub>O, S2 = acetone with the corresponding values of the  $\chi_M T$  product (cm<sup>3</sup> mol<sup>-1</sup> K)

	T/K	γ́ нs	$\chi_{\rm M} T$	⟨Fe−O⟩	$Fe-N_{am}$	$\langle Fe\!-\!N_{im}\rangle$	$\langle Fe-L \rangle$	$\langle C - O \rangle$	$\langle C - C \rangle$	C19–C24	C21–C22
1a	293	0.86	3.823	1.93	2.182(4)	2.12	2.07	1.333	1.39	1.422(6)	1.398(6)
1a	100	0.09	0.794	1.90	2.018(3)	1.98	1.96	1.335	1.39	1.422(5)	1.391(5)
1b	293	0.83	3.699	1.92	2.153(4)	2.08	2.04	1.32	1.39	1.426(7)	1.375(8)
1b	100	0.02	0.530	1.89	1.995(3)	1.96	1.94	1.33	1.39	1.422(5)	1.404(5)
2a acetone	173	1	4.292	1.935	2.191(5)	2.123	2.07	1.33	1.39	1.430(9)	1.394(10)
2b	293	0.80	3.632	1.91	2.138(13)	2.113	2.05	1.356	1.40	1.47(2)	1.36(2)
2b	123	0.03	0.806	1.89	1.993(6)	1.93	1.93	1.339	1.39	1.427(12)	1.415(13)
$2c \cdot H_2O$	123	0.02	0.470	1.89	1.990(3)	1.96	1.94	1.330	1.40	1.422(5)	1.403(5)
2d·H <sub>2</sub> O	293	0.71	3.264	1.91	2.129(5)	2.08	2.03	1.330	1.395	1.405(8)	1.395(9)
$2d \cdot H_2O$	100	0.01	0.480	1.89	1.992(9)	1.96	1.94	1.32	1.39	1.39 (2)	1.431(19)

bond lengths (see Table 3) span over the ranges 1.32-1.36 Å and 1.39-1.40 Å, respectively. These characteristics are comparable to those reported for a number of Fe<sup>III</sup>–catecholate systems.<sup>14</sup> However this analysis shows the existence of some borderline values of  $\langle C-C \rangle$  (for **2b** and **2c**·H<sub>2</sub>**O** samples) and rather high C19–C24 *and* C21–C22 bond length values (1.403-1.427 Å) in the low temperature data (see for example, **2c**·H<sub>2</sub>**O**, **1b** and **2b**). These discrepancies are mainly observed with complexes of group **2**. They might be indicative of a very small contribution of the Fe(II)semiquinonate configuration within the ground state.

# Molecular structures of 1a, 1b, 2b, $2c \cdot H_2O$ and $2d \cdot H_2O$ in the LS form

As shown in Tables 2 and 3, the metal-donor atom bond lengths of the FeN<sub>4</sub>O<sub>2</sub> cores are significantly shortened and the deviation of bond angles to 90 and 180° are reduced when the temperature decreases from room temperature to 123 or 100 K. These observations that reflect the net increase of the ligand field strength associated to the  $(t_{2g})^3(e_g)^2 \leftrightarrow (t_{2g})^5$ conversion of the metal ion,15 are consistent with the magnetic data (vide infra). Indeed, the variation of bond lengths and angles roughly compare with those characterised for ferric spin crossover complexes with similar FeN<sub>4</sub>O<sub>2</sub> coordination core in the LS state.  $^{16\text{--}18}$  Note that the variation of the  $N_4 Fe N_3$ bond angle and the Fe-N1 bond length (N1 =  $N_{amin_s}$ ) are equal or larger than 10° (see for example 2b) and 0.14 Å (2b,  $2d \cdot H_2O$ ) respectively. Consequently, they can be considered as good probes for analysing the spin crossover process. Merkel and coworkers<sup>12</sup> have reported the crystalline structure of [(TPA)Fe(TCC)]ClO<sub>4</sub>·nH<sub>2</sub>O (with n = 0.25) at 170 K. These data which are comparable to those here reported for  $2c \cdot H_2O$ characterise a low-spin metal ion (from the magnetic data, the HS fraction at 170 K is equal to 0.06). The LS Fe<sup>III</sup> catecholate systems are characterised by the following mean values: (Fe- $N_{amine}$  = 1.990–2.018 Å, (Fe– $N_{imine}$ ) = 1.935–1.977 Å, (Fe–  $O\rangle = 1.885-1.896$  Å. If the difference of HS fractions in the temperature range used for the X-ray measurements is taken into account, the variation of the mean metal-donor atom bond length (Fe-L) can be extrapolated for a complete spin crossover process to 0.123 (1b) < 0.128 (1a)  $\sim$  0.129 (2d·H<sub>2</sub>O) < 0.156 Å (2b) (the value determined from optimised geometries of 3a is 0.157 Å).6 These variations span over the range reported for the Schiff base ferric complexes undergoing a spin crossover, (0.12–0.15 Å).<sup>17,18</sup> As it can be noted for **3a**, the variations of the mean metal-donor atom bond lengths observed for 1a and **1b** are associated to a large change of the Fe–N1 (N1 =  $N_{amine}$ ) and Fe-N2 bonds that are located trans to the Fe-O bonds (i.e.:  $\Delta Fe-N1 > \Delta Fe-N2 > \Delta Fe-N3$  and  $\Delta Fe-N4$ ). For **2b**, the change of the bond lengths takes place through very large Fe-N2 and Fe-N3 variations, whereas for 2d·H<sub>2</sub>O, it involves rather small Fe-N1 and Fe-N4 variations.

#### Molecular packing of 1a and 1b at 100 K

The molecular packing of 1b at 100 K consists of pairs of cationic complexes with anions. As shown in Fig. 2, the NO<sub>2</sub> groups are twisted by 40.3 and 39.3° with respect to the catecholate aromatic plane that can be accounted for by the steric effect and the different molecular contacts with aromatic carbon atoms (O4-C8; 3.199, O5-C10; 3.220, O5-C19; 3.301 and O5-C24; 3.218 Å). The non-coplanarity precludes any significant  $\pi$ -stacking interactions between the catecholate rings although they are located in quasi-parallel planes. For 1a, the packing is similar but the cationic complexes are more efficiently separated by the bulky BPh<sub>4</sub><sup>-</sup> anions. The presence of molecular contacts between the NO<sub>2</sub> group and the pyridine rings may contribute to stabilise this NO2 group close to the aromatic plane. The second one is found to be significantly twisted (twist angles 21.7 and  $57.6^{\circ}$ ). As a general feature in the molecular packing of **1b** and 1a, some aromatic rings are found in almost parallel planes but the distances between the ring centroids ( $\delta_g > 4.11$  and 4.27 Å for 1a and 1b, respectively) and the dihedral angles between the planes correspond to very small  $\pi$ -stacking interactions. In contrast, a number of intermolecular contacts are observed in both structures.



Fig. 2 The intermolecular contacts involving the  $NO_2$  groups of 1b at 100 K.

#### Molecular packing of 2a.acetone, 2b and 2d.H2O

The molecular packing of complexes **2b** (shown in Fig. 3 at 123 K) and **2d**·H<sub>2</sub>O consists of layers of anions (including the solvent molecules for the solvated complexes) alternating with layers of cations organised in pairs. This latter is made up of complexes with opposite orientations along their N1–Fe–O1 axis which results in some assembling of the hydrophobic TCC groups of the two complexes and the polar coordination cores with the sheets of anions. Although the different pairs of cations



**Fig. 3** The molecular packing of **2b** at 123 K in the *ab* plane. The displacement ellipsoids are shown at the 50% probability level.

are regularly spaced with almost parallel aromatic rings in the interlayer space, no significant  $\pi$ -stacking interactions can be detected. For example, a weak interaction between the pyridine rings is observed for  $2d \cdot H_2O$  with  $\delta_g = 3.892$  Å and  $a = 4.97^{\circ}$  at 100 K. A moderate hydrogen bonding interaction is identified for  $2d \cdot H_2O$  between the oxygen atoms of the H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> molecules. This interaction, characterised by O6w–O4 distances of 2.849 Å and N5–O4–O6w angles of 122.05°, contributes to stabilise the anionic layer. In the molecular packing of  $2a \cdot acetone$ , the cations [(TPA)Fe(TCC)]<sup>+</sup> are well separated from each other by the bulky BPh<sub>4</sub><sup>-</sup> anions. The most significant  $\pi$ -stacking interaction is found between the two pyridine rings bearing the N4 atom (at 293 K,  $\delta_g = 3.627$  Å and  $a = 0.00^{\circ}$ ).

The molecular packing of  $2c \cdot H_2O$  at 123 K compares with those determined at 293 K for 2b and  $2d \cdot H_2O$ . A moderate hydrogen bonding interaction is observed between  $ClO_4^-$  and the water molecule (Ow–O6 distance of 2.709(7) Å and Ow–O6– Cl5 134.84°, Ow–O4(2–x,1–y,1–z) 2.850(6) Å, O4–Ow–O6 115.1(2) °). A number of intermolecular contacts are observed for 2b, 2d·H<sub>2</sub>O, 2a·acetone and 2c·H<sub>2</sub>O. The relative variation of the unit cell volume is found between 3.9 (1a) and 5.7% ( $2d \cdot H_2O$ ). These values are similar to those reported for ferrous and ferric spin crossover complexes.<sup>15</sup>

## Magnetic properties

In Fig. 4a,b is shown the temperature dependence of the  $\chi_M T$ product ( $\chi_M$  being the molar magnetic susceptibility corrected for the diamagnetic contributions) for solid samples of 1a-d, 2b**d**. S, **4a** and **5a** (S =  $H_2O$  for **2c** and **2d**). In Fig. 4b, the magnetic properties of [(TPA)Fe(Cat)]BPh<sub>4</sub> 3a previously reported<sup>4</sup> are plotted for comparison. The magnetic measurements are superimposable in the cooling and the heating modes and no hysteresis effect is detected. In Table 4 are gathered the  $\chi_M T$  values observed in the high and low temperature limits together with an estimation of the transition temperature  $T_{1/2}$  (corresponding to the half conversion of the metal ions  $\gamma_{\rm HS} = \gamma_{\rm LS} = 0.5$ ) and the residual HS fraction at low temperature.<sup>19</sup> These magnetic data reveal that the compounds of general formula [(TPA)Fe(R-Cat)]X undergo a thermal spin crossover process as a general feature. Indeed, [(TPA)Fe(TCC)]BPh<sub>4</sub> acetone is the only example of a complex existing in the HS state at any temperature. In contrast to the transition curve reported for 3a, those of 1a-d,2b-d. S, 4a and 5a are of continuous type as they spread over a temperature range equal to or larger than 200 K.

The weak cooperative character of the transition curves can be accounted for by the absence of any significant  $\pi$ stacking interactions observed in the molecular packing of the studied compounds. This feature contrasts to the solid state characteristics of **3a** for which strong  $\pi$ -stacking interactions and numerous intermolecular contacts lead to a cooperative transition.<sup>6</sup>

The thermodynamical parameters of the transition process can be estimated from the Slichter and Drickamer equation based on the regular solution model.<sup>20,21</sup> The enthalpy and entropy variations (see Table 4) are found in the range of 5.3–11.2 kJ mol<sup>-1</sup> and 26–51 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. The  $\Delta S$  values exceed the pure electronic contribution Rln(6/2) = 9.13 J mol^{-1} K^{-1} resulting from the difference in the spin degeneracies of the HS and LS states of a ferric complex. In addition, they are in agreement with those previously reported for ferric complexes ( $\Delta S = 16-18$  and 34-41 J mol<sup>-1</sup> K<sup>-1</sup>).<sup>22</sup> As expected for gradual transformations, the interaction parameter  $\Gamma$  is relatively small as it varies between 0 and  $RT_{1/2}$ . We note that this treatment, based on the regular solution model proposed by Slichter and Drickamer, fails to give reasonable thermodynamical parameters (with a non negative value of  $\Gamma$ ) for 1d·H<sub>2</sub>O, 4a and 5a. The absence of structural data for these compounds precludes any analysis of these results.

The transition temperatures increase as  $5a < 3a < 1a < 4a \sim 1c \cdot H_2O < 2b < 1b < 2d \cdot H_2O < 2c \cdot H_2O \sim 1d \cdot H_2O$ . The complexes [(TPA)Fe(R-Cat)]BPh<sub>4</sub> (noted a, as X<sup>-</sup> = BPh<sub>4</sub><sup>-</sup>) with catecholate bearing electron-donating and electron-withdrawing

**Table 4** Experimental  $\chi_M T$  values measured at low and high temperatures. Analysis of these data according to ref. 19. Estimation of the fraction of residual HS species and determination of the thermodynamical parameters ( $T_{1/2}$ ,  $\Delta H/kJ \text{ mol}^{-1}$ ,  $\Gamma/J \text{ mol}^{-1}$  and  $\Delta S/J \text{ mol}^{-1} \text{ K}^{-1}$ ) according to the Slichter and Drickamer method.<sup>20,21</sup>

Compound	T/K	$\chi_{\rm M} T/{\rm cm^3 mol^{-1}} {\rm K}$	$\gamma_{\rm HS}$ at low $T$	T/K	$\chi_{\rm M} T/{ m cm^3 mol^{-1} K}$	$T_{1/2}/K$	$\Delta H/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\gamma/kJ mol^{-1}$	$\Delta S/J \text{ mol}^{-1} \text{ K}^{-1}$
1a	10	0.449	0.02	293	4,188	143	7.2	0.200	51
1b	10	0.465	0.02	350	4.021(3.757)	224	11.2	0.519	50
1c·H <sub>2</sub> O	10	0.580	0.05	300	3.933	172	6.2	0.812	36
1d·H <sub>2</sub> O	10	0.579	0.05	350	3.670(3.164)	257			
2a · acetone	55			300	4.296				
2a	10	3.603		300	4.013				
2b	5	0.698	0.08	300	3.661	204	5.3	0.907	26
2c·H <sub>2</sub> O	5	0.400	0.01	300	3.394	253	9.1	1.434	36
2d·H <sub>2</sub> O	10	0.453	0.02	350	3.734(3.351)	245	9.8	0.907	40
4a -	5	0.634	0.06	300	3.874	168			
5a	5	0.682	0.07	300	3.818	84	_	_	



Fig. 4 (a, b): Temperature dependence of the  $\chi_M T$  product for solid samples of  $1a(\Phi)$ ,  $1b(\Phi)$ ,  $1c \cdot H_2O(\Box)$ ,  $2b(\diamond)$ ,  $2c \cdot H_2O(\Box)$ ,  $2d \cdot H_2O(\Box)$ ,

substituents are characterised either by a spin crossover process or by a HS ground state (2a). The sequence of transition temperatures 4a > 1a > 3a > 5a (for 2a-acetone,  $T_{1/2} = 0$ ) clearly shows that the spin crossover processes are dominated by solid state effects rather than the molecular characteristics. No correlation can be found for example with the Hammett constants ( $\sigma$  (NO<sub>2</sub>)>  $\sigma$  (Cl)>  $\sigma$  (H)>  $\sigma$  (CH<sub>3</sub>)>  $\sigma$  (OCH<sub>3</sub>) corresponding to  $NO_2$  (1), Cl (2), H (3), CH<sub>3</sub> (5) and  $OCH_3$ (4) substituents) which indicate in this order the decrease of the electron-withdrawing character of the R groups and hence some increase of the electronic density of the catecholate ring.<sup>23</sup> Accordingly, this feature contrasts with the analysis of some electronic spectral and electrochemical data collected in solution which confirm the relationship between the low-energy LMCT bands and the Lewis basicity of the catecholate groups.<sup>24,25</sup> One of the unexpected solid state effects can be the twist of the two  $NO_2$  groups characterised in the crystal structure of 1a, that accounts for a very small electron-withdrawing effect. It has been verified from the 293 K powder X-ray diffraction patterns that no common structural feature can be found for the series of compounds [(TPA)Fe(R-Cat)]BPh<sub>4</sub> (see ESI<sup>†</sup>).

In Fig. 5 is plotted the unit cell volume per spin crossover molecule (V/Z) as a function of the transition temperature  $T_{1/2}$ . It shows that the larger the unit cell volume, the lower the  $T_{1/2}$  value. The unit cell volume obviously decreases with the size of the monovalent anion (a  $(BPh_4) > b (PF_6) > c$  $(ClO_4^-) > d(NO_3^-))$ .<sup>26</sup> It turns out that the spin crossover cation undergoes a larger chemical pressure in solids formed with smaller anions.<sup>27</sup> The general tendency shown by these data is an increase of the transition temperatures under the effect of the lattice pressure. Consistently, the compound 2a acetone characterised by a HS ground state contains both the larger spherical anion BPh<sub>4</sub><sup>-</sup> and an acetone molecule which also plays a role of spacer. However, these effects of chemical pressure do not rule out weaker contributions due to the anion or solvent molecules whose subtle effects were first identified in the study of [Co(trpy)<sub>2</sub>]<sup>2+</sup>, [Fe(paptH)<sub>2</sub>]<sup>2+</sup> and [Fe(pic)<sub>3</sub>]<sup>2+</sup>.<sup>28</sup>

To sum up, the molecular electronic effects due to different catecholate substituents cannot account for the magnetic behaviours observed for these complexes in the solid state. The latter are dominated by lattice effects (packing and chemical pressure, arrangement and intermolecular contacts).

#### Mössbauer measurements

Variable temperature <sup>57</sup>Fe Mössbauer spectra were recorded for **2b**, **4a**, **5a**. In Table 5 are provided the least-squares fitting parameters. In Fig. 6 are shown the Mössbauer spectra of **4a** taken at 130 and 78 K. In the studied temperature range, the



**Fig. 5** Plot of the unit cell volume per metal ion  $(V(T)/Z \text{ in } \text{Å}^3)$  as a function of the transition temperature  $T_{1/2}$ . When the crystal structure was solved at two temperatures corresponding to prevailing HS and LS species, the two values of the volume were reported. The dotted line was drawn in order to show the main tendency.

superposition of two distinct quadrupole doublets indicates that the interconversion between the spin states is slow relative to the hyperfine frequencies ( $\approx 10^8$  Hz) associated with the nuclear energy schemes.

The compounds are characterised in the low- and high-temperature phases by specific Mössbauer parameters  $(\Delta E_{\rm Q}(\rm LS) = 1.5-2.0 \text{ mm s}^{-1}; \delta_{\rm IS}(\rm LS) = 0.20-0.27 \text{ mm s}^{-1} \text{ and}$  $\Delta E_{\rm O}({\rm HS}) = 0.4-1.1 \text{ mm s}^{-1}; \delta_{\rm IS}({\rm HS}) = 0.24-0.37 \text{ mm s}^{-1}).$  These data roughly compare to those observed for **3a**,<sup>6</sup> except that the  $\Delta E_{\rm o}({\rm HS})$  and  $\delta^{\rm IS}({\rm HS})$  values are found to be smaller for the complexes with R-substituted catecholate. In addition, the set of  $\Delta E_{\rm o}(\rm LS)$  and  $\delta^{\rm IS}(\rm HS)$  parameters are slightly smaller for this family of catecholate complexes than those reported for ferric complexes of biological interest<sup>29</sup> with [Fe<sup>III</sup>N<sub>4</sub>O<sub>2</sub>] coordination cores (for the LS state,  $\Delta E_Q = 2.0-3.0 \text{ mm s}^{-1}$ ;  $\delta^{IS} = 0.10-0.25 \text{ mm s}^{-1}$  and the HS state,  $\Delta E_Q = 0.5-1.5 \text{ mm s}^{-1}$ ;  $\delta^{IS} =$ 0.40–0.60 mm s<sup>-1</sup>). The observation, that the area fraction in the 130 K spectrum of 4a (Fig. 6) is not fully covered by the fitting, may well be due to a valence tautomerism process<sup>30</sup> or to an extensive quantum mixing between the Fe(III)-catecholate and the Fe(II)-semiquinonate configurations as recently shown for 3a.<sup>6</sup> Indeed, the UV-vis data collected in solution<sup>24</sup> show

Compound	T/K	$\delta^{\rm IS}({\rm LS})/{\rm mm~s^{-1}}$	$\Delta E_{\rm Q}({\rm LS})/{\rm mm~s^{-1}}$	$\delta^{\rm IS}({\rm HS})/{\rm mm~s^{-1}}$	$\Delta E_{\rm Q}({ m HS})/{ m mm~s^{-1}}$	γ́нs
[(TPA)Fe(TCC	)]PF <sub>6</sub> <b>2b</b>					
	293 200 100	 0.20(1) 0.212(2)	1.51(23) 2.019(4)	0.249(34) 0.25(35) —	0.826 0.89(30) —	1 0.77 0
[(TPA)Fe(MeO	Cat)]BPh4	4a				
	130 78	0.267(15) 0.268(15)	1.634(25) 1.618(25)	0.367(22)	0.932(22)	0.43 0
[(TPA)Fe(MeC	at)]BPh <sub>4</sub> 5a	I				
	210 30	0.255(2)	1.764(2)	0.342(16)	1.052(14) —	1 0

**Table 5** Selected <sup>57</sup>Fe Mössbauer fitted parameters of complexes [(TPA)Fe(R-Cat)]X. Isomer shifts are relative to  $\alpha$ -iron. The HS fraction is based on the evaluation of the areas  $A_{\rm HS}$  and  $A_{\rm LS}$  of the HS and LS resonance lines, assuming equal Lamb–Mössbauer factors for the two spin states



Fig. 6 Mössbauer spectra of 4a recorded at 130 and 78 K.

that the charge transfer between the catecholate group and the metal ion of compound 4a, is reinforced by the presence of the electron-donating CH<sub>3</sub>O group in comparison to 3a. These hypotheses should be investigated by using detailed Mössbauer measurements in the presence of a magnetic field and an enriched <sup>57</sup>Fe compound.

## Conclusion

The complexes [(TPA)Fe(R-Cat)]X were synthesised with different anions and catecholate ligands. They form a family of systems exhibiting spin crossover processes in the solid state. The magnetic behaviours, determined from variable temperature magnetic susceptibility measurements, consist of very smooth  $S = 1/2 \leftrightarrow S = 5/2$  transition curves (R-Cat<sup>2-</sup> = DNC<sup>2-</sup> and TCC<sup>2-</sup>) which indicate weak cooperative interactions. Although the electron-donating or electron-withdrawing character of the catechol substituents leads to different Fe<sup>III</sup>  $\leftarrow$  Cat charge transfer interactions and reactivities, it cannot account for the observed shift of the transition temperatures. The analysis of the structural data obtained for some  $\mathrm{Fe}^{\text{\tiny III}}\text{-}\mathrm{TCC}$  and  $\mathrm{Fe}^{\text{\tiny III}}\text{-}$ DNC complexes allowed a correlation between the  $T_{1/2}$  values and the unit cell volume to be shown. This feature means that the relative stabilisation of the LS state is mainly due to the chemical pressure experienced by the complex under the effect of the lattice. From these crystal structures, the characteristics of the dioxolene groups substituted with electron withdrawing groups (Fe<sup>III</sup>–TCC and Fe<sup>III</sup>–DNC complexes) and the FeN<sub>4</sub>O<sub>2</sub> core appear to be closer to those of a ferric catecholate configuration than a quantum mixing between the catecholate and semiquinonate forms observed with the more donating catecholate Cat<sup>2-</sup>.<sup>6</sup> The data recorded at low temperatures show that the changes of metal–ligand bond lengths and bond angles are consistent with the spin crossover process characterised by the magnetic measurements.

It is of interest to note that a spin crossover process due to species with a prevailing Fe<sup>III</sup>Cat character is here identified with the less donating catecholate groups. The results obtained with the more donating catecholate groups should be further analysed and discussed with regard to these ones. Indeed the spin crossover process is also exhibited by a compound described by a strong quantum mixing of the Fe<sup>III</sup>Cat and Fe<sup>IIS</sup>Q configurations and a coupling between spin-crossover and charge transfer, *i.e.* the valence tautomerism cannot be discarded for the more donating catecholate groups.

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