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### Abstract

Reaction of various phenols with benzoyl chloride afforded derivatives of phenyl benzoate that subsequently underwent Fries rearrangement. Obtained 2-hydroxybenzophenone analogues were combined with linear aliphatic triamines which afforded formation of pentadentate Schiff base ligands. Nine new iron(III) complexes of the general formula  $[Fe(L_n)X]$  (where  $L_n$  is dianion of pentadentate Schiff base ligand N,N'-bis((2-hydroxy-5-methylphenyl)phenyl)methylidene-1,5diamino-3-azapentane= $H_2L_1$ ), N,N'-bis((2-hydroxy-3,5-dimethylphenyl)phenyl)methylidene-1,5diamino-3-azapentane=H<sub>2</sub>L<sub>2</sub>), N,N'-bis((2-hydroxy-5-chlorophenyl)phenyl)methylidene-1,5-diamino-3-azapentane= $H_2L_3$ ), N,N'-bis((2-hydroxy-4-methylphenyl)phenyl)methylidene-1,5-diamino-3-N,N'-bis((2-hydroxy-5-bromophenyl)phenyl)methylidene-1,7-diamino-4azapentane= $H_2L_4$ ), azaheptane= $H_2L_5$ ), N,N'-bis((2-hydroxy-5-bromophenyl)phenyl)methylidene-1,7-diamino-4-methyl-4azaheptane= $H_2L_6$  and X is chlorido, azido or isocyanato terminal ligand) have been synthesized and characterized by elemental analyses, IR, and UV-VIS and the crystal structures of all complexes have been determined by X-ray diffraction. Magnetic investigation revealed high spin state behaviour in all reported compounds. DFT calculations and analysis of magnetic functions allowed to extract absolute values of zero field splitting parameters and exchange coupling constants.

*Keywords:* 2-hydroxybenzophenone derivative, Schiff base ligands; Iron(III) complexes; Exchange coupling; DFT; SQUID magnetometry.

### 1. Introduction

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# Spin-crossover (SCO) between the low-spin (LS) and high-spin (HS) state is a phenomenon that occurs in complexes usually with $3d^4$ - $3d^7$ electronic configuration of central atom wherein the spin state transition of the metal centre can be activated by temperature, pressure, light irradiation, magnetic field or their combination.<sup>1-3</sup> Such case of molecular bistability triggered by external stimuli opens the possibility of application in future memory devices,<sup>4</sup> displays<sup>5</sup> or sensors.<sup>6</sup> The SCO is essentially a single molecule phenomenon, however, interactions between switching moieties have direct impact on the shape of thermal or photo-induced LS $\leftrightarrow$ HS transition curves. With respect to this, the interesting SCO behaviour is usually found in the complexes that create intermolecular interactions, such as hydrogen bonding and $\pi$ - $\pi$ stacking within the crystal lattice.<sup>7</sup> This brought a motivation for investigation of compounds with increased potential for H-bonding and/or $\pi$ - $\pi$ stacking interactions and impact of contacts on the magnetochemical behaviour.

When miscellaneous derivatives of salicylaldehyde react with symmetric aliphatic triamines (e.g. N-(2-aminoethyl)ethane-1,2-diamine, N-(3-aminopropyl)propane-1,3-diamine, N-(3-aminopropyl)-N-methylpropane-1,3-diamine), or asymmetric N-(2-aminoethyl)propane-1,3-diamine triamine one arrives to a pentadentate N<sub>3</sub>O<sub>2</sub>-donor Schiff-base ligands. The following complexation with ferric chloride allows the formation of corresponding mononuclear complexes of general formula [Fe(L)Cl]. Thus, the rational design and synthesis of Schiff-base ligands present important steps in the bottom-up synthesis of SCO compounds and series of corresponding [Fe(L)Cl] complexes can be prepared as precursors for further modification of coordination sphere. The bond between iron(III) central atom and terminal chlorido ligands<sup>10</sup>, with N-donor aromatic ligands (i.e. pyridine derivatives),<sup>11</sup> or by metalocyanates.<sup>12</sup> Our group has already shown that the presence of chlorido terminal ligand in [Fe(L)Cl] complexes results always in the HS state behaviour,<sup>11,12</sup> while the corresponding [Fe(L)CN] complexes show LS behaviour.<sup>11,12</sup> However, if the chlorido ligand is replaced by N-donor terminal pseudohalide anions e.g. azide, cyanate, thiocyanate or selenocyanate, the iron(III) coordination centre is then surrounded with N<sub>4</sub>O<sub>2</sub>-donor set supporting the presence of SCO phenomenon.

The number of so far prepared [Fe(L)X] complexes (X=NCS<sup>-</sup>, NCSe<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>) allows us to compare impact of ligand structure on the presence of SCO behaviour.<sup>10</sup> When a Schiff bases were prepared from salicylaldehyde or 3-ethoxysalicylaldehyde and symmetric triamines, appropriate [Fe(L)NCS] complexes revealed pure HS behaviour. <sup>10a,12b,13</sup> Compounds with Schiff bases containing symmetric amines and azide or cyanate terminal ligands have not been reported yet. When 3-methoxysalicylaldehyde, 3-ethoxysalicylaldehyde or 2-acetyl-1-hydroxynaphthalene were reacted with asymmetric N-(2-aminoethyl)propane-1,3-diamine, the HS state was found in the corresponding azido complexes.<sup>10a-d</sup> On the contrary, if the Schiff base ligand of azido iron(III) complexes started

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from 1-hydroxynaphthalene-2-carbaldehyde or 5-bromosalicylaldehyde, the SCO was presente<sup>40b,d</sup>cte Online DOI: 10.1039/C7NJ00617A Similar trend has been noticed in the next example of isocyanato complexes [Fe(L)NCO], where L contained aliphatic part derived from N-(2-aminoethyl)propane-1,3-diamine. If Schiff base ligands contain an aromatic part originated from 3-methoxysalicylaldehyde or 5-chlorosalicylaldehyde, the iron(III) central atom stays in the HS state.<sup>10c,d</sup> On the other hand, if naphthalenic carbaldehyde is used in this sake, the SCO phenomenon does occur in the corresponding [Fe(L)NCO] compound.<sup>10d</sup>

It follows from previous observations that Schiff bases derived from symmetric triamines lead to pure HS behaviour, while asymmetric triamine along with extended aromatic part of Schiff base promotes the occurrence of SCO phenomenon. Therefore, the extension of "conventional" aldehydes to benzophenone analogues seemed to be promising way of rational design of Schiff base ligand. The formal substitution of hydrogen atom of aldehyde group with phenyl or other aromatic unit was motivated by the idea that potentially enhanced  $\pi$ - $\pi$  interactions and cooperativeness can bring about abrupt and hysteretic SCO. Furthermore, Schiff bases derived from the same amine can adopt different configuration and appropriate complexes exhibit different magnetic behaviour, when 2hydroxybenzophenone derivative is used instead of substituted salicylaldehyde.<sup>14</sup> This motivated us to use such extended aromatic ketones with symmetric triamines and pseudohalides.

Despite from plenty of successful modifications discussed above, our assumptions were not fulfilled and only pure HS compounds were obtained. Herein we report on the synthesis of nine iron(III) complexes of general formula [Fe(L<sub>n</sub>)X], where L<sub>n</sub> is a deprotonated pentadentate Schiff base ligand prepared by condensation of derivative of 2-hydroxybenzophenone and aliphatic triamine (where n=1-6, and X refers either to chlorido, azido or isocyanato terminal ligand, see Fig. 1.). All prepared compounds have been characterized by elemental analyses, IR and UV–VIS spectroscopy and the single crystal X-ray diffraction analysis confirmed their expected molecular structure. In addition, the magnetic properties have been measured and interpreted using the spin Hamiltonian approach and DFT calculations.

### 2. Experimental part

### 2.1. Materials and physical measurements

All solvents and chemicals were purchased from commercial sources and used without further purification. Elemental analysis was performed by using Eager 300 (Carlo Erba) elemental analyser. UV-VIS spectra were obtained on a Specord 250 plus, Analytical Jena spectrophotometer. Infrared spectra (ATR technique) were measured on a Magna FT- IR 750, Nicolet spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C spectrum was recorded with a Bruker DPX 500 (500 MHz). Chemical shifts are reported in ppm relative to CDCl<sub>3</sub> as an internal standard.

Data collection and cell refinement of **C1-C9** were made by Stoe StadiVari diffractometer Vising Cle Online Dol:101039/CR100617A Pilatus 300K HPAD detector and microfocus source Xenocs FOX3D with CuKα. The structures were solved by direct or charge-flipping methods using SHELXT,<sup>16</sup> SIR-2011,<sup>17</sup>, or SUPERFLIP<sup>18</sup> and refined by the full-matrix least-squares procedure with SHELXL (version 2016/6).<sup>19</sup> Geometrical analyses were performed with SHELXL. The structures were drawn using the OLEX2 package.<sup>20</sup> Crystal data and conditions of data collection and refinement are reported in Tab. 1 The bispropyleneamine group of **8** and N-methyl-bispropyleneamine group of **9** are disordered in two positions. The occupancy factors of two parts of disordered groups are 0.507(3)/0.493(3) and 0.576(3)/0.424(3) for **8** and **9**, respectively. The crystal structures of **2**, **8** and **9** contain also disordered solvent molecules, which have been modelled using solvent-masking in OLEX2 package. The all constrains and restrains used for refinement of crystals structures are given in CIF file.

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indso	Tab. 1. Crystallog	raphic data for the	e reported compo	unds.						
of W	Compound	C1	C2	С3	C4	C5	C6	C7	C8	С9
rsitv	Empirical formula	$C_{32}H_{31}CIFeN_3O_2$	C34H35ClFeN3O2	C <sub>34</sub> H <sub>35</sub> FeN <sub>6</sub> O <sub>2</sub>	C35H35FeN4O3	$C_{30}H_{25}Cl_2FeN_6O_2$	$C_{31}H_{25}Cl_2FeN_4O_3$	$C_{32}H_{31}FeN_6O_2$	$C_{32}H_{29}Br_2FeN_6O_2$	C33H31Br2FeN6O2
nive	Formula weight	580.91	608.95	615.53	615.52	628.31	628.30	587.48	745.28	759.31
hv I l	Temperature (K)	100(2)	110(2)	110(2)	110(2)	100(2)	100(2)	100(2)	110(2)	110(2)
ded	Wavelength (Å)	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186
vnlos	Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
Do	Space group	P21/n	P-1	P21/n	P21/n	P21/n	P21/n	Pbca	P-1	P-1
017	a (Å)	10.3034(3)	10.9490(3)	10.2617(3)	10.1275(3)	9.6274(3)	9.4543(3)	18.7577(5)	9.8877(2)	10.1152(3)
Aav C	b (Å)	15.3208(4)	11.8076(3)	15.2514(3)	15.4288(4)	15.2106(3)	15.3791(4)	18.8838(6)	12.8918(2)	13.0131(3)
1 00	c (Å)	18.1489(6)	13.3882(3)	19.5057(5)	19.3778(6)	19.5026(7)	19.5339(5)	16.1938(4)	13.8494(2)	13.8985(4)
տ խ	α (°)	90	97.761(2)	90	90	90	90	90	102.1670(10)	101.157(2)
hishe	β(°)	101.693(3)	104.537(2)	105.111(2)	103.679(2)	97.639(3)	95.402(2)	90	97.8370(10)	96.653(2)
Put	γ(°)	90	109.503(2)	90	90	90	90	90	109.2430(10)	110.337(2)
	V (Å <sup>3</sup> )	2805.46(15)	1533.21(7)	2947.19(13)	2942.00(15)	2830.59(15)	2827.59(14)	5736.1(3)	1588.28(5)	1649.33(8)
	Z, $\rho_{calc}$ g.cm <sup>-3</sup>	4, 1.373	2, 1.319	4, 1.387	4, 1.390	4, 1.474	4, 1.476	8, 1.361	2, 1.558	2, 1.529
	Radiation type	Cu-Kα	Cu-Kα	Cu-Kα	Cu-Kα	Cu-K <sub>a</sub>	Cu-K <sub>α</sub>	Cu-K <sub>a</sub>	Cu-Kα	Cu-K <sub>a</sub>
	μ (mm⁻¹)	5.456	5.015	4.442	4.456	6.336	6.350	4.539	7.070	6.819
	F(000)	1212.0	638.0	1292.0	1292.0	1292.0	1292.0	2456.0	750.0	766.0
	2θ Ranges (°)	7.62 to 176.15	7.03 to 142.74	7.46 to 142.38	7.41 to 142.60	7.40 to 143.00	7.33 to 142.71	8.60 to 143.19	6.70 to 142.68	6.62 to 143.03
	Reflections collected	37250	34231	59381	35699	41976	43503	51484	57949	36401
	Data/restrains/p arameters	5286/0/355	5745/0/374	5639/0/392	5477/0/392	5405/0/370	5378/0/370	5512/0/372	5978/483/410	6192/486/427
	Final R indices	$R_1 = 0.0404$	$R_1 = 0.0288$	R <sub>1</sub> = 0.0268,	$R_1 = 0.0258$	$R_1 = 0.0458$	R <sub>1</sub> = 0.0328	R <sub>1</sub> = 0.0307	R <sub>1</sub> = 0.0329	$R_1 = 0.0303$
	[I > 2σ(I)]	wR <sub>2</sub> = 0.1097	wR <sub>2</sub> = 0.0728	wR <sub>2</sub> = 0.0651	wR <sub>2</sub> = 0.0470	wR <sub>2</sub> = 0.1257	wR <sub>2</sub> = 0.0941	wR <sub>2</sub> = 0.0686	wR <sub>2</sub> = 0.08983	wR <sub>2</sub> = 0.0788
	R indices	R <sub>1</sub> = 0.0458	R <sub>1</sub> = 0.0328	R <sub>1</sub> = 0.0338, 2	R <sub>1</sub> = 0.0395	R <sub>1</sub> = 0.0555	R <sub>1</sub> = 0.0362	R <sub>1</sub> = 0.0468	R <sub>1</sub> = 0.0352	R <sub>1</sub> = 0.0348
	(all data)	wR <sub>2</sub> = 0.1126	wR <sub>2</sub> = 0.0738	wR <sub>2</sub> = 0.0671	wR <sub>2</sub> = 0.0481	wR <sub>2</sub> = 0.1347	wR <sub>2</sub> = 0.0984	wR <sub>2</sub> = 0.0717	wR <sub>2</sub> = 0.0908	wR <sub>2</sub> = 0.0801
	S	1.054	0.965	1.007	0.820	1.082	1.077	0.878	1.123	0.959
	CCDC number	1525798	1525799	1525800	1525801	1525802	1525803	1525804	1525805	1525806

All herein reported magnetic measurements were performed on a SQUID magnetometeric Online Del: 10.1039/C/NJ00617A (Quantum Design, model MPMS-XL-7). In all cases, the temperature dependence of magnetization

was recorded at B = 0.1 T as an external magnetic field. The temperature dependence of magnetization and was the same for cooling and heating mode. Gelatine capsules were used as sample containers for the measurement in the temperature range  $1.8 \leftrightarrow 300$  K. The very small diamagnetic contribution of the gelatine capsule and high-temperature sample holder had a negligible contribution to the overall magnetization. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants.<sup>21</sup>

The fitting of the magnetic susceptibility and magnetization was performed with the help of a home-made program.

The DFT calculations of g-factors were carried out using the package ORCA 3.0.3<sup>22</sup> on the geometries obtained from the X-ray analysis. The GGA functional PBE was selected<sup>23</sup> and the scalar relativistic correction was included applying the second order Douglass-Kroll-Hess approach (DKH).<sup>24</sup> The relativistically recontracted Ahlrich's def2-TZVP basis set was employed for all atoms.<sup>25</sup> The chain-of-spheres approximation (RIJCOSX)<sup>26</sup> was set on using an automatically generated auxiliary basis set.

Subsequently, the optimization of the positions of hydrogen atoms was performed for supramolecular dimers using the basis set def2-SVP and the empirical dispersion correction D3BJ.<sup>27</sup> The exchange coupling calculations were carried out using the package ADF 2016<sup>28</sup> on the geometries with optimized hydrogen atoms. The hybrid functional X3LYP was selected<sup>29</sup> and the Slater-type orbital (STO) basis set of TZP quality was employed for the Fe atoms; while for other atoms DZP quality was used.<sup>30</sup> The "small core" option and increased integration quality (level 5 in ADF convention) were set.

### 2.2. Synthesis and spectral properties

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The substituted phenyl benzoates (**3a-e**) were prepared by benzoylation of phenol derivatives (**1a-e**) with benzoyl chloride (**2**) in aqueous solution of sodium hydroxide.<sup>15</sup> The derivatives of 2-hydroxybenzophenone (**4a-e**) were prepared by Fries rearrangement of appropriate phenyl benzoate (**3a-e**) in molten and anhydrous aluminium chloride (Fig S1, top).<sup>15</sup> Herein reported Schiff base ligands  $H_2L_n$  (n=1-6) have been synthesized without isolation, purification or characterisation. *In situ* prepared ligands were reacted with iron(III) chloride in the presence of triethylamine as a base and appropriate sodium salt of counteranion that leaded to complex of general composition [Fe(L<sub>n</sub>)X] (Fig. 1, Fig. S1 bottom).



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Fig. 1 Scheme of syntheses of complexes C1–C9. For C1 (and corresponding ligand  $H_2L_1$ )  $R_1 = R_2 = R_4 = H$ ,  $R_3 = CH_3$ , n = 2, X = Cl; for C2–C4 (and corresponding ligand  $H_2L_2$ )  $R_1 = R_3 = CH_3$ ,  $R_2 = R_4 = H$ , n = 2 and X = Cl (C2),  $N_3$  (C3) or NCO (C4); for C5 and C6 (and corresponding ligand  $H_2L_3$ )  $R_1 = R_2 = R_4 = H$ ,  $R_3 = Cl$ , n = 2 and  $X = N_3$  (C5) or NCO (C6); for C7 (and corresponding ligand  $H_2L_4$ )  $R_1 = R_3 = R_4 = H$ ,  $R_2 = CH_3$ , n = 2 and  $X = N_3$ ; for C8 (and corresponding ligand  $H_2L_5$ )  $R_1 = R_2 = R_4 = H$ ,  $R_3 = Br$ , n = 3 and  $X = N_3$ ; for C9 (and corresponding ligand  $H_2L_6$ )  $R_1 = R_2 = H$ ,  $R_3 = Br$ ,  $R_4 = CH_3$ , n = 3 and  $X = N_3$ .

### General procedure for phenyl benzoates preparation

The Erlenmeyer flask was charged with appropriate derivative of phenol (100 mmol), water (150 mL) and 10 % sodium hydroxide solution (60 mL). Ice (ca. 150 g) was added to the solution and benzoyl chloride (11.6 mL, 100 mmol) was poured in small portions while the reaction mixture was vigorously stirred. The product that solidified upon stirring as off-white solid was filtered off and washed with water (200 mL). Purification of product with activated charcoal and subsequent isothermal crystallization from ethanol afforded products in white polycrystalline powder.

### General procedure for 2-hydroxybenzophenone derivatives preparation

250 ml round-bottom flask was charged with derivative of phenyl benzoate (100 mmol, 1 eq.) and anhydrous aluminium chloride (16.7 g, 125 mmol, 1.25 eq.). The melted reaction mixture was slowly stirred at 160-180 °C for 3 hours, cooled down to room temperature and quenched with ice-cold water (170 mL) and 10 % aqueous solution of hydrochloric acid (85 mL). Dichloromethane (200 mL) was added and mixture was shaken well until it completely dissolved. The solution was transferred to a separatory funnel, aqueous layer was separated from the organic one and extracted two more times (2x200 mL). Combined organic layers were concentrated to ca. 150 mL under reduced pressure, transferred back to separatory funnel and extracted with 2.5 % sodium hydroxide solution (4x250 mL). Combined alkaline water layers were acidified with 10 % sulphuric acid (pH  $\approx$ 1, ca 300 mL). When the product that precipitates as yellow crystalline solid, it was filtered off and dried in the air. On the other hand, if product separates as yellow oil, it was extracted from water layer with dichloromethane (3x500 mL). Combined organic layers were dried with anhydrous magnesium sulphate and concentrated on rotary evaporator to dryness. The yellow oil or solid of product was

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dissolved in methanol, purified with activated charcoal and the solution was set for isothermalce Online DOI: 10.1039/C/NJ00617A crystallization that afforded product as yellow polycrystalline powder

### Syntheses and spectral properties of complexes

**C1** ([Fe(L<sub>1</sub>)Cl]): 4a (0.849 g, 4.0 mmol, 2 eq.) was combined with solution of N-(2-aminoethyl)ethane-1,2-diamine (0.206 g, 2 mmol, 1 eq.) in methanol:acetonitrile mixture (1:1 v/v, 25 mL) in Erlenmeyer flask. The reaction mixture was refluxed for 45 minutes. In the second step, a solution of anhydrous iron(III) chloride (0.324 g, 2.0 mmol, 1 eq.) in methanol:acetonitrile mixture (1:1 v/v, 25 mL) and triethylamine (0.405 g, 4 mmol, 2 eq.) were added and the resulting mixture was refluxed for another 45 minutes. The solution was filtered and set for controlled crystallisation at laboratory temperature. Single crystals suitable for X-Ray diffraction were collected after few days. Yield 55 %. <u>FT–IR</u> (ATR,  $\tilde{v}_{max}$ /cm<sup>-1</sup>): 3121 (w, N-H), 2936 (w, C-H<sub>alif</sub>), 2899 (w, C-H<sub>alif</sub>), 1608 (s, C=N). UV-VIS (nujol,  $\lambda_{max}$ /nm): 515, 464, 333, 247. Elemental analysis for C<sub>32</sub>H<sub>31</sub>ClFeN<sub>3</sub>O<sub>2</sub> (580.91 g.mol<sup>-1</sup>): Found % (Calc. %): C 65.70 (66.16), H 5.53 (5.38), N 7.20 (7.23).

**C2** ([Fe(L<sub>2</sub>)Cl]): Complex **C2** was prepared in the same manner as **C1**, however, **4b** (0.905 g, 4.0 mmol, 2 eq.) was used instead of **4a**. Yield 57 %. <u>FT–IR</u> (ATR,  $\tilde{v}_{max}/cm^{-1}$ ): 3137 (w, N-H), 2932 (w, C-H<sub>alif</sub>), 2912 (w, C-H<sub>alif</sub>), 1607 (s, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 541, 472, 334, 246. Elemental analysis for C<sub>34</sub>H<sub>35</sub>ClFeN<sub>3</sub>O<sub>2</sub> (608.95 g.mol<sup>-1</sup>): Found % (Calc %): C 67.12 (67.06), H 6.05 (5.79), N 7.85 (6.90).

**C3** ([Fe(L<sub>2</sub>)N<sub>3</sub>]): Preparation of complex **C3** departed in the same manner as **C1**, however, starting with **4b** (0.905 g, 4.0 mmol, 2 eq.) instead of **4a**. After addition of triethylamine, the reaction mixture was stirred for another 15 min and sodium azide NaN<sub>3</sub> (0.300 g, 4.6 mmol, 2.3 eq.) was added. The final solution was refluxed for 45 minutes and filtered. Single crystals suitable for X-Ray diffraction were collected after few days of controlled crystallisation at laboratory temperature. Yield 60 %. <u>FT–IR</u> (ATR,  $\tilde{v}_{max}$ /cm<sup>-1</sup>): 3154 (w, N-H), 2943 (w, C-H<sub>alif</sub>), 2915 (w, C-H<sub>alif</sub>), 2900 (w, C-H<sub>alif</sub>), 2052 (s, N<sub>3</sub>), 1607(s, C=N). UV-VIS (nujol,  $\lambda_{max}$ /nm): 521, 443, 326, 252. Elemental analysis for C<sub>34</sub>H<sub>35</sub>FeN<sub>6</sub>O<sub>2</sub> (615.53 g.mol<sup>-1</sup>): Found % (Calc %): C 66.90 (66.34), H 5.88 (5.73), N 13.79(13.65).

**C4** ([Fe(L<sub>2</sub>)NCO]): Complex C4 was prepared in the same manner as C1, however, starting with 4b (0.905 g, 4.0 mmol, 2 eq.) instead of 4a and sodium cyanate NaNCO (0.300 g, 4.6 mmol, 2.3 eq.) was used instead of sodium azide. Yield 64 %. <u>FT–IR</u> (ATR,  $\tilde{v}_{max}/cm^{-1}$ ): 3184 (w, N-H), 2936 (w, C-H<sub>alif</sub>), 2899 (w, C-H<sub>alif</sub>), 2193 (s, NCO), 1607(s, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 522, 471, 337, 251. Elemental analysis for C<sub>35</sub>H<sub>35</sub>FeN<sub>4</sub>O<sub>3</sub> (615.52 g.mol<sup>-1</sup>): Found % (Calc %): C 67.51 (68.30), H 5.75 (5.73), N 9.05 (9.10).

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**C5** ([Fe(L<sub>3</sub>)N<sub>3</sub>]): Complex **C5** was prepared in the same manner as **C3**, however, starting with the same manner as **C3**,

**C6** ([Fe(L<sub>3</sub>)NCO]): Complex C6 was prepared in the same manner as C4, however, 4c (0.931 g, 4.0 mmol, 2 eq.) was used instead of 4b. Yield 58 %. <u>FT-IR</u> (ATR,  $\tilde{v}_{max}/cm^{-1}$ ): 3121 (w, N-H), 2936 (w, C-H<sub>alif</sub>), 2903 (w, C-H<sub>alif</sub>), 2185 (s, NCO), 1606(s, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 503, 457, 341, 246. Elemental analysis for C<sub>31</sub>H<sub>25</sub>Cl<sub>2</sub>FeN<sub>4</sub>O<sub>3</sub> (628.30 g.mol<sup>-1</sup>): Found % (Calc %): C 58.90 (59.26), H 3.99 (4.01), N 8.74 (8.92).

**C7** ([Fe(L<sub>4</sub>)N<sub>3</sub>]): Complex **C7** was prepared in the same manner as **C3**, however, starting with **4d** (0.849 g, 4.0 mmol, 2 eq.) instead of **4b**. Yield 40 %. <u>FT–IR</u> (ATR,  $\tilde{\nu}_{max}/cm^{-1}$ ): 3244 (w, N-H), 3051 (w, C-H<sub>a</sub>), 2936 (w, C-H<sub>alif</sub>), 2903 (w, C-H<sub>alif</sub>), 2051 (s, N<sub>3</sub>), 1600(s, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 505, 436, 332, 247. Elemental analysis for C<sub>32</sub>H<sub>31</sub>FeN<sub>6</sub>O<sub>2</sub> (587.48 g.mol<sup>-1</sup>): Found % (Calc %): C 65.11 (65.42), H 5.45 (5.32), N 14.40 (14.31).

**C8** ([Fe(L<sub>5</sub>)N<sub>3</sub>]): Complex **C8** was prepared in the same manner as **C3**, however, starting with **4e** (1.109 g, 4.0 mmol, 2 eq.) instead of **4b** and N-(3-aminopropyl)propane-1,3-diamine (0.262 g, 2.0 mmol, 1 eq.) was used instead of N-(2-aminoethyl)ethane-1,2-diamine. Yield 52 %. <u>FT-IR</u> (ATR,  $\tilde{v}_{max}/cm^{-1}$ ): 3256 (w, N-H), 3059 (w, C-H<sub>ar</sub>), 2953 (w, C-H<sub>alif</sub>), 2866 (w, C-H<sub>alif</sub>), 2046 (s, N<sub>3</sub>), 1578(sh, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 505, 454, 321, 245. Elemental analysis for C<sub>32</sub>H<sub>29</sub>Br<sub>2</sub>FeN<sub>6</sub>O<sub>2</sub> (745.28 g.mol<sup>-1</sup>): Found % (Calc %): C 51.50 (51.57), H 3.92 (4.09), N 11.28 (11.63).

**C9** ([Fe(L<sub>6</sub>)N<sub>3</sub>]): Complex **C9** was prepared in the same manner as **C3**, however, starting with **4e** (1.109 g, 4.0 mmol, 2 eq.) instead of **4b** and N,N-di-(3-aminopropyl)-N-methyl-amine (0.291 g, 2.0 mmol, 1 eq.) was used instead of N-(2-aminoethyl)ethane-1,2-diamine. Yield 56 %. <u>FT-IR</u> (ATR,  $\tilde{v}_{max}/cm^{-1}$ ): 3059 (w, C-H<sub>ar</sub>), 2957 (w, C-H<sub>alif</sub>), 2928 (w, C-H<sub>alif</sub>), 2883 (w, C-H<sub>alif</sub>), 2043 (s, N<sub>3</sub>), 1601 (s, C=N). UV-VIS (nujol,  $\lambda_{max}/nm$ ): 513, 456, 338, 244. Elemental analysis for C<sub>33</sub>H<sub>31</sub>Br<sub>2</sub>FeN<sub>6</sub>O<sub>2</sub> (759.31 g.mol<sup>-1</sup>): Found % (Calc %): C 51.86 (52.20), H 4.22 (4.12), N 11.64 (11.07).

### 3. Results and discussion

### 3.1. Syntheses and spectral characterisation

The synthesis of Schiff base ligands consisted of three steps. At first, the corresponding derivative of phenol (**1a-e**) reacted with benzoyl chloride (**2**) in sodium hydroxide solution at lowered

temperature. Substituted analogues of phenyl benzoate (3a-e) precipitated as off-white solid vertice online isothermal crystallization from ethanol afforded pure products in the reasonable yield (72-85 %). In the next, **3a-e** were combined with powdered anhydrous aluminium chloride, the reaction mixture was melted upon the heating which afforded formation of 2-hydroxybenzophenone derivatives (4ae) by Fries rearrangement. Products 4a-e were isolated by extraction with sodium hydroxide solution and after the neutralisation they were isothermally crystallized from methanol as yellow solids and the yields varied between 40-91 %. Schiff base ligands  $H_2L_1-H_2L_6$  were prepared via the condensation of 2-hydroxy-5-methylbenzophenone (4a,  $H_2L_1$ ), 2-hydroxy-3,5-dimethylbenzophenone (4b,  $H_2L_2$ ), 5chloro-2-hydroxybenzophenone (4c, H<sub>2</sub>L<sub>3</sub>), 2-hydroxy-4-methylbenzophenone (4d, H<sub>2</sub>L<sub>4</sub>) or 5-bromo-2-hydroxybenzophenone (4e,  $H_2L_5$ ,  $H_2L_6$ ) with 1,5-diamino-3-azapentane ( $H_2L_n$ , n=1-4), 1,7-diamino-4azaheptane  $(H_2L_5)$  or 1,7-diamino-4-methyl-4-azaheptane  $(H_2L_6)$  in mixture of methanol and acetonitrile (1:1, v/v). The yellow solutions of ligands were prepared in situ and used for the further complexation without any purification and characterisation. Complexes C1-C9 of general formula [Fe(L<sub>n</sub>)X] (where n=1 for C1, n=2 for C2-C4, n=3 for C5, C6, n=4 for C7, n=5 for C8 and n=6 for C9) were prepared by complexation of Schiff bases with anhydrous iron(III) chloride in the presence of triethyl amine as a base. In the case of C3-C9, chloride ligand anion was exchanged either with sodium azide (C3, C5, C7-C9) or sodium cyanate (C4, C6). The dark violet crystals suitable for the diffraction analysis were obtained after several days of controlled evaporation of solution at laboratory temperature.

Newly prepared organic and coordination compounds were characterised by FTIR spectroscopy (see supporting information Fig. S2-S4). In the case of **3a-e**, vibrational bands of hydrogen atoms attached to benzene ring Ar-H can be found in range 3072-3006 cm<sup>-1</sup>. Vibrational bands of aliphatic C-H bonds are observed in range 2917-2924 cm<sup>-1</sup> in case of methylated esters **3a**, **3b**, and **3d**. One can also observe peaks of C=O bond from ester groups at 1724, 1727, 1731, 1730 and 1728 cm<sup>-1</sup> for **3a-e** respectively. Infrared spectra of 4a-e (see supporting information Fig. S4-S6) show vibrational bands of Ar-H in the range 3070-3033 cm<sup>-1</sup>. Presence of methyl groups in 4a, 4b, and 4d leads to observation of C-H bands in almost the same range 2917-2914 cm<sup>-1</sup> as for the corresponding benzoates. Vibrational bands of C=O group of benzophenone unit are observed at 1626, 1614, 1623, 1622 and 1620 cm<sup>-1</sup> for **4a-e**, respectively. N-H vibrational modes located in interval 3256-3117 cm<sup>-1</sup> are identified for complexes C1-C9 (see supporting information Fig. S7-S11). Peaks of aromatic C-H vibrations are observed at 3051, 3059 and 3059 cm<sup>-1</sup> for **C7**, **C8** and **C9**, respectively, while in other complexes these bands are combined with vibrations of N-H and aliphatic C-H groups. One can also find symmetric and asymmetric vibrations of aliphatic C-H bonds in the ranges 2928-2957 cm<sup>-1</sup> and 2866-2912 cm<sup>-1</sup>, respectively. Peaks corresponding to NCO terminal ligand are located at 2193 and 2185 cm<sup>-1</sup> for **C4** and **C6**, respectively. On the other hand, bands that can be assigned to azido

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terminal ligand are found at 2052, 2052, 2051, 2046 and 2043 cm<sup>-1</sup> in the IR spectra of **C3**, **C5**, **C7**, **WC8** cle Online DOI: 10.1039/C7NJ00617A and **C9**, respectively. Imino -C=N vibrations are found in the spectral region 1600-1615 cm<sup>-1</sup> for **C1-C7** and **C9**, however, in case of complex **C8** this band is combined with a band of skeletal vibrations of aromatic rings and reaches a maximum at 1578 cm<sup>-1</sup>.

The solid state electronic absorption spectra of **3a**-**e** exhibit very similar features (see supporting information Fig. S12, left). One can observe a band at 232-234 nm that belongs to  $\pi \rightarrow \pi^*$  transition with two shoulders in intervals 272-277 nm and 280-284 nm that correspond to another  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  excitations. In case of **4a**-**e** (see supporting information Fig. S12, right) bands at 218-226 nm (blue shift in range 8-15 nm compared to **3a**-**e**) and 259-273 nm (blue shift in range 3-15 nm compared to **3a**-**e**) are observed that belong both to  $\pi \rightarrow \pi^*$  transitions. Another band corresponding to  $n \rightarrow \pi^*$  excitation is located at 339-362 nm (red shift in range 59-80 nm compared to **3a**-**e**). The solid state electronic absorption spectra of **C1-C9** (see supporting information Fig. S13) exhibit four bands: two of them that belong to  $\pi \rightarrow \pi^*$  transitions are found in intervals 244-252 nm and 321-341 nm, the third one is dedicated to a charge transfer appears in 436-472 nm region and band in the visible region at 503-541 nm corresponding to charge transfer bands which obscure forbidden d-d transition bands of iron(III) central atom (<sup>6</sup>A<sub>1g</sub>  $\rightarrow$  <sup>4</sup>T<sub>1g</sub> and <sup>6</sup>A<sub>1g</sub>  $\rightarrow$  <sup>4</sup>T<sub>2g</sub>).

In the <sup>1</sup>H NMR spectra of compounds **3a-e** (see supporting information Fig. S14-S18) hydrogen atoms of benzoyl parts gain comparable values in ranges 8.26-8.18, 7.67-7.58 and 7.57-7.47 ppm for those in ortho, para and meta positions, respectively. The aromatic protons signals of substituted phenyl moiety differ due to the position and nature of substituents. In methylated **3a** two well separated doublets appear in ranges 7.21-7.20 ppm and 7.10-7.08 ppm. In chlorinated analogue **3c**, two multiplets in slightly higher regions 7.42-7.39 ppm and 7.20-7.17 ppm are found. In brominated **3e**, one of the signals is elevated even higher to the region 7.57-7.51 ppm such that it is combined with the signal of protons from benzoyl unit. The other doublet at 7.14-7.11 ppm is detected in **3e**. In unsymmetrically methylated **3d** a triplet at 7.36-7.33 ppm, a doublet at 7.13-7.11 ppm and a multiplet at 7.08-7.05 ppm are observed. The signals are combined into one complex multiplet appearing in lower region between 7.11 and 7.03 ppm in **3b** with two methyl substituents. Moreover, signals of aliphatic methyl groups are found at 2.36 ppm, at 2.36 and 2.22 ppm and at 2.43 ppm in spectra of **3a**, **3b** and **3e**, respectively.

In <sup>1</sup>H NMR spectra of **4a-e** (see supporting information Fig. S19-S23, upper) a singlet appears in region 12.18-11.88 corresponding to OH phenyl group. Signals of benzoyl parts are found in regions 7.77-7.65, 7.64-7.56 and 7.56-7.46 ppm for hydrogen atoms in ortho, para and meta positions, respectively. These signals are slightly lowered compared with **3a-e**. The aromatic protons of substituted phenyl units appear in **4a** at 7.37 ppm as singlet, and at 7.34-7.32 and 7.00-6.98 ppm as doublets. In case of analogous compound **4c** a signal of one proton is combined with a signal from

protons of benzoyl moiety. Two doublets appear in region 7.47-7.44 and 7.05-7.03 ppm and obevice Online values higher than those of **4a**. Spectrum of brominated analogue **4e** exhibits multiplet at 7.77-7.66 ppm with even higher value than **4c**. One of the doublets appears in region 7.59-7.58 ppm that is slightly higher than previous two compounds. The other doublet obeys values in range 7.00-6.98 ppm, comparable with **4a** and **4c**. In spectrum of **4d** one can observe a multiplet in region 7.51-7.46 ppm, a singlet at 6.89 ppm and a doublet at 6.69-6.67 ppm that are the peaks with lowest observed value. In **4b** only one complex multiplet at 7.21-7.20 ppm is observed. Singlets of aliphatic methyl groups gain values lower compared with **3a**, **3b** and **3d** and were found at 2.26 ppm in **4a**, at 2.30 and 2.22 ppm in **4b** and at 2.38 ppm in **4d**.

In <sup>13</sup>C NMR spectra of compounds **3a-e** (see supporting information Fig. S14-S18, bottom) peaks of C=O carbon of ester group appear at 165.6, 165.4, 165.3, 165.5, 165.2 ppm for **3a-e**, respectively. Methyl groups are found at 21.2 ppm in **3a**, at 21.2 and 16.5 ppm in **3b** and at 21.6 ppm in **3d**. The other aromatic carbons are observed in region 151.2-118.9 ppm. Similarly, in <sup>13</sup>C NMR spectra of compounds **4a-e** (see supporting information Fig. S19-S23, bottom) signals of carbon of C=O group are found at 201.9, 202.2, 201, 201.4 and 200.9 ppm for **4a-e**, respectively. Methyl groups exhibit peaks at 20.8 ppm in **4a**, at 20.8 and 15.9 ppm in **4b** and at 22.3 ppm in **4d**. Peaks in the region 163.7-110.6 ppm are assigned to the aromatic carbons of two benzene rings.

### 3.2. Description of crystal structures

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Complexes C1 and C3-C6 crystallize in centrosymmetric monoclinic space group P2<sub>1</sub>/n, C2, C8 and **C9** crystallize in triclinic P-1 space group and complex **C7** in orthorhombic Pbca space group. Within this series of compounds, three isomorphic groups can be recognised: the first includes compounds C1, C3 and C4, the second C5 and C6, and the third one is C8 and C9. Selected crystallographic parameters are listed in Tab. 1. Asymmetric unit in each crystal structure contains one molecule of corresponding complex (Fig. 2 - Fig. 10) and the unit cell contains four asymmetric units in case of monoclinic structures of C1, C3-C6, two asymmetric units for triclinic structures of C2, **C8-C9** and eight asymmetric units in the orthorhombic structure of **C7**. The iron(III) coordination environment contains two imino (N<sub>im</sub>) and one amino (N<sub>am</sub>) nitrogen donor atoms, two oxygen donor atoms and the sixth coordination place is occupied by terminal either chlorido (C1, C2) or nitrogen donor atom ( $N_{ps}$ ) of pseudohalogenido ligand (**C3-C9**). Thus, the coordination chromophore can be expressed as  $\{Fe(N_{im})_2N_{am}O_2Cl\}$  for C1 and C2 and  $\{Fe(N_{im})_2N_{am}N_{DS}O_2\}$  for C3-C9. In agreement with our previous observations,<sup>10a,11a,12b</sup> compounds C1-C7 with short N,N-bis(ethylene)amine aliphatic part of Schiff bases always adopt the facial configuration of three nitrogen and *cis* arrangement of two oxygen donor atoms. In cis-O<sub>2</sub> and fac-N<sub>3</sub> configuration one of N<sub>im</sub> atoms is always in axial position with respect to the terminal ligand and all seven compounds C1-C7 contain Schiff base ligand

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wreathed around the iron(III) central atom in right hand  $\Delta$  configuration (see supporting information of the online DOI: 10.1039/C7NJ00617A Fig. S33). We have also reported number of examples with *cis*-O<sub>2</sub> and *mer*-N<sub>3</sub> configuration where

*N*,*N*-bis(propylene)amine or *N*-methyl-*N*,*N*-bis(propylene)amine aliphatic parts were included in the molecular structure of corresponding Schiff base ligands. However, compounds **C8** and **C9** adopt very scarce *trans*-O<sub>2</sub> and *fac*-N<sub>3</sub> configuration where N<sub>am</sub> donor atom are always in the axial position with respect to the terminal pseudohalide anion.

The HS state is evident from values of iron-nitrogen bond distances which vary in the ranges 2.17-2.35Å (Fe-N<sub>am</sub>) and 2.10-2.22Å (Fe-N<sub>im</sub>) (see Tab. 2). The Fe1-O1 and Fe1-O2 bonds lengths are less sensitive to the spin state variation of central atom and are the shortest one within the coordination chromophore with values in the range 1.88-2.01Å. The axial Fe-Cl bonds of **C1** and **C2** are the longest and weakest with values 2.25Å and 2.33Å, respectively. In the case of **C3-C9** with pseudohalido ligands, Fe-N<sub>ps</sub> bond distances acquire values from range 1.99Å-2.02Å (see Tab. 2) typical for the HS state of central atom<sup>10,12a</sup> and apparently they are independent on the type of N<sub>3</sub><sup>-</sup> and NCO<sup>-</sup> terminal ligand anions.

Coordination polyhedra of reported compounds can be expressed as deformed tetragonal bipyramid (for selected bond angles see Tab. S2).  $\Sigma$  and  $\Theta$  distortion parameters are suitable quantities for the detection of the spin state of central atom and for the recognition between various isomeric configurations of coordination polyhedral.<sup>32</sup> Values of both distortion parameters for **C1-C7** are comparable with values for other similar HS mononuclear complexes with *cis*-O<sub>2</sub>, fac-N<sub>3</sub>,<sup>10a</sup> and for all seven compounds there is possible to observe good correlation between the  $\Sigma$  and  $\Theta$  values (see supporting information Fig. S34). In this series of complexes, the lowest degree of deformation is observed for complex **C7** which contains Schiff base ligand with methyl substituent introduced in the position 4 of benzene ring. Compounds **C8** and **C9** with *trans*-O<sub>2</sub> and mer-N<sub>3</sub> configuration of coordination polyhedral acquire significantly lower values of  $\Sigma$  and  $\Theta$  parameters.

In addition, crystal structures of **C1-C7** contain similar hydrogen bonded interconnection of two neighbouring complex molecules via N<sub>am</sub> and oxygen donor atoms (for supramolecular dimers see Fig S24 and Fig. S25, for whole packing see Fig. S26-Fig. S32) with distances from the range 2.84-3.02Å (Tab. S3). Formation of hydrogen bonded pseudo-dimers allows communication between the paramagnetic centres which results usually in the antiferromagnetic exchange coupling (*vide infra*). The expected  $\pi$ - $\pi$  interactions between aromatic parts of Schiff base ligand were thus suppressed due to the edge to face (T-shaped) mutual orientation of benzene rings of two neighbouring molecules of complex.

	C1	C2	C3	C4	C5
Fe1-O1	1.8775(15)	1.9428(11)	1.9595(10)	1.9605(11)	1.972(2)
Fe1-O2	2.0109(16)	1.8977(11)	1.8987(10)	1.8988(11)	1.907(2)
Fe1-N1 <sub>(im)</sub>	2.1489(19)	2.2177(11)	2.1817(12)	2.1715(13)	2.176(3)
Fe1-N2 <sub>am</sub>	2.349(2)	2.2166(13)	2.1960(12)	2.2093(14)	2.172(3)
Fe1-N3	2.1650(18)	2.1973(13)	2.2016(12)	2.2165(13)	2.193(3)
Fe1-X <sup>a</sup>	2.2460(6)	2.3315(4)	2.0206(13)	2.0078(14)	2.017(3)
Σ /°15	104	93	111	105	104
Θ/°15	226	243	262	244	241
	C6	C7	C8A	C8B	С9
Fe1-01	1.9718(14)	1.9436(12)	1.9610(16)	1.9610(16)	1.9561(15)
Fe1-O2	1.9025(14)	1.90812(12)	1.9389(17)	1.9389(17)	1.9362(16)
Fe1-N1	2.1781(16)	2.1434(14)	2.1066(19)	2.1066(19)	2.1039(19)
Fe1-N2	2.1717(17)	2.1967(15)	2.237(3)	2.237(3)	2.2949(19)
Fe1-N3	2.1999(17)	2.1616(15)	2.1173(19)	2.1173(19)	2.1104(19)
Fe1-X <sup>a</sup>	1.9926(19)	2.0207(15)	2.010(2)	2.010(2)	2.016(2)
Σ/° <sup>15</sup>	97	83	54	54	48
Θ/°15	221	185	68	77	82

Tab. 2. Selected bond lengths and metric parameters of C1-C9

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<sup>a</sup> X is Cl1 for C1 and C2, N4 for C3-C9 respectively

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Fig. 2 Asymmetric unit of complex C1.

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Fig. 3 Asymmetric unit of complex C2.



Fig. 4 Asymmetric unit of complex C3.



Fig. 5 Asymmetric unit of complex C4.





Fig. 6 Asymmetric unit of complex C5.



Fig. 7 Asymmetric unit of complex C6.



Fig. 8 Asymmetric unit of complex **C7**.

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Fig. 9 Asymmetric unit of complex C8.



Fig. 10 Asymmetric unit of complex **C9**.

### 3.3. Magnetic properties

Magnetic behaviour of reported complexes **C1-C9** was investigated in detail. The temperature dependence of magnetic properties is presented as effective magnetic moment and the field dependence as magnetization, both of them in units of Bohr magnetons per centre. In all nine complexes, the effective magnetic moment acquires values about 5.9  $\mu_B$  in the temperature range 50-300K and the molar magnetisation at 2 K and 7 T reaches almost 5  $\mu_B$ . Thus, both functions prove permanent HS state behaviour of **C1-C9**. As discussed above, a supramolecular dimer motif can be found in the structures of **C1-C7** motivating thus a general anisotropic two-centre approach including the magnetic exchange coupling. The postulated spin Hamiltonian reads<sup>21</sup>

$$\hat{H} = -\frac{J}{2}(\vec{S}_1 \cdot \vec{S}_2) + D\hat{S}_{1z}^2 + \hat{S}_{1z}\mu_B gB$$
<sup>(1)</sup>

where *J* is the parameter of the isotropic exchange coupling interaction, *D* is the parameter of the axial zero-field splitting, *B* is the absolute value of the magnetic field induction and *g* is the isotropic gyromagnetic factor. The spin operators act on the neighbouring sites of the supramolecular dimer. In cases **C5-C9** the *temperature independent magnetism* was introduced as correction of the slope of the high-temperature part of the curve. Regarding the sign of the axial zero-field splitting the

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magnetic properties of powder samples are inconclusive,<sup>31</sup> especially in the case of small splittingcle Online typical for iron(III) systems, therefore both, positive and negative values, were tested. The alternative model where the small parameter of zero field splitting was replaced by the weak magnetic exchange from surrounding molecules (i.e. molecular field) was tested, too, however, for system C2 where the D parameter gains highest absolute value no better fits can be found with such model (see Fig S36). To keep the consistency we use therefore the Hamiltonian (1) for all systems. The experimental functions with their best fits are displayed in Fig. 11 and Fig. S35 and the resulting optimum parameters along with the relative errors of fitting are presented in the Tables 3 and 4. All parameter values span the range expected for this class of compounds. It is interesting to note, that both sets of D parameters are apparently invariant upon the degree of angular deformation of coordination polyhedral (see supplementary information, Fig. S37). It can be also seen, that the pairs C1-C2, C3-C4 and C5-C6 possess similar values of exchange coupling which correlates with their structural kinship. Moreover, the pairs with stronger antiferromagnetic coupling show also lower dihedral angle Fe-N-O-Fe and within all pairs the shorter is the Fe-Fe distance the stronger is the coupling. (see Tab. 5). This is in accordance with expectation since both mentioned structural parameters enhance the overlap of interacting orbitals along the superexchange pathway.<sup>33</sup>

Tab. 3. Summary of fitted magnetic parameters of systems **C1-C9** and the corresponding relative errors for the alternative with **negative** value of the *D* parameter.

Complex	J(-)/cm⁻¹	g(-)	<i>D</i> (-)/cm <sup>-1</sup>	$\chi$ тім $^{[a]}$	$R(\chi)/R(M)$
C1	-0.491	1.97	-0.57	0.00	0.030/0.021
C2	-0.707	1.94	-0.75	0.00	0.005/0.024
C3	-0.312	1.97	-0.67	0.00	0.016/0.022
C4	-0.312	1.98	-0.53	0.00	0.023/0.027
C5	-0.374	1.98	-0.37	15.94	0.011/0.027
C6	-0.370	1.98	-0.37	15.48	0.005/0.019
С7	-0.224	1.93	-0.56	13.60	0.025/0.014
C8	-	1.90	-0.42	-2.08	0.041/0.030
С9	-	1.95	-0.60	-2.53	0.027/0.053

<sup>[a]</sup> In units of  $10^{-9}$  m<sup>3</sup> mol<sup>-1</sup>.

Tab. 4. Summary of fitted magnetic parameters of systems **C1-C9** and the corresponding relative errors for the alternative with **positive** value of the *D* parameter.

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Complex	J(+)/cm <sup>-1</sup>	g(+)	<i>D</i> (+)/cm⁻¹	<b>X</b> тім <sup>[а]</sup>	$R(\chi)/R(M)$	View Article Online DOI: 10.1039/C7NJ00617A
C1	-0.522	1.96	0.65	0.00	0.022/0.018	
C2	-0.678	1.96	0.95	0.00	0.040/0.025	
С3	-0.371	2.00	0.81	0.00	0.027/0.021	
C4	-0.311	1.98	0.58	0.00	0.001/0.027	
C5	-0.423	2.00	0.33	9.92	0.023/0.035	
C6	-0.390	2.00	0.48	10.16	0.012/0.024	
C7	-0.276	1.96	0.73	4.66	0.003/0.17	
C8	-	1.90	0.44	-0.30	0.041/0.027	
С9	-	1.95	0.70	-4.74	0.032/0.045	

<sup>[a]</sup> In units of 10<sup>-9</sup> m<sup>3</sup> mol<sup>-1</sup>.

Tab. 5. Dihedral angles Fe-N-O-Fe and distances Fe-Fe for systems C1-C7.

Complex	J(-)/cm⁻¹	<i>J</i> (+)/cm <sup>-1</sup>	dihedral angle	d/Å
C1	-0.491	-0.522	40.8°	5.12
C2	-0.707	-0.678	44.3°	5.09
C3	-0.312	-0.371	50.4°	5.04
C4	-0.312	-0.311	51.1°	5.10
C5	-0.374	-0.423	45. 1°	4.99
C6	-0.370	-0.390	47.3°	5.03
С7	-0.224	-0.276	65.7°	4.95





Fig. 11 Magnetic functions for **C1-C9** and their theoretical analysis with D(-) alternative, effective magnetic moment *vs* temperature (left), magnetization *vs* magnetic field (right), magnetic susceptibility *vs* temperature (inset); grey circles: experimental data, solid line: fitted.

### 3.4. DFT calculations

Both, the *g*-factors and exchange coupling parameters can be easily calculated with the help of Density Functional Theory (DFT). The *g*-factors were obtained with the help of coupled-perturbed Kohn-Sham approach.<sup>34</sup> Because of its efficiency and reliability, the GGA functional PBE was chosen in this work. Resulting *g*-factors are collected in Table 6. One can see that the values are very similar each other and in all cases slightly higher compared to those extracted from experimental curves. The exchange coupling parameters can be obtained employing the *Ginsberg-Noodleman approach*.<sup>35</sup> In this work its *weak bonding* variant was used, which regarding to convention from Eq. (1) leads to formula

$$J = \frac{2(E_{BS} - E_{HS})}{S^2}$$
(2)

where  $E_{HS}$  and  $E_{BS}$  is the energy of the high spin state (HS) and the broken-symmetry state (BS), respectively, and *S* is the value of the total spin of the HS state, i.e. *S* = 5. The functional X3LYP was shown to perform well for the H-bonds energy<sup>36</sup> motivating thus its employment in this work. The resulting calculated values of magnetic exchange coupling are collected in Table 6. Very good agreement with the fitted values can be concluded.

The accurate calculation of very small zero-field splitting parameters is still very challenging task<sup>37</sup> which exceeds the scope of present work, therefore we leave the question on their correct sign open.

Complex	J/cm⁻¹	g
C1	-0.361	2.013
C2	-0.649	2.012
С3	-0.490	2.010
C4	-0.373	2.010
C5	-0.471	2.011
C6	-0.447	2.009
C7	-0.324	2.010
C8	-	2.010
С9	-	2.011

Tab. 6. Summary of calculated magnetic parameters of systems C1-C9.

### Conclusions

14.

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### View Article Online DOI: 10.1039/C7NJ00617A

In the summary, nine novel mononuclear iron(III) complexes have been prepared and their structural and magnetic properties were investigated in detail. The target-directed synthesis of Schiff base ligands was focused on the formation of 2-hydroxybenzophenone derivatives capable to condensate with aliphatic triamines and to form pentadentate N<sub>3</sub>O<sub>2</sub>-donor ligands with enhanced degree of aromaticity. Iron(III) complexation with corresponding Schiff bases allowed us to prepare series of mononuclear compounds with terminal chlorido, azido or isocyanato ligand anions. Unfortunately, despite our best efforts to create  $\pi$ - $\pi$  contacts in the supramolecular structures of presented compounds, the H-bonding interconnection between two complex molecules took the place more preferably. Phenyl rings of neighbouring H-bonded pseudodimers are arranged in the face-to-edge fashion to each other making the formation of  $\pi$ - $\pi$  contacts impossible.

All nine complexes exhibit permanent HS state behaviour which was confirmed by structural as well as magnetic investigation. A zero-field splitting with very small absolute value ( $D \approx 0.5 \text{ cm}^{-1}$ ) was found in all complexes, however, its sign cannot be determined with employed methods. A small magnetic exchange coupling was also determined by fitting experimental magnetic functions and its H-bond pathway was confirmed by DFT calculations. Despite its small value a correlation between the coupling and structural motif of related H-bonded pseudodimers was proven.

The presence of SCO phenomenon in the ferric complexes with N<sub>4</sub>O<sub>2</sub>-coordination environment is anticipated.1 However, this is not the case in herein reported compounds. Putting this into perspective, over the fifty similar examples of iron(III) complexes with pentadentate Schiff bases and pseudohalido terminal ligands can be found in the CCDC database. Among them, however, only less than a half exhibits thermally induced SCO effect and it seems that the presence of asymmetric N,N-(ethyl)propylamine aliphatic part of the pentadentate Schiff base ligands is a common structural feature in this family of SCO complexes. To the best of our knowledge, so far reported iron(III) complexes containing either the symmetric aliphatic parts of Schiff base ligands (N,N-bis(propyl)amine or N,N-bis(ethyl)amine moiety) lack the SCO bistability in favour of the HS state behaviour. So it looks, that symmetry of pentadentate Schiff base ligands plays a crucial role and presence of N,N-(ethyl)propylamine aliphatic bridge is necessary requirement for the observation of SCO phenomenon. The synthesis of this type of ligands and iron(III) complexes is an ongoing work in our laboratory.

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