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Impact of the Schiff Base Ligand Substituents on the Solid State CONJO3087E and Solution Properties in Eleven Iron(III) Complexes

Lukáš Pogány,^{*a*} Barbora Brachňaková,^{*a*} Petra Masárová,^{*a*} Ján Moncol,^{*a*} Ján Pavlik,^{*a*} Miroslav Gál,^{*b*} Milan Mazúr,^{*c*} Radovan Herchel,^{*d*} Ivan Nemec,^{*d*} Ivan Šalitroš,^{*a*,d*}

- a) Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Bratislava SK-81237, Slovakia, *e-mail: <u>ivan.salitros@stuba.sk</u>
- b) Department of Inorganic Technology, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava-81237, Slovakia
- c) Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Bratislava SK-81237, Slovakia
- d) Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, 771 46 Olomouc, Czech Republic

Abstract:

Investigations on a series of mononuclear iron(III) Schiff base complexes of general formula [Fe(L)Cl] \cdot S (where L²⁻ is Schiff base ligand anion, S is a solvent molecule) are reported. Derivatives of salicylaldehyde or 2-hydroxy-1-naphtaldehyde were used in combination with a linear either symmetrical or non-symmetrical aliphatic triamines to synthesize the Schiff base ligands and the consecutive reactions with iron(III) chloride afforded various [Fe(L)Cl] complexes. Compounds were characterized by conventional techniques and the crystal structures of all complexes have been determined as well. Structural study has revealed relationship between the spatial arrangement of N₃O₂-donor atom set and length of the aliphatic part of Schiff base ligand. Magnetic and EPR investigation confirmed the high spin state behaviour in all reported compounds and their analysis allowed to quantify the parameters of spin Hamiltonian. Formation of hydrogenbonded pseudodimers with antiferromagnetic exchange coupling was found in the complexes with the shortest aliphatic part of Schiff base ligands. Experimental exchange coupling constants are in good agreement with those obtained from DFT calculation and correlate with the strength of the hydrogen bonds. Cyclic and square wave voltammetry were employed to investigate the redox properties of reported compounds and the experimental redox potentials were compared with those obtained from the DFT calculations.

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Keywords: Iron(III) complexes, Schiff base ligand, Crystal structure, EPR spectroscopy, DFT, Electrochemistry

Introduction

Schiff base (SB) ligands play an important role in the coordination chemistry. The low prices and good availability of the starting chemicals, the simple preparation or variety of coordination possibilities of SB ligands provide many research opportunities in inorganic and organic chemistry. The SB condensation between carbonyls and primary amines results into formation of imines which offer participation in binding with metal ions via nitrogen lone pair electrons. If the starting materials contain additional functional groups with potential donor atoms, the corresponding SBs might become polydentate ligands capable to stabilize metal ions in various oxidation states, controlling the performance of metals in a large variety icte Online of useful catalytic transformations,¹ in microbiological process simulations,² or their luminescence properties.³ Special attention is paid on coordination compounds containing polydentate chelating SB ligands exhibiting magnetic activity. Miscellaneous examples of SB metal complexes were reported to date in which magnetic ordering,⁴ spin crossover properties,⁵ single molecule magnetism⁶ or magnetocaloric effect⁷ were investigated. Multiple denticity and chelating effect of SBs allow the formation of stable coordination compounds⁸ whose magnetic properties can be tuned by the counter anion variation or by goal-directed introduction of substituents on the ligand skeleton.⁹

Iron(III) complexes with salen (N,N'-bis(salicylidene)ethylenediamine) or saldien (N,N'bis(salicylidene)diethylenetriamine) type of ligands present well-established family of coordination compounds in which two or one coordination site, respectively, are still available for other bridging ligands.¹⁰ Such strategy of synthesis might end up with the formation of discrete oligo/polynuclear complex compounds¹¹ or with the coordination polymers with 1D,¹² 2D,¹³ or 3D¹⁴ supramolecular structures. Our group has already explored a wide pallet of ferric complexes with N₃O₂-pentadentate SB ligands H₂L, prepared by the condensation of aliphatic triamines and aromatic 2-hydroxycarbaldehyde derivatives. The iron(III) complexation with H_2L results in to the formation of high spin [Fe(L)Cl] complexes in the first step, and consecutive chlorido ligand replacement allows to prepare mononuclear complexes with pseudohalido terminal ligands [Fe(L)X] ($X^{-} = CN^{-}$, NCS⁻, N₃⁻, NCS⁻, NCO⁻ etc.).¹⁵⁻¹⁷ Depending on the nature of used pseudohalides, one can tune the ligand field of iron(III) central atom and prepare low spin,¹⁵ high spin¹⁶ or spin crossover^{16b,17} compounds. Another synthetic approach involves hydroxido, cyanido, metallocyanido or bipyridine Ndonor bridging ligands capable to merge two or more $\{Fe(L)\}^+$ moieties into the oligomeric/polynuclear complex compounds.¹⁸ Based on our thorough research in this field, there is apparent that substituents introduced on the aromatic ring as well as the length and/or symmetry of the aliphatic triamine part of H_2L pentadentate ligands have a significant impact on the structural and magnetic properties of resulted coordination compounds. For instance, magnetism of six similar heptanuclear mixed-valence complexes $[{(L)Fe^{III}NC}_6-Fe^{II}]Cl_2$ prepared from corresponding ferric precursors [Fe(L)Cl] and potassium ferrocyanide strongly depends on the molecular architecture of used pentadentate ligand H₂L.¹⁹ In general, the structure of $[{(L)Fe^{III}NC}_6-Fe^{II}]^{2+}$ contains six ferric centres bonded with N₃N'O₂ donor atom set supporting the spin crossover event. However, only one heptanuclear analogue exhibits thermally induced low spin \leftrightarrow high spin bistability.^{19a} Another five heptanuclear compounds contain permanently high spin iron(III) centres, but, again the nature of the intramolecular magnetic exchange interaction strongly depends on the type of the used (L)²⁻ ligand.^{19b-e}

In order to understand how the substituent variation in pentadentate SB ligands affect the structural and other physical properties in corresponding iron(III) complexes, we decided to investigate a wide family of mononuclear ferric complexes of [Fe(L)Cl] type. N₃O₂-donor atoms of $(L)^{2}$ -ligand anion can be arranged in four possible configurations (Figure 1) which have a significant impact on the degree of angular distortion of coordination polyhedra. Moreover, particular alignment of N₃O₂-donor atoms can influence the spectral properties, intermolecular interactions, magnetic anisotropy and magnetic exchange coupling. Herein we report on the synthesis, structural, spectral and magnetic properties of numerous mononuclear complexes with pentadentate SB ligands and chlorido terminal ligand. Altogether, we prepared and characterized eleven novel compounds [Fe(L)Cl] where pentadentate SB ligand dianions $(L)^{2-}$ contain variously substituted aromatic rings. Four aliphatic triamines have been chosen for the SB condensation and their different length and symmetry control the configuration of donor atoms, degree of angular distortion of coordination polyhedra or type

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59 60 of the intermolecular interactions. Magnetic and EPR investigation confirmed high spin Vir Addice Online behaviour in all reported compounds. Parameters of magnetic anisotropy and exchange coupling interaction were extracted from experimental data, compared with theoretical ones obtained from DFT calculations and related to the structural features. Electrochemistry investigation in the solution has been performed and experimental as well as calculated redox potential have been related with the corresponding molecular structures of reported complexes.



Figure 1 Four possible configurations of pentadentate SB ligand in octahedral [Fe(L)Cl] coordination compounds. Two phenolic oxygen atoms and three nitrogen donor atoms (two imino and one amino) gain chiral cis-O₂/fac-N₃ when axial position occupied by one of imino nitrogen atom (*a*), cis-O₂/fac-N₃ with axial position occupied by amino nitrogen atom (*b*, so far not reported, thus hypothetical configuration, chiral only if SB ligand is asymmetric), chiral *trans*-O₂/*mer*-N₃ (*c*) and chiral *cis*-O₂/*mer*-N₃ (*d*).

Results and discussion

Synthesis, spectral properties and solid-state structures

The pentadentate ligands H_2L_n (n=1-10) (Figure 2) were synthesized by a SB condensation between corresponding aliphatic triamines and 1-(2-hydroxyphenyl)ethan-1-one, derivatives of the 2-hydroxybenzaldehyde or 2-hydroxynaphthaldehyde, respectively (see Experimental part S1 in electronic supporting information (ESI)). Complexation with iron(III) chloride afforded formation of mononuclear complexes of the general formula $[Fe(L_n)Cl]$ and their single crystals were obtained after the recrystallization of polycrystalline powders from acetone (1, 6, 8, 7c, 9, 10), methanol (2, 3 and 5) or from methanol-acetonitrile mixture (4, 7t) in 67-92 % yield. Infrared spectroscopy supports the structural characterization of 1-10 (see Experimental part S1 in ESI). N-H vibrations were detected in the expected region 3270-3130 cm⁻¹ for complexes containing secondary amino groups (1-8) and those of them which involve amino groups in H-bonding (vide infra) exhibit vibrations shifted below 3210 cm⁻¹. Aromatic and aliphatic C-H vibrations have been detected for all reported complexes in the region 3100-3000 cm⁻¹ and 3000-2800 cm⁻¹, respectively. The most intense vibrational bands are assigned to imino C=N and Car-Car located between 1635–1500 cm⁻¹. In addition, signals of co-crystallized water (8, 10), methanol (4) and acetone (1) solvent molecules have been identified as well. Generally, UV-VIS absorption spectra of the high-spin iron(III) complexes provide information about their electronic structures and in the case of solution spectra of 1-10, three major absorption bands can be distinguished. The *d*-*d* transitions of the high-spin iron(III) complexes with the ground state ${}^{6}A_{1}$ are banned by formal spin and Laporte rule and often overlapped by intense metal-to-ligand (MLCT) charge transfer bands in the visible light region (\approx 500 nm). The next two bands are located in the UV region and most probably present intraligand $n \rightarrow \pi^*$ (≈ 300 nm) and $\pi \rightarrow \pi^*$ (≈ 230 nm) electronic transitions.

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Figure 2 Molecular structures of ligands H_2L_n which are used for the preparation of complexes 1-10. Ligands and compounds prepared from DET amine are in blue, PET in red and DPT or DPTM in black colour.

Molecular structures of reported complexes have been confirmed by single-crystal X-ray diffraction analysis and selected crystallographic parameters are listed in

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Table 1. X-ray diffraction experiments have been carried out at 293 K (for 3, 5(P21/1), (jew) attice Online 8, 9, and 10), 150 K (4, 5(P-1), 7c) and at 100 K (1, 2, 10). Temperature variation did not cause any symmetry change of 10 which maintain the same monoclinic $P2_1/c$ space group at both temperatures, but the position of acetone solvent molecule was not possible to localize at 293 K. However, the room temperature monoclinic structure of $5(P2_1/c)$ has reversibly changed upon the cooling to lower triclinic *P*-1 symmetry (denoted as 5(*P*-1)). Complex 7t crystallizes in non-centrosymmetric orthorhombic space group **Pna2**₁. Crystal structure of four complexes contain co-crystallized lattice solvent molecules (complex 1 $[Fe(L1)Cl] \cdot CH_3COCH_3$; complex 4 - $[Fe(L4)Cl] \cdot CH_3OH$; complex 8 - $[Fe(L8)Cl] \cdot H_2O$; complex 10 - $[Fe(L10)Cl]_2 \cdot 2H_2O \cdot CH_3COCH_3)$ and the other seven crystal structures (2, 3, 5, 6, 7t, 7c, 9) are solvent-free. Nine structures contain one complex molecule [Fe(L_n)Cl] and corresponding lattice solvent molecules in their asymmetric unit (complexes 1 -[Fe(L1)Cl]·CH₃COCH₃, **2** - [Fe(L2)Cl], **3** - [Fe(L3)Cl], **5**(*P***2**₁/c) - [Fe(L5)Cl], **6** - [Fe(L6)Cl], 7t and 7c - [Fe(L7)Cl], 8 - [Fe(L8)Cl] \cdot H₂O and 9 - [Fe(L9)Cl]), while two complex molecules with corresponding solvents in the asymmetric unit have been found in the crystal structure of 4 $({[Fe(L4)Cl]_2 (CH_3OH)_2}),$ 5(P-1) $({[Fe(L5)Cl]_2})$ and 10 $({Fe(L10)Cl}_2 \cdot (H_2O)_2 \cdot CH_3COCH_3).$

In general, all reported compounds exhibit similar structural motif. The iron(III) central atom is coordinated by N₃O₂-donor atoms of the SB ligand and the sixth coordination site is occupied by chlorido terminal ligand (Figure 1). Despite the seemingly uneventful structural variability, the shape and arrangement of {FeN₃O₂Cl} coordination chromophore depends strongly on the gentle variation of the SB ligand molecular design. In particular, the configuration of three nitrogen donor atoms strongly depends on the length of its aliphatic part. Two imino and one amino nitrogen donor atoms are placed in the facial fashion (fac-N₃; Figure 1a) when corresponding SB ligand contains the shortest "N,N-bis(ethylene)amino" aliphatic bridging part (derived from N-(2-aminoethyl)ethane-1,2-diamine, abr. DET; compounds 1-4; Figure 3a and Table S3.1 in ESI). The meridional (mer-N₃) arrangement has been found in the structures 5-10 (Figure 3b-e and Table S3.1 in ESI)) with longer either asymmetric "N,N-ethylene-propyleneamino" (derived from N-(2-aminoethyl)propane-1,3diamine, abbr. PET) or symmetric "N-bis(1,3-propylene)amino" (derived from N-(3aminopropyl)propane-1,3-diamine, abbr. DPT) and "N-methyl-N-bis(1,3-propylene)amino" (derived from N-(3-aminopropyl)-N-methylpropane-1,3-diamine, abbr. DPTM) aliphatic bridges of SB ligands. The trans configuration of phenolato oxygen donor atoms is observed only in the case of compound 7t (trans-O₂/mer-N₃; Figure 3c and Table S3.1 in ESI)), while all other complexes 5-10 show *cis*-O₂/*mer*-N₃ arrangement.

Table S3.1 (see ESI) contains full list of bond distances and angles of coordination polyhedra. Average values of Fe–N^{im} and Fe–N^{am} distances are typical for high spin iron(III) coordination centres and vary in the ranges 2.07–2.16 Å and 2.15–2.30 Å, respectively (Table 2). In accordance with structures of the previously reported complexes,¹⁵⁻¹⁹ the shortest Fe–O and the longest Fe–Cl bond distances of coordination polyhedra obey typical average values in the ranges 1.90–1.97 Å and 2.31 Å – 2.41 Å, respectively (Table 2). Deviation of {FeN₃O₂Cl} coordination chromophore from ideal octahedron can be quantitatively expressed by Σ and Θ structural parameters (Table 2, Table S3.1, Figure S3.1 see ESI).²⁰ Both distortion parameters reflect the angular deviation of *cis* and torsion angles from ideal octahedral geometry of coordination polyhedra, respectively, and their values divide reported compounds into three groups sorted according to the symmetry and the length of aliphatic parts of SB ligands. Complexes 1-4 with the shortest DET aliphatic moiety and *cis*-O₂/*fac*-N₃ configuration exhibit the most distorted coordination polyhedra and their Σ and Θ parameters range in 80°–93° and 181°–231°, respectively. The lowest distortion has been

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noticed for compounds containing DPT and DPTM aliphatic parts where those with the view Article Online $O_2/mer-N_3$ configuration (7c and 8-10) acquire Σ and Θ values in the range 37°-46° (Σ) and 88°–93° (Θ), while compound 7t with the *trans*-O₂/*mer*-N₃ configuration exhibits the highest distortion in this group ($\Sigma = 41^{\circ}$) and ($\Theta = 105^{\circ}$). Σ and Θ intermediate values of 5(*P*-1), $5(P2_1/c)$ and 6 with asymmetric PET derived SB ligands present a crossing region between the DPT/DPTM and DET group of complexes. In addition, linear correlation between Σ and Θ has been observed and one can conclude that the lowest and the highest angular distortion of coordination polyhedron have been noticed for 7c and 3, respectively (Figure S3.1a,c, see ESI). Distortion from reference polyhedron can be expressed also by symmetry measure parameter proposed by Avnir.²¹ Continuous shape measurement and derived symmetry parameters describe a degree of deformation from the shape of ideal polyhedron (Table 2; Table S3.2, see ESI). For instance, symmetry measures $S(O_h)$ and $S(D_{3h})$ introduced by Alvarez et al. can quantify degree of Bailar twisting between regular octahedron (O_h) : $S(O_h)=0$ and trigonal prism $(D_{3h}; S(O_h)=16.737)$, but they are also sensible to further types of distortions or to the spin state variation of central atom.²² All herein reported structures contain coordination polyhedra with shapes close to the regular octahedron, since the range of $S(O_h)$ spans from 0.56 to 2.50 and because the next lowest parameter $S(D_{3h})$ acquires already too high values indicating the major deviation from trigonal prism symmetry. It is also interesting to point out, that variation of temperature in the case of complex 10 or phase transition in complex 5 does not have significant influence on the values of symmetry measure parameters.

The previously reported halido/pseudohalido iron(III) complexes with pentadentate SB ligands exhibited two basic types of supramolecular contacts: 1) centrosymmetric supramolecular dimers held by two N-H...O hydrogen bonds between the amine group hydrogen and phenolate oxygen atoms, which is typical for mononuclear complexes with DET aliphatic bridge of SB ligand.^{16,19e} 2) 1D zig-zag chain substructure held by N-H···X or $N-H\cdots S\cdots X$ contacts (X = halido or atom from pseudohalido terminal ligand, S = solvent molecule). Both types of synthons can be found in the presented series of compounds, too (Figure S3.2, Table S3.3, see ESI). The supramolecular dimerization via N-H \cdots O hydrogen bonds was observed in compounds 1, 2, 3 and 4 ($d(N \cdots O) = 3.245(3)$ for 1, 3.003(2) for 2, 2.906(4) for 3 and 2.846(2) Å for 4; Figure 3a). In 1 the N-H. O hydrogen bonds are bifurcated by another acceptor – coordinated chloride ligand $(d(N \cdots Cl) = 3.474(2) \text{ Å})$. The N-H···Cl chain is observed in 5(P-1) ($d(N \cdots Cl) = 3.248(3)$ and 3.345(3) Å) and this motif survives the phase transition to $5(P2_1/c)$ ($d(N \cdots Cl) = 3.399(18)$ Å). However, the supramolecular chains held by hydrogen bonding are found also in other compounds from the present series. In 6, such chain substructure is formed by the N-H...O hydrogen bonds $(d(N \cdots O) = 3.061(4) \text{ Å})$ between the amine group hydrogen and methoxy oxygen atoms (Figure 3b). In other compounds, the "bridging" function between the complex molecules in chain substructures is held by the solvent molecules. In 8 the supportive role is taken by the water molecule which interconnects two [Fe(L8)Cl] molecules by N-H...O (amine group...water molecule. d(N...O) = 2.960(8) Å) hydrogen bonding and two O-H...O hydrogen bonds (water molecule...phenolate/methoxy oxygen atom. $d(O \cdots O) =$ 2.888(8)/2.970(8) Å). In 10, two lattice water molecules interconnect two [Fe(L10)Cl] molecules but without propagation of this motif to the chain substructure. Both water molecules form bifurcated O-H···O hydrogen bonds with phenolate and methoxy oxygen atoms (acceptors) from adjacent complex molecules and they both are linked together by O-H···O hydrogen bond of moderate strength ($d(O \cdots O) = 2.899(3)$ Å, structure measured at 100 K; Figure 3e). Furthermore, the water molecule which is acceptor of water water hydrogen bond forms relatively long O-H···Cl non-covalent contact with coordinated

chlorido ligand ($d(O \cdots Cl) = 3.522(2)$ Å). The compounds 7c, 7t and 9 do not possession of the significant hydrogen bonds.

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Table 1 Selected crystallographic data for 1 - 10

Compound	1 K	2 K	3 K	4 K	5 K	5 K	6 K
Empirical formula	C29H29ClFeN3O3	C28H27ClFeN3O2	C20H23ClFeN3O4	C19H21Br2ClFeN3O3	C23H29ClFeN3O4	C23H29ClFeN3O4	C ₂₁ H ₂₃ Br ₂ ClFeN ₃ C
Formula weight	558.85	528.82	460.71	590.51	502.79	502.79	632.54
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic Triclinic Monoclinic Triclinic		Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	PĪ	P21/c	PĪ	$P2_1/n$
T [K]	100(1)	100(1)	293(1)	150(1)	293(1)	150(1)	293(1)
a [Å]	16.0970(15)	18.021(3)	10.8572(4)	11.5360(4)	9.9944(2)	9.8897(6)	12.185(1)
b [Å]	7.0994(4)	7.448(5)	10.4047(3)	12.6730(4)	22.3122(5)	10.8138(6)	16.5136(9)
c [Å]	24.040(2)	18.822(2)	18.9387(7)	16.2456(5)	10.9698(2)	22.2761(13)	13.1192(9)
α [°]	90	90	90	94.651(2)	90	90.162(5)	90
β [°]	104.105(7)	96.64(1)	101.464(4)	101.474(3)	107.526(2)	91.327(5)	114.409(9)
γ [°]	90	90	90	106.584(3)	90	107.242(5)	90
V [Å ³]	2664.4(4)	2509.5(18)	2096.75(13)	2206.59(13)	2332.68(9)	2274.5(2)	2403.9(3)
Ζ	4	4	4	4	4	4	4
$\rho_{\rm calc}$ [g.cm ⁻³]	1.393	1.400	1.459	1.778	1.432	1.468	1.748
<i>u</i> [mm ⁻¹]	5.749	0.738	0.878	4.451	6.527	0.816	4.096
Crystal size [mm]	0.22 x 0.08 x 0.06	0.16 x 0.16 x 0.12	0.26 x 0.26 x 0.08	0.45 x 0.30 x 0.23	0.50 x 0.16 x 0.05	0.31 x 0.22 x 0.20	0.40 x 0.14 x 0.06
Data/restrains/parameters	5135/0/336	5108/0/318	4145/0/265	9005/0/527	4496/524/345	9274/433/584	4904/0/294
S	0.834	1.032	1.240	0.940	0.801	0.988	1.019
$R_1 [I \ge 2\sigma(I)]$	0.03863	0.0387	0.0665	0.0290	0.0339	0.0500	0.0478
w R_2 (all data)	0.0882	0.0855	0.1006	0.0596	0.0799	0.1258	0.0922
CCDC	1062787	1062788	1062789	1062791	1507222	1062792	1062793
Compound	7 c K	7t K	8 K	9 K	10	K	
Empirical formula	$C_{20}H_{21}Br_2ClFeN_3O_2$	$C_{20}H_{21}Br_2ClFeN_3O_2$	$C_{20}H_{27}Br_2ClFeN_3O_5$	C29H29ClFeN3O2	$C_{46}H_{54}Br_4Cl_2Fe_2N_6O_8.2H_2C$	$C_{49}H_{65}Br_4Cl_2Fe_2N_6O_{11}$	
Formula weight	586.52	586.52	664.58	542.85	1357.18	1416.31	
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	
Space group	<i>P</i> 2 ₁ /c	$Pna2_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	
<i>T</i> [K]	293(1)	150(1)	293(1)	293(1)	293(1)	100(1)	
a [Å]	7.6216(5)	15.733(5)	12.0070(10)	7.5539(4)	18.8416(3)	18.7064(8)	
b [Å]	12.2155(7)	15.024(5)	16.9410(10)	23.432(1)	27.6317(4)	27.4015(14)	
c [Å]	23.4460(10)	10.024(5)	13.6630(10)	14.244(1)	11.0612(2)	10.9938(3)	
α [°]	90	90	90	90	90	90	

β [°]	98.896(5)	90	112.820(10)	95.577(5)	99.7690(10)	104.105(7)
γ [°]	90	90	90	90	90	90
V [Å ³]	2156.6(2)	2369.4(16)	2561.7(4)	2509.3(2)	5675.24(16)	5675.24(16)
Ζ	4	4	4	4	4	4
$ ho_{ m calc}[m g.cm^{-3}]$	1.806	1.644	1.723	1.437	1.588	1.694
$\mu [{ m mm}^{-1}]$	4.551	4.142	3.850	0.740	3.478	3.559
Crystal size [mm]	0.50 x 0.20 x 0.08	0.45 x 0.22 x 0.11	0.50 x 0.12 x 0.04	0.20 x 0.12 x 0.08	0.55 x 0.46 x 0.11	0.55 x 0.46 x 0.11
Data/restrains/parameters	4404/0/262	2980/1/263	5134/11/308	5042/0/325	11592/0/637	11341/0/673
S	1.022	0.961	1.088	1.138	1.062	1.051
R_1 [I>2 σ (I)]	0.0353	0.0381	0.0939	0.0728	0.0391	0.0221
w R_2 (all data)	0.0832	0.0954	0.1843	0.1045	0.0908	0.0564
CCDC	1063388	1062794	1062795	1062796	1062798	1062799







Figure 3 Molecular structures and hydrogen bonds (black dashed lines) for complex **4** (*a*) with DET aliphatic part of SB ligand; **6** (*b*) with PET type of SB ligand; **7t** (*c*) and **7c** (*d*) polymorphs with DPT type of SB ligands and compound **10** (*e*) with DPTM type of SB ligands. Colour code: orange-Fe; blue-N; red-O; grey-C; white-H; brown-yellow - Br.

Table 2. Summary of selected bond distances and distortion parameters of coordination polyhedra in $1 - 10$
(Fe1 and Fe2 are denoted as two independent metal centres. A and B symbols are used for the characterization
of disordered coordination polyhedra with occupancy)

	1 (100 K)	1(100 K) $2(100 K)$		4 (150 K)		5(P2 ₁ / c) (293 K)	
	I (100 K)	2 (100 K)	Fe1 Fe2		Fe2	(0.35)*	A(0.65)*
(Fe-O)avg	1.95	1.95	1.93	1.94	1.95	1.94	1.94
(Fe-N _{im})avg	2.12	2.14	2.14	2.15	2.15	2.11	2.11
Fe-N _{am}	2.24	2.21	2.23	2.20	2.20	2.21	2.21
Fe-Cl	2.32	2.32	2.33	2.31	2.31	2.40	2.40
Σ^{20} / °	87	80	92	93	92	78	54
Θ ²⁰ / °	211	181	249	231	221	199	199
$S(O_h)$	2.06	1.67	2.73	2.50	2.35	1.	50
$S(D_{3h})$	11.13	11.72	9.08	10.45	10.40	11	.27

	5	(P-1) (150 K	.)	6	7t (150 K)	7c
	Fe1	Fe2A* (0.48)	Fe2B* (0.52)	(293 K)		(293K)
(Fe-O)avg	1.94	1.90	1.97	1.93	1.93	1.95
(Fe-N _{im})avg	2.10	2.07	2.13	2.11	2.06	2.11
Fe-N _{am}	2.20	2.29	2.29	2.19	2.20	2.25
Fe-Cl	2.40	2.39	2.39	2.35	2.40	2.33
Σ^{20} / °	54	84	58	57	41	36
$\Theta^{20/\circ}$	159	213	167	169	105	52
$S(O_h)$	1.34	1.	71	1.47	1.29	0.561
$\mathbf{S}(D_{3h})$	11.62	10	.90	11.75	14.90	16.406

	8 (293 K)	0 (202 IZ)	10 (293 K)		10 (100K)	
		9 (293 K)	Fe1	Fe2	Fe1	Fe2

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(Fe-O)avg	1.95	1.94	1.96	1.95	1.95	1.96
(Fe-Nim)avg	2.10	2.10	2.10	2.10	2.11	2.11
Fe-Nam	2.20	2.30	2.27	2.26	2.25	2.26
Fe-Cl	2.34	2.36	2.33	2.36	2.34	2.36
Σ^{20} / °	40	42	41	37	43	35
Θ ²⁰ / °	86	86	88	92	93	93
$S(O_h)$	0.73	0.79	0.79	0.79	0.76	0.80
$S(D_{3h})$	15.38	15.31	14.97	14.72	15.22	14.66

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*occupancy factor of disordered structures

Magnetic properties

The temperature and field dependent magnetism of 1-10 was studied in detail. At temperature range above 50 K all eleven complexes possess the value of effective magnetic moment close to 5.9 $\mu_{\rm B}$ per centre and their magnetisation converges to value close to 5.0 $\mu_{\rm B}$ per centre at low temperature and high magnetic field. Such limiting behaviour indicates permanent high spin state with total spin per centre S = 5/2.

As a rule, in octahedral high spin iron(III) complexes a weak zero-field splitting (ZFS) is present.²³ Further, based on the structural analysis (*vide supra*), the oligomeric and polymeric supramolecular motifs can be recognized in each of systems **1-10** which motivate introduction of weak magnetic exchange interactions.²⁴ Weak interactions of polymeric topology can be usually well approximated by a mean-field interaction, called in this context *molecular field*.²⁵ On top of it, magnetic exchange interaction of dimeric topology transmitted through H-bonds can be assumed for systems **1-4**. In this spirit, a spin Hamiltonian normalized to one centre was postulated as follows

$$\hat{H} = \frac{1}{2} \Big(-J(\hat{S}_{1} \cdot \hat{S}_{2}) + D(\hat{S}_{1z}^{2} + \hat{S}_{2z}^{2}) \Big) + \frac{1}{2} \sum_{a=x,y,z} (\hat{S}_{1a} + \hat{S}_{2a}) \Big(\mu_{\rm B} g B_{a} - (zj) \big\langle S_{a} \big\rangle_{T} \Big)$$
(1)

Here J is the parameter of isotropic magnetic exchange interaction between neighbouring centres, D is the parameter of axial ZFS parameter and B_a is the *a*-th component of the vector of magnetic field. The *g*-tensor was considered isotropic and represented thus by only one quantity *g*. The molecular field is quantified by the renormalized parameter (*zj*). The calculated susceptibility is corrected by empirical *temperature independent magnetism*²⁵ as follows

$$\chi_{\rm corr} = \chi_{\rm mol} + \chi_{\rm TIM} \tag{2}$$

For systems 1-4 a decrease of magnetic moment below 4 μ_B (or, equivalently, a maximum at the susceptibility curve) at low temperature is apparent (Figure 4a, Figure S4.1-S4.4), which indicates presence of dominant antiferromagnetic exchange interaction. Less dramatic decrease of magnetic moment for compounds 5-10 (Figure 4b-e, Figure S4.5-S4.11) can be well explained by weak antiferromagnetic molecular field and/or weak ZFS. The apparent deflection of the curve of magnetization vs. magnetic field from the Brillouin-like shape, which is well visible for systems 3, 7t and 9, indicates ZFS with absolute value of *D* parameter higher than 0.5 cm⁻¹. The sign of this parameter cannot be reliably extracted from magnetic functions if its value is lower than ≈ 1.0 cm⁻¹.²⁶

The fitted optimum values of spin Hamiltonian parameters for the alternative with negative ZFS are collected in Table S4.1 and for the alternative with positive value of *D* in Table S4.2 (see ESI) along with the corresponding fitting residuals ($R(\chi)$ and R(M)). The reconstructed

curves for the former alternative are displayed in Figure 4 (compounds 4, 6, $7t_{D}7c_{10}1009(2000)$) and both alternatives are viewed in Figure S4.1-S4.11 for all reported compounds (see ESI). All optimum values of parameters span the range expected for this family of high spin [Fe(L)X] complexes (where X= Cl⁻ or pseudhalido terminal ligands), as is obvious from the Table S4.4 (see ESI) presenting the magnetic parameters observed for the similar reported systems.^{16a}



Figure 4 Magnetic functions for compounds 4 (*a*), 6 (*b*), 7t (*c*), 7c (*d*) and 10 (*e*): effective magnetic moment vs. temperature (left), magnetization vs. magnetic field (right), magnetic susceptibility vs. temperature (inset); grey circles: experimental data, solid line: fitted data for negative D alternative.

As it was shown elsewhere,²⁷ the miscellaneous structural features of coordination polyhedra might influence the magnetic anisotropy of the complex compounds containing the hexacoordinated 3d transition metal ions. In order to bring more light to the evolution of ZFS within the series of reported compounds 1-10, the obtained values of *D* parameters were correlated with the angular distortion parameters Σ and Θ . From all four dependencies (both *D*-negative or positive *D*+ variants vs Σ and Θ , respectively; Figure 5a and Figure S4.12, see ESI) is evident that the lowest absolute values of *D* were found for compounds with asymmetric SB ligands prepared from PET amines (compound 5 and 6) and for View Article Online complexes 2 and 4 with the shortest DET type of ligands. As it was already emphasised (vide supra), those four compounds contain the intermediate (5 and 6) and high degree (2 and 4) of angular distortion in the 1-10, respectively. On the other hand, the highest values of |D| were obtained for next two complexes with DET type of SB ligands (1 and 3) which show high angular distortion as well as for whole group of complexes containing the DPT and DPTM type of SB ligands (7-10) exhibiting the lowest angular distortion. This leads to the conclusion that angular deviation of coordination polyhedra is only one of the several effects which influence the magnetic anisotropy in the hexacoordinated iron(III) complexes.

Magnetic exchange coupling parameters can be easily assessed with the help of density functional theory (DFT) by employing the strategy of *broken symmetry*.²⁸ In this approach the value of parameter J is estimated from comparison of the energy of broken symmetry state $E_{\rm BS}$ and high spin state $E_{\rm HS}$ of a system. Since from the magnetic measurements it was concluded that all couplings are very weak (coupling constants lower than 1.0 cm⁻¹), following variant of the formula was adopted.29

$$J = \frac{2\left(E_{BS} - E_{HS}\right)}{S^2} \tag{3}$$

where S is the value of the total spin of the HS state, i.e. in all studied systems S = 5. The hybrid exchange-correlation functional X3LYP was selected for calculation of energy as it was designed for study of H-bonds and weak interactions³⁰ and has proven its reliability previously.^{16a,31} The resulting calculated values of magnetic exchange coupling are collected in Table S4.3 (see ESI) along with the optimum fitted values. Somehow lower values were obtained from DFT calculation for systems 1 and 4, while excellent mutual agreement with fitted values can be concluded for systems 2 and 3. Both, the calculated and experimental exchange coupling constants J, correlate with the strength of the hydrogen bonds of supramolecular dimers in 1-4 (Figure 5b). Thus, the hypothesis of magnetic exchange interaction transmitted through H-bonds leading to the formation of supramolecular magnetic dimers can be considered legitimate.



Figure 5 Magnetostructural correlation of reported compounds 1-10: (a) Evolution of axial zero-field splitting parameter D (negative alternative) upon the variation of Σ distortion parameter. Datapoints of compounds containing the shortest DET aliphatic part are marked with blue, PET with red and DPT or DPTM with black colour. (b) Correlation of calculated and experimentally obtained exchange coupling constants J with the N \cdots O hydrogen bond distances of complexes 1-4.

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EPR spectroscopy

Figure S5.1 shows the X-band EPR spectra of powder iron(III) complexes 1 - 6 and 8 - 10 recorded at temperature of 293 K and 98 K. It is obvious that no significant differences in the spectral features were found comparing the corresponding EPR spectra recorded at 293 and 98 K, except that the EPR signal intensity slightly increased at 98 K. In addition, at low temperature, the resonance lines in the EPR spectra of samples 1 and 2 are better resolved. Hence, we can describe the EPR spectra obtained at both temperatures jointly.

In the EPR spectra of the complexes **3**, **4**, **6** and **10**, the dominant resonance line is a broad signal down field near the effective g-value of $g_{eff} \approx 4.3$. Comparing to this, spectra of **8** contain the relative less broad, dominant resonance appeared down field near $g_{eff} \approx 6.0$ and in the case of **4**, the additional resonance of much lower intensity down field near $g_{eff} \approx 2.0$ was detected. Unfortunately, in the EPR spectra of sample **5**, the above-mentioned resonances are not very well resolved which is caused by the very broad line width of the individual signals. Finally, in the case of complex **9**, the signal intensity of wide resonance up field near $g_{eff} \approx 2.0$ significantly decreased at 98 K.

Table 3 collects the g_{eff} values of the dominant resonances, which were refined by computer simulation. The g_{eff} values of complexes 3, 4, 6 and 10 (the first group) hit the relatively narrow range of 3.53 - 4.16. Furthermore, the corresponding g_{eff} values were temperature independent (within experimental error).

Table 3 The effective g-factor (g_{eff}) values of the dominant resonance EPR signals obtained for the first (3, 4, 6, 10) and the second (5, 8, 9) group of the complexes. The g_{eff} - values, which were evaluated from the experimental EPR spectra recorded at temperature of 293 K and 98 K, were further refined by computer simulation.

Iron(III) Complexes			The firs	st group		The second group			
Com	piexes	3	4	6	10	5	8	9	
$g_{ m eff}$	at 293 K	3.80(3)	3.53(3)	3.96(3)	4.16(3)	3.30(3)	6.13(3)	3.86(3); 2.11(3)	
	at 98 K	3.81(3)	3.55(3)	3.96(3)	4.16(3)	3.30(3)	6.10(3)	3.85(3); 2.14(3)	

In the case of complex 1 and mainly complex 2, the line shape of the EPR spectra is substantially different than those obtained for the other iron(III) complexes 3 - 10. Therefore, the EPR spectral features are discussed separately. In the EPR spectra of complex 1, the dominant resonance is again a broad signal down field near $g_{\rm eff} \approx 4.3$, but with the addition of a broad shoulder up field near $g_{\rm eff} \approx 6.0$ and a wide resonance up field near $g_{\rm eff} \approx 2.0$. The dominant resonances in the EPR spectra of complex 2 are two broad signals, the first one up field near $g_{\rm eff} \approx 2.0$ at both temperatures, and the second one up field near $g_{\rm eff} \approx 4.3$ at 293 K and down field near $g_{\rm eff} \approx 4.3$ at 98 K. Additionally, the relatively sharp resonance line appeared down field near $g_{\rm eff} \approx 10.0$ at both temperatures. However, such simple analysis does not describe satisfactorily the experimental EPR spectra of complexes 1 and 2. Therefore, the computer simulation of the EPR line shape was performed by the original program "Spin", ³² which was created for the high spin systems (S > 1/2). The following spin Hamiltonian parameter values were obtained from the best computer fit to the experimental EPR spectral line: (i) In the case of complex 1, $g_{eff} = 2.19(3)$ and the axial zero field splitting parameter, D = 0.061(3) cm⁻¹ at 293 K; and $g_{eff} = 2.28(3)$ and D = 0.062(3) cm⁻¹ at 98 K. We note that the calculated D-values are relatively very small. (ii) In the case of complex 2, $g_{\rm eff}$ = 4.33(3) and D = 0.290(3) cm⁻¹ at 293 K; and $g_{eff} = 4.15(3)$ and D = 0.290(3) cm⁻¹ at 98 K. For both complexes, the rhombic zero field splitting parameter (E) was estimated to span the

range 0.001 cm⁻¹ or less. It is clear that, for the given complex, the *D* values were temperature online independent (within experimental error). All the zero field splitting parameters are presented in their absolute values, since the resulting line shape of computed EPR spectrum is almost sign independent.

In Figure S5.2, the EPR spectra of complexes 7c and 7t measured at 293 and 98 K are compared. The resonance lines of the given complex are very similar at both temperatures, except that the better signal intensity was obtained at low temperature. However, the significant differences are seen in the line shape of complex 7c vs. 7t. Using the computer simulation of the line shape, the best fit to the experimental EPR spectra was obtained for the effective g-values as follows: (i) In the case of complexes 7c and 7t, $g_{eff} = 2.01(3)$, at both temperatures. (ii) In the case of complex 7c (for relative narrow, downfield signal of small intensity), $g_{eff} = 4.25(3)$ at 293 K and $g_{eff} = 4.27(3)$ at 98 K. (iii) In the case of complex 7t (for broad downfield signal), $g_{eff} = 4.46(3)$ at 293 K and $g_{eff} = 4.48(3)$ at 98 K.

The small, sharp line that is present in the EPR spectra in the Figures S4.1 and S4.2 (*-marked) at $g_{\text{eff}} \approx 2.00$ and superimposed on the broad resonance lines located in this region, is due to a low concentration of irremovable impurity present on the microwave cavity walls and is not connected with the iron(III) EPR spectra.

It is obvious, that the first derivative X-band EPR spectra of powder complexes 1 - 10 recorded at 293 K and 98 K exhibited the broad resonance signals near the effective g-values of 2.0, 4.3 and 6.4. However, the line shape seen in the EPR spectra of complex 1 and mainly complex 2 is essentially different compared with those of complexes 3 - 10. Additionally, comparing the line shape of the corresponding EPR spectra of complexes 1 - 10, which were recorded at high and low temperature indicates, that no spin-crossover transition ($S = 5/2 \leftrightarrow 1/2$) was detected in the temperature interval from 293 K to 98 K.

In accordance with the literature,³³ all the resonance signals detected in the EPR spectra of powdered complexes 1 - 10 are attributed to the high spin (S = 5/2) magnetically active iron(III) state. The inhomogeneous broad line width could be caused by the combined effect of the *g*- and *D*- strain. The above mentioned effective *g*-factor values and zero field splitting values are in good accordance with those found for the similar high spin iron(III) complexes (S = 5/2) presented in the literature.³⁴

Electrochemistry

The redox behaviour of iron(III) complexes was studied by cyclic and square wave voltammetry in 0.1 M LiCl solution in dry ethanol. Both cyclic voltammetry and square wave voltammetry confirmed a quasi-reversible one-electron transfer reaction which is in good agreement with previous studies.³⁵ The expected direct relationship between both, the electron withdrawing and electron donating character of the individual substituents and its reduction potential, was recorded. Therefore, proceeding from compound 10 to compound 1, the reduction increases in power from $E_{p/2} = -669$ to -830 mV vs. ferrocenium/ferrocene (Fc⁺/Fc) couple (Table 6, column $E_{p/2}$ - $E_{p/2}$ (Fc),Figure S6.1 and Figure S6.3 see ESI). Compounds 6, 7, 8 and 10 containing bromo-substituted benzene rings in the SB ligands show the highest redox potential (from -669 to -732 mV vs. Fc^+/Fc). Apparently, naphthalene rings in 9 might have the similar impact on the redox potential as 5-Br or 6-Br substituents of 6, 7, 8 and 10. Two couples (6-8 and 7-4) with the same substituents introduced on the benzene rings exhibit notable difference in their reduction power which was therefore tentatively attributed to the different length of aliphatic parts of their SB ligands. Thus, the prolongation of aliphatic part from PET to DPT in case of 6 and 8 with 3-methoxy and 6bromo substituted benzenes, or the shortening from DPT to DET in 7 and 4 with 5-bromo substituents decreases the redox potential from -669 mV to -732 mV vs. Fc⁺/Fc in the first

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couple and from -680 mV to -793 mV vs. Fc⁺/Fc in the second couple (Table 4). On the off deficie Online hand, the compounds with DET aliphatic spacer (1-4) are reduced at more negative potentials than those with longer aliphatic substituents introduced in their SB ligands. The most negative redox potential was detected in the case of the compounds 1 and 2 containing the naphthalene aromatic moieties. Thus, if the reduction potentials of compounds 1 with DET aliphatic part on one side, and compounds 10 with DPTM aliphatic part on the second side are compared, the effect of spacer length on the redox properties of the respective compounds seems to be also important. Figure S6.1 suggests a trend in which compounds with shortest DET spacer have more negative $E_{p/2}$ and the complexes with the longest DPT and DPTM moieties show the weakest reduction power.

The redox properties were studied also by DFT method, where the thermodynamic cycle shown in Figure S6.2 (see ESI) was employed. In accord with this Born-Haber cycle, the standard Gibbs free energy of a redox half reaction in solution, ΔG_{solv} , was obtained by calculating the change in free energy of redox reaction in gas phase, ΔG_{g} , and solvation free energies of each of the species, $\Delta G_{solv}(Ox)$ and $\Delta G_{solv}(Red)$, by employing this equation

$$\Delta G_{\text{solv}}^{o} = \Delta G_{g}^{o} + \Delta G_{\text{solv}}^{o} (\text{Red}) - \Delta G_{\text{solv}}^{o} (\text{Ox})$$
(4)

In next step, the reduction potential was calculated with Nernst equation assuming transfer of one electron as

$$E_{\rm Ox/Red}^{\rm o} = -\Delta G_{\rm solv}^{\rm o} / F \tag{5}$$

where F is Faraday constant. With the aim to acquire reliable reduction potential for the iron(III) complexes under study, we used an internal reference system to minimize the error between calculated and experimental values.³⁶ Thus, the ferrocenium/ferrocene (Fc⁺/Fc) redox pair was selected as internal reference, as suggested also by IUPAC for the experimental work.³⁷ The ωB97X-D3 range-separated hybrid GGA functional with empirical dispersion correction³⁸ was chosen, because it provided accurate results for other iron-based complexes.³⁹ The molecular geometries of iron(III) and iron(II) complexes 1-10 were optimized in vacuo followed by calculations of the molecular vibrations. Then, gas-phase zero-point energies, thermal corrections, and entropic corrections were calculated using the standard formulas for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation for T = 298.15 K resulting in the respective Gibbs free energies. The respective solvation Gibbs free energies were calculated with the SMD solvation model⁴⁰ setting solvent to ethanol according to the experimental conditions. The computational results are listed in Table 4 and calculated and experimental redox potentials relative to Fc⁺/Fc redox couple are compared in Figure 6. Sufficiently good linear correlation (except of compounds 2 and 7t) between the calculated and experimental redox potentials was found. Large deviation of 7t from this trend might suggest that compound 7 is present as cis-isomer (see the position of 7c in Figure 6) in ethanol solution. The deviation of the compound 2 from the overall trend can be explained by the fact that this is the only compound within the series, which possess methyl group on imine bond. Since, the computation of the solvation Gibbs free energy is in general problematic, we also computed the electron affinity E_{ea} of the complexes following IUPAC convention as energy required to detach an electron from the singly charged negative ion

$$[\operatorname{Fe}(L^5)\operatorname{Cl}]^-(g) \to [\operatorname{Fe}(L^5)\operatorname{Cl}](g) + e^-$$
(7)

and the results are listed in Table 4 and depicted in Figure 7. Evidently, the electron affinity nicely correlate with the experimental redox potentials, only the value for complex 4 slightly

deviates. Thus, such simplified calculations are also suitable to predict trends in the reduction of the coordination compounds.

Table 4 Calculated Gibbs free energies, electron affinities and redox potentials compared to the experim	ental
redox potentials	

$\Delta G_{ m g}^{ m o}$	$\Delta G_{ m solv}^{ m o}({ m Ox})$	$\Delta G_{\rm solv}^{\rm o}({\rm Red})$	$\Delta G_{ m solv}^{ m o}$	$E^{ m o}_{ m Ox/Red}$	$E^{\rm o}_{\rm Ox/Red} - E^{\rm o}_{\rm Fc^+/Fc}$	$E_{p/2}$ - $E_{p/2}$ (Fc)	E_{ea}
kcal/mol	kcal/mol	kcal/mol	kcal/mol	V	mV	mV	eV
-49.713	-34.346	-71.665	-87.035	3.774	-1478	-830	2.010
-48.199	-33.984	-68.997	-83.214	3.609	-1644	-802	1.903
-47.512	-30.069	-68.454	-85.898	3.725	-1528	-822	1.922
-54.241	-30.011	-63.905	-88.137	3.822	-1431	-793	2.217
-50.315	-31.861	-68.748	-87.204	3.782	-1471	-768	2.037
-57.061	-25.065	-58.433	-90.431	3.922	-1331	-669	2.348
-53.348	-26.860	-58.280	-84.770	3.676	-1577	-680	2.162
-56.350	-26.323	-58.232	-88.262	3.827	-1425	-680	2.306
-52.888	-25.005	-60.517	-88.403	3.834	-1419	-732	2.142
-52.559	-30.074	-65.258	-87.746	3.805	-1448	-726	2.136
-53.770	-25.162	-59.665	-88.275	3.828	-1425	-690	2.186
-166.219	-54.450	-9.353	-121.126	5.253	0	0	7.225
	ΔG_{g}° kcal/mol -49.713 -48.199 -47.512 -54.241 -50.315 -57.061 -53.348 -56.350 -52.888 -52.559 -53.770 -166.219	ΔG_{g}° $\Delta G_{solv}^{\circ}(Ox)$ kcal/molkcal/mol-49.713-34.346-49.713-33.984-47.512-30.069-54.241-30.011-50.315-31.861-57.061-25.065-53.348-26.860-56.350-26.323-52.888-25.005-52.559-30.074-53.770-25.162-166.219-54.450	ΔG_{g}° $\Delta G_{solv}^{\circ}(Ox)$ $\Delta G_{solv}^{\circ}(Red)$ kcal/molkcal/molkcal/mol-49.713-34.346-71.665-48.199-33.984-68.997-47.512-30.069-68.454-54.241-30.011-63.905-50.315-31.861-68.748-57.061-25.065-58.433-53.348-26.860-58.280-56.350-26.323-58.232-52.888-25.005-60.517-52.559-30.074-65.258-53.770-25.162-59.665-166.219-54.450-9.353	ΔG_{g}° $\Delta G_{solv}^{\circ}(Ox)$ $\Delta G_{solv}^{\circ}(Red)$ ΔG_{solv}° kcal/molkcal/molkcal/molkcal/mol-49.713-34.346-71.665-87.035-48.199-33.984-68.997-83.214-47.512-30.069-68.454-85.898-54.241-30.011-63.905-88.137-50.315-31.861-68.748-87.204-57.061-25.065-58.433-90.431-53.348-26.860-58.280-84.770-56.350-26.323-58.232-88.262-52.888-25.005-60.517-88.403-52.559-30.074-65.258-87.746-53.770-25.162-59.665-88.275-166.219-54.450-9.353-121.126	ΔG_{g}° ΔG_{solv}° (Θx) ΔG_{solv}° (\mathbb{Red}) ΔG_{solv}° $E_{Ox/Red}^{\circ}$ kcal/molkcal/molkcal/molkcal/molV-49.713-34.346-71.665-87.0353.774-49.713-34.346-71.665-87.0353.609-47.512-30.069-68.454-85.8983.725-54.241-30.011-63.905-88.1373.822-50.315-31.861-68.748-87.2043.782-57.061-25.065-58.433-90.4313.922-53.348-26.860-58.280-84.7703.676-56.350-26.323-58.232-88.2623.827-52.888-25.005-60.517-88.4033.834-52.559-30.074-65.258-87.7463.805-53.770-25.162-59.665-88.2753.828-166.219-54.450-9.353-121.1265.253	ΔG_{sc}° ΔG_{solv}° (Ox) ΔG_{solv}° (Red) ΔG_{solv}° $E_{Ox/Red}^{\circ}$ $E_{Ox/Red}^{\circ} - E_{Fe+/Fe}^{\circ}$ kcal/molkcal/molkcal/molkcal/molVmV-49.713-34.346-71.665-87.0353.774-1478-48.199-33.984-68.997-83.2143.609-1644-47.512-30.069-68.454-85.8983.725-1528-54.241-30.011-63.905-88.1373.822-1431-50.315-31.861-68.748-87.2043.782-1471-57.061-25.065-58.433-90.4313.922-1331-53.348-26.860-58.280-84.7703.676-1577-56.350-26.323-58.232-88.2623.827-1425-52.888-25.005-60.517-88.4033.834-1419-52.559-30.074-65.258-87.7463.805-1448-53.770-25.162-59.665-88.2753.828-1425-166.219-54.450-9.353-121.1265.2530	ΔG_{g}° ΔG_{solv}° (Red) ΔG_{solv}° $E_{0x/Red}^{\circ}$ $E_{fe/Fe}^{\circ}$ $E_{fp/2}^{\circ}$ $E_{p/2}^{\circ}$ $E_{p/2}^$



Figure 6 The correlation plot calculated vs. experimental relative redox potentials of the respective compounds. The red line corresponds to linear equation y = -922 + 0.694x. Compounds 2 and 7t were excluded from the linear fit.





Figure 7 The correlation plot for calculated electron affinity vs. experimental relative redox potentials of the respective compounds.

Summary

A series of novel iron(III) SB complexes was structurally, spectrally and magnetically characterized. Eleven mononuclear compounds of general formula [Fe(L)Cl] contain pentadentate ligand anion L prepared by SB condensation between miscellaneous derivatives of salicylaldehyde and linear aliphatic triamines. Thus, each central atom is surrounded by N_3O_2Cl donor atom set which supports the high spin state electronic configuration.

Structural investigation revealed interesting impact of the length and symmetry of SB ligands on the stereochemistry of coordination polyhedra. In the line with our previous findings,¹⁵⁻¹⁷ compounds containing the shortest aliphatic bridge derived from DET amine adopt the *cis*- $O_2/mer-N_3$ configuration. Such arrangement of SB ligand donor atoms causes the highest angular distortion of coordination polyhedra among the reported compounds and promote the formation of antiferromagnetically coupled hydrogen bonded pseudodimers within the crystal lattice. It is interesting to note that experimental and DFT calculated magnetic exchange coupling constants are in good agreement to each other.

Compounds with the longer either asymmetric PET or symmetric DPT and DPTM aliphatic bridges introduced on the SB ligand skeleton prefer the *cis*-O₂/*mer*-N₃ arrangement of donor atoms and their angular distortion of coordination polyhedra decreases in the order PET > DPT, DPTM. Complex 7 with DPT type of ligand exists in two isomeric forms adopting either *cis*-O₂/*mer*-N₃ or *trans*-O₂/*mer*-N₃ configuration and complex 5 with PET asymmetric SB ligand exhibits reversible monoclinic-triclinic phase transition upon the temperature variation. Interestingly, neither the isomerism nor phase transition has significant impact on their physical properties.

Magnetic and EPR study confirmed the high spin behaviour of the iron(III) central atoms in all cases, too, with indication of weak zero-field splitting with a small absolute value (|D| < 1 cm⁻¹); however, its sign cannot be determined with the employed methods. The first derivative EPR spectra of powdered complexes **1** - **10** measured at two temperatures confirm the high spin (S = 5/2) magnetically active iron(III) state as well.

Redox properties of reported compounds in the solution are also significantly dependent on the molecular design of SB ligand. One can conclude that reduction power increases with the

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shortening of the aliphatic spacer in order DPT, DPTM < PET < DET and decreases with effect online introduction of bromo substituents on the aromatic part of chelating ligands. Redox potentials were also calculated by DFT method employing the Born-Haber cycle to consider solvation effects which resulted in the good agreement between the experimental and theoretical values.

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A series of novel iron(III)–Schiff base complexes has been prepared and structuraly characterised. The stereochemical, magnetic and redox properties were corelated with the molecular design of the corresponding N_3O_2 -pentadentate Schiff base ligand.