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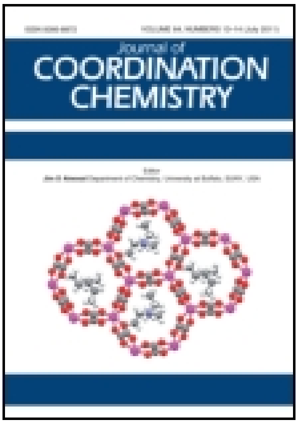

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Crystal structure and magnetic properties of two dinuclear iron(III) complexes with multidentate Schiff-base ligands

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Crystal structure and magnetic properties of two dinuclear iron(III) complexes with multidentate Schiff-base ligands

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Two dinuclear iron(III) compounds, $[Fe_2(HL_1)_2(L_1)_2]\cdot MeOH$ (**1**) and $[Fe_2(\mu\text{-}L_1')_3]$ (**2**) [$L_1 =$ N-(2-hydroxypropyl)(3-methoxysalicylaldimine) and $L_1' =$ 1,2-bis(2-hydroxybenzylidene) hydrazine], have been synthesized and characterized. Structural analysis of **1** shows that the six-coordinate Fe(III)'s are linked by two alkoxo oxygen atoms from two Schiff-base ligands to form a rectangular arrangement of metal ions and oxygen atoms. The distance of these two Fe(III) ions is 3.2122(8) Å. In **2,** three Schiff-base ligands coordinate two Fe(III) ions in a tetradentate mode; each iron is six coordinate with octahedral geometry. The Fe–Fe distance is 3.9304(10) Å. Magnetic susceptibility (2–300 K) indicates an antiferromagnetic interaction between the two oxygen-bridged Fe(III) ions with $J = -13.6\,\text{cm}^{-1}$ for **1**.

Keywords: Dinuclear iron(III) complexes; Schiff-base ligands; Crystal structure; Magnetic property

1. Introduction

Schiff bases have been extensively studied in coordination chemistry due to their facile syntheses, tunable steric and electronic properties, high purity, and good solubility. The flexible coordination could be useful to generate dinuclear or multinuclear complexes [1–8].

The design, synthesis, and characterization of iron complexes with Schiff-base ligands are important in bioinorganic, materials chemistry, and catalytic chemistry due to their importance as synthetic models for iron-containing enzymes [9], molecule-based magnetic materials [10–19], oxidation catalysts [20–22], and bistable molecular materials based on temperature-, pressure-, or light-induced spin-crossover behaviors [23–25]. Dinuclear complexes were treated as models for understanding the effect of structural parameters in determining the sign and magnitude of exchange coupling interactions between two iron centers [26].

We have synthesized two new dinuclear iron(III) complexes containing Schiff-base bridging ligands. Our strategy is using multidentate Schiff-base ligands to control

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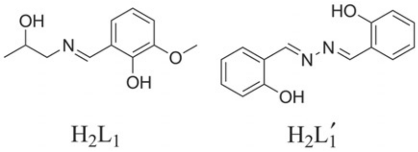

Scheme 1. The structures of H_2L_1 and $H_2L'_1$.

nuclearity of the complexes. Herein, N-(2-hydroxypropyl)(3-methoxysalicylaldimine) (H_2L_1) and 1,2-bis(2-hydroxybenzylidene) hydrazine ($H_2L'_1$; scheme 1) were used as bridging ligands to construct dinuclear iron(III) complexes. We report here the synthesis, crystal structures, and magnetic properties of $Fe_2(HL_1)_2(L_1)_2 \cdot MeOH$ (**1**) and $Fe_2(\mu\text{-}L'_1)_3$ (**2**).

2. Experimental

2.1. *Chemicals and preparation of the ligands and complexes*

o-Vanillin, iso-propanol amine, hydrazine, salicylaldehyde, methanol (MeOH, anhydrous), and $FeCl_3 \cdot 6H_2O$ were obtained from Aldrich and Alfa Aesar. All of the above chemicals were used as received.

The Schiff base H_2L_1 [H_2L_1 = N-(2-hydroxypropyl)(3-methoxysalicylaldimine)] was synthesized by condensation between o-vanillin 152 mg (1 mmol) and iso-propanol amine 75 mg (1 mmol) in methanol (10 mL). The mixture was refluxed for 2 h. The resulting light yellow precipitate was filtered. The Schiff base $H_2L'_1$ [$H_2L'_1$ = 1,2-bis(2-hydroxybenzylidene) hydrazine] was synthesized by condensation between hydrazine 50 mg (1 mmol) and salicylaldehyde 244 mg (2 mmol) in methanol (10 mL). The mixture was refluxed for 2 h. The resulting dark red precipitate was filtered.

$[Fe_2(HL_1)_2(L_1)_2] \cdot MeOH$ (**1**) was prepared as follows: a solution of Schiff base (H_2L_1, 0.209 g, 1 mmol) in methanol (15 mL) was added to $FeCl_3 \cdot 6H_2O$ (135 mg, 0.5 mmol) dissolved in 10 mL of methanol under stirring. The mixture was further stirred for 30 min and then filtered. Several days later, well-shaped dark brown crystals that appeared were separated by filtration and washed with methanol, Yield: 111.8 mg (50% based on iron(III) chloride). The product was air dried at room temperature; single crystals suitable for X-ray diffraction were obtained. IR (cm^{-1}): 3415 (b), 3132 (s), 2067 (m), 1667 (m), 1621 (s), 1544 (w), 1469 (w), 1443 (m), 1400 (s), 1303 (m), 1250 (m), 1221 (m), 1038 (m), 974 (w), 859 (m), 742 (m), 619 (m), 475 (m). Anal. Calcd (found) for $C_{45}H_{58}Fe_2N_4O_{13}$ (%): C, 55.45 (55.39); N, 5.75 (5.59); H, 6.00 (6.10).

$[Fe_2(\mu\text{-}L'_1)_3]$ (**2**) was prepared as follows: A solution of $H_2L'_1$ (241 mg, 1 mmol) in methanol (20 mL) was added to $FeCl_3 \cdot 6H_2O$ (100 mg, 0.62 mmol) dissolved in 10 mL of methanol under stirring. The mixture was further stirred for 1 h and then filtered. Several days later, well-shaped brown crystals that appeared were separated by filtration and washed with methanol, Yield: 119.8 mg (47% based on iron(III) chloride). The products were air dried at room temperature giving single crystals suitable for X-ray diffraction. IR (cm^{-1}): 1607 (s), 1572 (s), 1526 (s), 1469 (s), 1450 (s), 1388 (w), 1295 (m), 1192 (s), 1162 (m), 1022 (w), 979 (w), 936 (w), 761 (s), 685 (w), 457 (m). Anal. Calcd (found) for $C_{42}H_{30}Fe_2N_6O_6$ (%): C, 61.04 (60.97); N, 10.18 (9.96); H, 3.60 (3.73).

2.2. *Crystal structure determination*

X-ray measurements for **1** and **2** were taken at room temperature on a Bruker ApexII CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), operating in ω–2θ scanning mode using suitable crystals for data collection. Lorentz-polarization correction was applied to the data. The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares on F^2 using SHELX-97 [27, 28]. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Crystallographic data and refinement details are given in table 1.

2.3. *Spectroscopic and variable temperature magnetic susceptibility measurements*

Fourier transform infrared (FTIR) spectra were recorded with a Vertex 70 FTIR spectrophotometer using the reflectance technique (4000–400 cm^{-1}). Samples were prepared as KBr discs. Variable temperature magnetic susceptibility measurements were performed from 2 to 300 K using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with 7 T magnet. Diamagnetic corrections for the compounds were estimated using Pascal's constants and magnetic data were corrected for diamagnetic contributions of the sample holder.

3. Results and discussion

3.1. *Crystal structure of* $[Fe_2(HL_1)_2(L_1)_2]\cdot MeOH$ *(1)*

Structural analysis shows that **1** crystallizes in the monoclinic space group $P2_1/c$ and each unit cell comprises four dinuclear units. A perspective view of the metal centers of the dinuclear core of **1** is depicted in figure 1; selected bond lengths and angles are presented in table 2. The structure of **1** consists of well-separated molecules of $[Fe_2(HL_1)_2(L_1)_2]$ and crystallization methanol. The metal centers of the dinuclear core are linked by two alkoxo oxygen atoms from two ligands to form a rectangular arrangement of iron atoms and oxygen atoms. The central $Fe_2(\mu\text{-}O)_2$ ring is almost symmetric, angles at oxygen (104.55(12), 103.39(11)°) and iron (74.5(1), 76.26(10)°) are typical for a symmetrical Fe–O–Fe–O ring. The Fe–Fe distance is 3.2122(8) Å and the dihedral angle between the Fel–O3–Fe2 and Fel–O6–Fe2 planes is 13.80(155)°.

Fe(1) and Fe(2) are in a FeN_2O_4 coordination environment composed of two nitrogen atoms, two phenoxido oxygen atoms, and two alkoxo oxygen atoms from the ligands with a moderately distorted octahedron. Two of the four iso-propanol groups are neutral and uncoordinated, but a surprising feature of the structure is that the chelates containing the two iso-propoxides are attached to the same iron. All N–Fe(III) and O–Fe(III) bond distances are within the normal range observed in other iron(III) complexes [26, 29, 30].

Table 1. Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{45}H_{58}Fe_2N_4O_{13}$	$C_{42}H_{30}Fe_2N_6O_6$
Formula weight	974.65	826.42
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/c$	R-3
Unit cell dimensions (Å, °)		
a	17.658(4)	13.3837(19)
b	24.283(5)	13.3837(19)
c	11.007(2)	37.077(7)
α	90	90
β	103.21(3)	90
γ	90	120
Volume (Å^3), Z	4594.8(16), 4	5751.6(16), 6
Temperature (K)	293(2)	293(2)
Calculated density (g cm^{-3})	1.409	1.432
Absorption coefficient (mm^{-1})	0.699	0.813
F(000)	2048	2544
θ range (°)	$3.46 < \theta < 25.01$	$2.81 < \theta < 27.86$
Measured reflections	$-21 \leq h \leq 21$; $-28 \leq k \leq 28$; $-10 \leq l \leq 13$	$-13 \leq h \leq 17$;$-16 \leq k \leq 17$; $-48 \leq l \leq 41$
Reflections collected	28,704	15,828
Unique reflection, R_{int}	7917, 0.0985	3035, 0.0398
Goodness-of-fit on F^2	1.062	1.093
Final R indices [$I > 2\sigma(I)$]	$R^a = 0.0697$, $wR^b = 0.1751$	$R = 0.0488$, $wR^b = 0.1114$
R indices (all data)	$R = 0.0803$, $wR = 0.1838$	$R = 0.0569$, $wR = 0.1170$
Largest difference peak and hole (e Å^{-3})	0.884 and −0.478	0.547 and −0.545

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$.

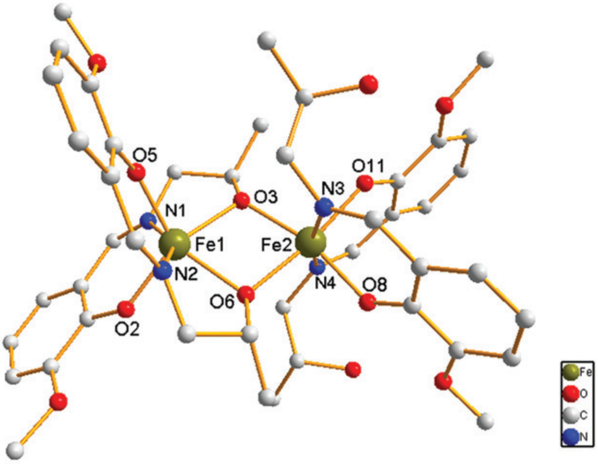

Figure 1. A perspective view of structure for $[Fe_2(HL_1)_2(L_1)_2] \cdot MeOH$. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Fe(2)–O(8)	1.959(3)	Fe(1)–O(2)	1.939(3)
Fe(2)–O(11)	1.975(3)	Fe(1)–O(5)	1.945(3)
Fe(2)–O(3)	1.993(3)	Fe(1)–O(6)	2.050(3)
Fe(2)–O(6)	2.043(3)	Fe(1)–O(3)	2.067(3)
Fe(2)–N(3)	2.147(4)	Fe(1)–N(2)	2.135(3)
Fe(2)–N(4)	2.153(4)	Fe(1)–N(1)	2.136(3)
O(8)–Fe(2)–O(11)	96.77(11)	O(2)–Fe(1)–O(5)	117.02(13)
O(8)–Fe(2)–O(3)	164.78(11)	O(2)–Fe(1)–O(6)	93.06(11)
O(11)–Fe(2)–O(3)	97.75(11)	O(5)–Fe(1)–O(6)	141.15(12)
O(8)–Fe(2)–O(6)	90.06(11)	O(2)–Fe(1)–O(3)	143.18(13)
O(11)–Fe(2)–O(6)	169.37(11)	O(5)–Fe(1)–O(3)	91.72(11)
O(3)–Fe(2)–O(6)	76.26(10)	O(6)–Fe(1)–O(3)	74.50(10)
O(8)–Fe(2)–N(3)	88.71(12)	O(2)–Fe(1)–N(2)	83.30(13)
O(11)–Fe(2)–N(3)	82.17(12)	O(5)–Fe(1)–N(2)	82.94(13)
O(3)–Fe(2)–N(3)	97.77(12)	O(6)–Fe(1)–N(2)	76.47(12)
O(6)–Fe(2)–N(3)	89.88(11)	O(3)–Fe(1)–N(2)	125.07(12)
O(8)–Fe(2)–N(4)	86.20(13)	O(2)–Fe(1)–N(1)	83.15(12)
O(11)–Fe(2)–N(4)	86.97(12)	O(5)–Fe(1)–N(1)	84.74(13)
O(3)–Fe(2)–N(4)	90.01(12)	O(6)–Fe(1)–N(1)	125.08(13)
O(6)–Fe(2)–N(4)	101.65(12)	O(3)–Fe(1)–N(1)	76.79(12)
N(3)–Fe(2)–N(4)	167.38(13)	N(2)–Fe(1)–N(1)	155.08(13)

3.2. *Crystal structure of* $[Fe_2(\mu\text{-}L'_1)_3]$ *(2)*

Structural analysis shows that **2** crystallizes in the trigonal space group *R*-3 and each unit cell has six dinuclear units. A perspective view of the dinuclear molecule with atom numbering is depicted in figure 2(a). Selected bond lengths and angles are presented in table 3. In this complex, three ligands coordinate the two metal ions *via* two phenolates and two imines. The coordination spheres of the Fe(III) ions in **2** are identical. Each is in a FeN_3O_3 octahedron, formed by three imine nitrogen atoms and three phenolate oxygen atoms. The salicylaldimine moiety is facial and connected by three diaza (=N–N=) bridges. The Fe $\cdots$ Fe distance in this complex is 3.9304(10) Å with ligands twisted along N–N single bonds to accommodate the two irons and consequently a triple helical structure is generated. The extent of twisting is slightly different for the three ligands. The dihedral angles between the two salicylaldimine moieties of the three ligands are 35.70(107)°, 38.06(150)°, and 33.01(50)°. All N–Fe(III) and O–Fe(III) bond distances are within the normal range observed in other iron(III) complexes [26, 29, 30].

3.3. *Magnetic properties*

The magnetic properties of **1** were studied to evaluate the magnetic interactions between the two paramagnetic centers. Variable temperature magnetic susceptibility measurements from 2 to 300 K under a constant magnetic field of 1 kOe were carried out.

The magnetism of **1** as $\chi_M T$ against T plots is shown in figure 3. Data were corrected for gelatin capsule sample holder as well as for diamagnetic and temperature independent paramagnetism. As shown in figure 3, the room temperature value of $\chi_M T$ (6.60 $cm^3 K mol^{-1}$) is slightly less than the sum value expected for two spin-only paramagnetic systems with $S = 5/2$ ($\chi_M T = 8.75\,cm^3\,K\,mol^{-1}$ assuming $g = 2$), and $\chi_M T$

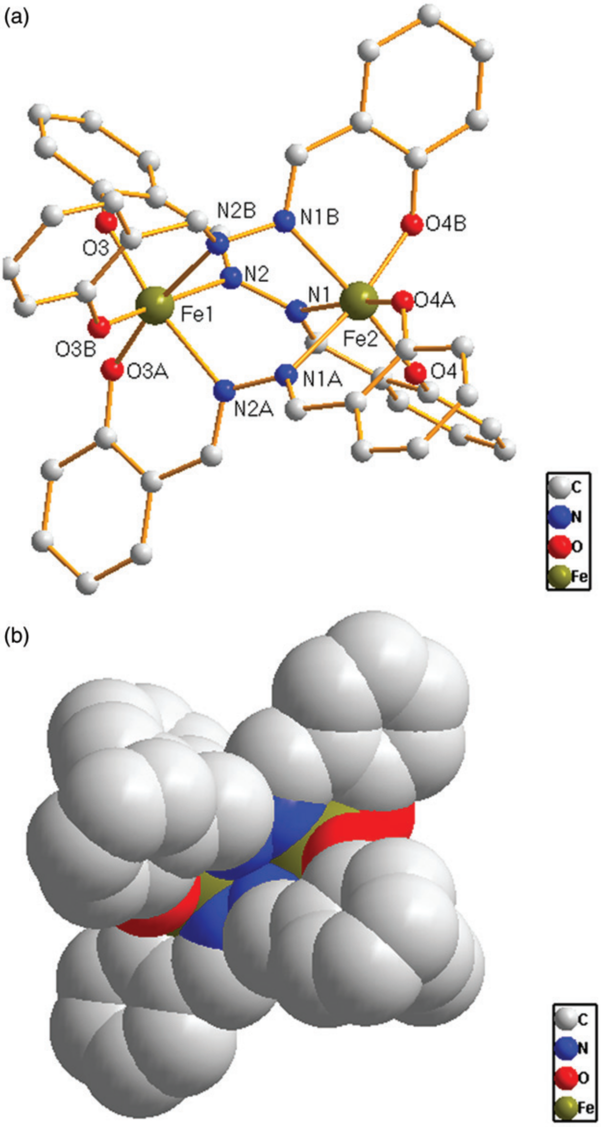

Figure 2. Molecular structure of $[Fe_2(\mu\text{-}L'_1)_3]$ (**2**). Hydrogen atoms are omitted for clarity: (a) diagram showing the perspective view of **2** with atom labels and (b) space-filling representation of the triple helical structure.

decreases rapidly upon lowering the temperature. This indicates antiferromagnetic coupling interaction between the two high-spin iron(III) ions in **1**.

For theoretical analysis of the magnetic behavior of **1**, the analytical expression based upon the Hamiltonian ($\hat{H} = -2J\hat{S}_1\hat{S}_2$) was used. The molar susceptibility of the Fe(III)–Fe(III) ($S_1 = S_2 = 5/2$) system is given in equation (1) [31].

$$\chi_M = (Ng^2\mu_B^2/kT)[A/B], \tag{1}$$

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

N(1)–Fe(2)	2.1829(19)	Fe(1)–N(2)#2	2.1685(18)
N(2)–Fe(1)	2.1686(18)	Fe(1)–N(2)#1	2.1686(18)
O(3)–Fe(1)	1.9255(16)	Fe(2)–O(4)#2	1.9178(18)
O(4)–Fe(2)	1.9178(18)	Fe(2)–O(4)#1	1.9178(18)
Fe(1)–O(3)#1	1.9255(16)	Fe(2)–N(1)#1	2.1830(19)
Fe(1)–O(3)#2	1.9256(16)	Fe(2)–N(1)#2	2.1830(19)
O(3)–Fe(1)–O(3)#1	98.02(6)	O(4)#1–Fe(2)–O(4)	96.34(7)
O(3)–Fe(1)–O(3)#2	98.02(6)	O(4)#2–Fe(2)–N(1)#1	170.54(7)
O(3)#1–Fe(1)–O(3)#2	98.02(6)	O(4)#1–Fe(2)–N(1)#1	84.72(7)
O(3)–Fe(1)–N(2)#2	89.63(7)	O(4)–Fe(2)–N(1)#1	92.88(7)
O(3)#1–Fe(1)–N(2)#2	170.88(7)	O(4)#2–Fe(2)–N(1)	92.88(7)
O(3)#2–Fe(1)–N(2)#2	85.74(6)	O(4)#1–Fe(2)–N(1)	170.54(7)
O(3)–Fe(1)–N(2)#1	170.88(7)	O(4)–Fe(2)–N(1)	84.72(7)
O(3)#1–Fe(1)–N(2)#1	85.74(7)	N(1)#1–Fe(2)–N(1)	85.84(7)
O(3)#2–Fe(1)–N(2)#1	89.64(7)	O(4)#2–Fe(2)–N(1)#2	84.72(7)
N(2)#2–Fe(1)–N(2)#1	85.98(7)	O(4)#1–Fe(2)–N(1)#2	92.88(7)
O(3)–Fe(1)–N(2)	85.73(7)	O(4)–Fe(2)–N(1)#2	170.55(7)
O(3)#1–Fe(1)–N(2)	89.64(7)	N(1)#1–Fe(2)–N(1)#2	85.84(7)
O(3)#2–Fe(1)–N(2)	170.88(7)	N(1)–Fe(2)–N(1)#2	85.84(7)
N(2)#2–Fe(1)–N(2)	85.98(7)	O(4)#2–Fe(2)–O(4)#1	96.34(7)
N(2)#1–Fe(1)–N(2)	85.98(7)	O(4)#2–Fe(2)–O(4)	96.34(7)

Symmetry transformations used to generate equivalent atoms: #1 x, $y+1$, z; #2 $-x$, y, z.

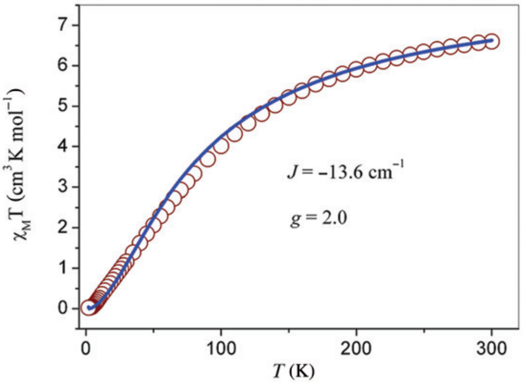

Figure 3. The plots of $\chi_M T$ *vs.* T for **1**; the solid line represents the best fit with $J = -13.6\,\text{cm}^{-1}$ and $g = 2.0$.

$$A = 2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x},$$
$$B = 1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x},$$
$$x = J/kT.$$

In these expressions, J is the magnetic coupling parameter, g is the Landé factor, and N, β and k have their usual meanings. Least-squares best-fit parameters are $J = -13.6\,\text{cm}^{-1}$, $g = 2.0$, and $R = 4.1 \times 10^{-4}$ (R is the agreement factor defined as $R = \Sigma[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \Sigma[(\chi_M)_{\text{obs}}]^2$). The calculated curve matches rather well with the magnetic data in the whole temperature range investigated. This indicates that the

Table 4. Selected magneto-structural data for dinuclear μ-O bridged iron(III) complexes.

Compound	Fe–O–Fe (°)	J_{exp} (cm^{-1})	Ref.
$[Fe_2(HL_1)_2(L_1)_2] \cdot MeOH$	104.6 (103.4)	−13.6	This work
$[Fe_2(HL_2)_2(OH)_2](ClO_4)_2$	100.7	−11.0	33
$[Fe(acac)L_3]_2 \cdot MeCN$	103.3	−16.1	32
$[FeL_3]_2$	104.5	−27.2	32
$[FeClL_4]_2$	105.4	−29.6	32
$[Fe_2(HO\text{-dipic})_2(H_2O)(OH)] \cdot 4H_2O$	103.2	−14.6	34
$[Fe_2(salen)_2(OH)_2] \cdot 2H_2O{\cdot}2py$	102.8	−20.8	35
$[Fe_2(dipic)_2(H_2O)_2(OH)_2]$	103.6	−22.8	34
$[Fe_2(Me_2Ndipic)_2(H_2O)_2(OH)_2] \cdot 2H_2O$	105.3	−23.4	35

Abbreviations used: H_2L_1 = N-(2-hydroxypropyl)(3-methoxysalicylaldimine); H_2L_2 = macrocyclic tetraaminodiphenol; N(R),N-(2-methylene-4,6-di-tert-butylphenol) aminoethan-1-ol (H_2L_3, R = Me and H_2L_4, R = H); HO-dipic = 4-hydroxo-2,6-pyridinedicarboxylate; salen = N,N′-ethylenebis-salicylaminate); py = pyridine; dipic = 2,6-pyridinedicarboxylate; Me_2Ndipic = 4-dimethylamino-2,6-pyridinedicarboxylate.

complex undergoes antiferromagnetic spin-exchange interaction between the irons. The magnitude of the antiferromagnetic coupling in **1** ($J = -13.6\,\mathrm{cm}^{-1}$) falls in the range 11.0 to $-29.6\,\mathrm{cm}^{-1}$ observed for other dinuclear μ-O bridged iron(III) complexes (table 4) [32–34]. According to the literature, a magneto-structural correlation exists between both the experimental and calculated J values and the Fe–O–Fe angle for these type complexes. It should be noted that such a strong correlation does not exist with other structural parameters (e.g., Fe–O or Fe···Fe distances), hence the main structural factor governing the magnetic exchange coupling between planar Fe(μ-O)$_2$Fe complexes is proven to be the Fe–O–Fe angle. The crossover point from AF to F interactions is predicted at 100.4° [35].

4. Summary and conclusion

We have synthesized and characterized two dinuclear complexes of N-(2-hydroxypropyl)(3-methoxysalicylaldimine) (H_2L_1) and 1,2-bis(2-hydroxybenzylidene) hydrazine ($H_2L'_1$). These Schiff-base ligands are bi-, tri-, or tetradentate donors in the new complexes. For **1**, metal centers of the dinuclear core are linked by two alkoxo oxygen atoms forming an almost symmetric Fe–O–Fe–O ring. In **2**, three ligands are twisted about the N–N single bond and coordinate to two irons in a helical fashion to generate the triple helical structure. The magnetic behavior of **1** shows a moderate antiferromagnetic interaction within the normal range observed in other oxygen-bridged diiron(III) complexes. Magneto-structural correlations between J values and the Fe–O–Fe angles for planar Fe(μ-O)$_2$Fe complexes are worthy of in-depth research; further studies are currently underway in our laboratory.

Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 827463 and 827464. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK or Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk.

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