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Synthesis, Crystal Structure, and Magnetic Properties of a Very Rare Double μ-1,1-Azido- and a μ-1,1-(OMe)-Bridged Fe^{III} Dimer Containing a N,N,O-Donor Tridentate Schiff Base Ligand

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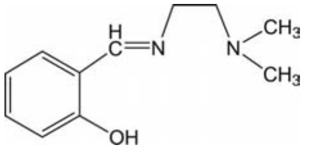
Two new Fe^{III} complexes, $[Fe_2L_2(\mu\text{-}OMe)_2(NCS)_2]$ (**1**) and $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$ (**2**), have been synthesized using a N,N,O-donor tridentate Schiff base ligand HL {2-[(2-dimethylaminoethylimino)methyl]phenol}, the condensation product of salicylaldehyde and *N*,*N*-dimethyl-1,2-diaminoethane. The complexes were characterized by X-ray structural analyses and variable-temperature magnetic susceptibility measurements. Both crystal structures are centrosymmetric dimers containing two Fe^{III} atoms, which are bridged in compound **1** by two methoxy anions and in compound **2** by two μ-1,1-azides. The chelating tridentate Schiff base and a terminal thiocyanato (for **1**) or azido (for **2**) group complete the hexacoordination of the distorted octahedral environment of each iron center. The magnetic properties of compound **1** show the presence of antiferromagnetic exchange interactions mediated by double methoxy bridges (J = –29.45 cm^{-1}). Compound **2** shows the presence of very weak ferromagnetic exchange interactions mediated by double μ-1,1-N_3 bridges (J = 1.08 cm^{-1}).

Introduction

The chemistry of iron(III) complexes is dominated by oxygen-bridged species because of the high oxygen affinity of the iron(III) ion.[1] This type of oxygen-bridged dinuclear iron(III) unit is also valuable to synthetic chemists because of its relevance in biological systems.[2] Such units are present at the active site of numerous non-heme metalloenzymes such as hemerythrin, a dioxygen carrier protein.[3] Synthetic efforts to prepare model complexes of iron proteins have yielded several unexpected and interesting oxygen-bridged polyiron compounds, the magnetic properties of which have motivated interesting studies concerning their unusual electronic structure.[4]

The tridentate Schiff base ligands, derived from the monocondensation of a diamine and salicylaldehyde derivative have been used extensively along with pseudohalides to construct various polynuclear complexes of Cu^{II} and Ni^{II} that show interesting structural and magnetic properties.[5–6] Among them the μ-1,1 (end-on) azido-bridged compounds are of special interest in designing new polynuclear species exhibiting ferromagnetic coupling as this bridging mode is a ferromagnetic coupler with M–N–M angles as wide as 108°.[7] However, such ligands have seldom been used to synthesize complexes with Fe^{III}. They usually afforded mononuclear bis(Schiff base) species,[8] except in a few cases where oxido-, alkoxido- or hydroxido-bridged dinuclear complexes resulted.[9] The mononegative tridentate Schiff bases along with two pseudohalide ions balance the charge of Fe^{III}, but one of the pseudohalide ions should act as a bridging ligand to complete the usual hexacoordination of Fe^{III}. Thus these groups of tridentate Schiff bases have the potential to produce pseudohalide-bridged Fe^{III} complexes although no such example is found in the literature.

In the present contribution, the tridentate N,N,O-donor Schiff base (HL), which results from the monocondensation of salicylaldehyde and 1,2-bis(dimethylamino)ethane (Scheme 1), has been used to synthesize the two new ferric compounds $[Fe_2L_2(\mu\text{-}OMe)_2(NCS)_2]$ (**1**) and $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$ (**2**). Herein, we present the syntheses, crystal structures, and variable-temperature magnetic properties of these two compounds. Complex **1**, a double methoxy-bridged dimer is antiferromagnetically coupled whereas complex **2** a double μ-1,1-azido-bridged dimer is ferromagnetically cou-



Scheme 1. The ligand HL.

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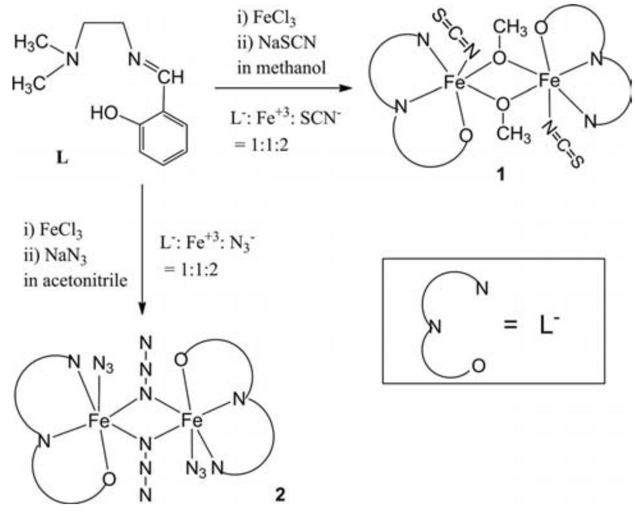
pled. To the best of our knowledge, complex **2** is only the third example of a μ-1,1-azido-bridged Fe^{III} species and the first one with a tridentate Schiff base as coligand.

Results and Discussion

Synthesis of the Complexes

The hydroxido- and oxido-bridged dinuclear Fe^{III} complexes with the monocondensed tridentate Schiff base ligand 2-[(2-dimethylaminoethylimino)methyl]phenol (HL) (Scheme 1) have been reported by us recently.[9d] In the present investigation we have used this ligand for the synthesis of two new Fe^{III} dinuclear complexes. The two metals are bridged by two methoxy anions in **1** and by two azides in **2**. Complex **1** has been synthesized by the reaction of $FeCl_3$, the Schiff base ligand (HL), and a coligand thiocyanate ion in a 1:1:2 molar ratio in a methanol medium (Scheme 2). When we tried to obtain complex **2** by the same procedure using azide instead of thiocyanate as coligand, we obtained a mixture of products: a good crystalline compound that turned out to be **2** along with a microcrystalline product. The elemental analysis and spectral study of the latter suggested that its formula was $[Fe_2L_2(OMe)_2(N_3)_2]$. As we could not synthesize it in pure form, we do not report details here. However compound **2** could be obtained as the sole product when $FeCl_3$, the Schiff base (HL), and sodium azide were allowed to react in an acetonitrile medium.



Scheme 2. Synthetic route to **1** and **2**.

IR and UV/Vis Spectra of the Complexes

The spectroscopic data and their assignments are given in the Experimental Section. The IR spectra of the two complexes are very similar to each other with regard to the tridentate L^- ligand. Both of them show a strong and sharp peak for ν(C=N) at 1616 and 1619 cm^{-1} for complexes **1** and **2**, respectively, indicating the presence of the Schiff base. In the spectrum of complex **1** a strong band at 2108 cm^{-1} is indicative of the presence of the *N*-coordinated thiocyanate.[10] While two overlapping but distinct peaks at 2051 to 2063 cm^{-1} for complex **2** corroborate the presence of two types of azido (terminal and μ-1,1 bridging, respectively) in the complex.[5b]

The electronic spectra of compounds **1** and **2** are recorded in methanol and acetonitrile solution, respectively. The spectrum of complex **1** shows one band in the visible (λ_{max} = 433 nm) and another in the near-UV (λ_{max} = 330 nm) region. The former (lower energy) band can be attributed to thiocyanato–Fe^{III} charge transfer and the latter (higher energy) band at 330 nm is a superposition of the azomethine π–π* transition band and the charge-transfer bands from oxygen to Fe^{III}.[9a,9e] The spectrum of **2** presents similar features to that of complex **1**. The higher energy band (near UV region) lies at λ_{max} = 325 nm, which is attributed to the π–π* transition of the azomethine linkage and the lower energy band (near the Vis region) λ_{max} = 425 nm corresponds to an azide-to-Fe^{III} charge-transfer band.

Description of Structures of the Complexes

Complex 1

Both the structures are centrosymmetric dimers in which the iron atoms have distorted six-coordinate octahedral environments. Bond lengths and bond angles are given in Table 1. The structure of **1** is shown in Figure 1 together with the atom numbering scheme in the metal coordination sphere.

Table 1. Dimensions in the metal coordination sphere, distances [Å], angles [°].

Bond lengths	**1**, X = O	**2**, X = N
Fe(1)–N(19)	2.134(2)	2.109(2)
Fe(1)–N(22)	2.252(1)	2.240(2)
Fe(1)–O(11)	1.913(1)	1.911(2)
Fe(1)–N(1)	2.061(2)	2.002(2)
Fe(1)–X(4)[a]	1.983(1)	2.088(2)
Fe(1)–X(4)	2.003(1)	2.137(2)
Bond angles		
O(11)–Fe(1)–X(4)[a]	100.27(5)	101.21(7)
O(11)–Fe(1)–X(4)	92.64(5)	91.40(7)
X(4)–Fe(1)–X(4)[a]	74.24(6)	72.21(9)
O(11)–Fe(1)–N(1)	92.12(6)	93.82(8)
X(4)[a]–Fe(1)–N(1)	93.42(6)	92.12(8)
X(4)–Fe(1)–N(1)	167.40(6)	164.19(8)
O(11)–Fe(1)–N(19)	86.06(6)	86.47(7)
X(4)[a]–Fe(1)–N(19)	171.34(5)	164.15(7)
X(4)–Fe(1)–N(19)	99.74(5)	93.94(7)
N(1)–Fe(1)–N(19)	92.23(6)	101.26(8)
O(11)–Fe(1)–N(22)	162.72(5)	163.03(7)
X(4)[a]–Fe(1)–N(22)	97.00(5)	95.60(7)
X(4)–Fe(1)–N(22)	92.52(5)	91.52(7)
N(1)–Fe(1)–N(22)	86.32(6)	87.83(8)
N(19)–Fe(1)–N(22)	76.81(5)	76.65(7)

Symmetry elements for **1**, a: 2 – *x*, 2 – *y*, 1 – *z*; for **2**, a: 1 – *x*, –*y*, 2 – *z*.

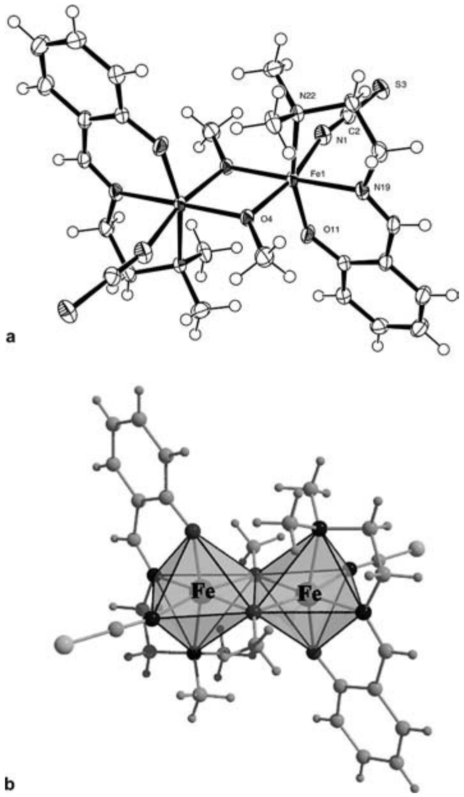


Figure 1. Structure of complex **1**. (**a**) The centrosymmetric structure with ellipsoids drawn at 50% probability. (**b**) Edge-sharing dimeric structure of **1**.

In **1** the iron atom is bonded to three atoms of the meridionally coordinated tridentate ligand with the following bond lengths: Fe–O(11) 1.913(1) Å, Fe–N(19) 2.134(2) Å, and Fe–N(22) 2.252(1) Å. The equatorial plane is completed by a bridging methoxy group with an Fe–O(4)^a bond length of 1.983(1) Å. In the axial positions a second methoxy group, O(4) with a bond length of 2.003(1) Å, and a terminal thiocyanato group, N(1) with a bond length of 2.032(3) Å, are present. Thus the two Fe^{III} octahedra are joined together by two bridging methoxy groups sharing an edge as shown in Figure 1 (b). The four donor atoms in the equatorial plane are nearly coplanar with an r.m.s. deviation of 0.066 Å. The iron atom is 0.041(1) Å from this plane in the direction of N(1). Within the dimer the Fe–Fe separation is 3.178(1) Å and the distance between the two bridging oxygen atoms is 2.405(4) Å, both of which are comparable with those reported previously in di-μ-methoxy-bridged diferric complexes.[9a,9b] The μ-OMe bridge in this complex leads to a perfectly planar $Fe_2(\mu\text{-}OMe)_2$ ring as the dimer sits on a crystallographic inversion center. The Fe–O–Fe angle [105.75(6)°] and O–Fe–O angle [74.25(6)°] also lie within the ranges of similar compounds.[9a,9b,11] The two Fe-μ-OMe bond lengths are slightly different making the Fe_2O_2 core asymmetric, which is a common feature for such dimers. The phenyl rings are almost perpendicular to the $Fe_2(\mu\text{-}OMe)_2$ core with a dihedral angle of 85.90(8)°. The longest Fe-μ-OMe [2.003(1) Å] bond is *trans* to the thiocyanato ligand, and the shortest Fe-μ-OMe bond [1.983(1) Å] is *trans* to the imino nitrogen atom.

In compound **1**, there are two weak intramolecular H-bonding interactions: one between the H22E and O11 atom (1 – *x*, –*y*, 2 – *z*) with dimensions C221···O11 3.251(2) Å, H22E···O11 2.33 Å, and C221···H22A···O11 161° and the other between the H5A and N1 atom (1 – *x*, –*y*, 2 – *z*) with dimensions C5···N1 3.184(3) Å, H5A···N1 2.57 Å, and C5···H5A···N1 122° (Figure S1). No significant intermolecular interactions have been found.

Complex 2

The structure of **2** is shown in Figure 2 together with the atomic numbering scheme. Bond lengths and bond angles are given in Table 1. Complex **2** differs from **1** only in that the bridging groups and one of the coligands are azido rather than methoxy. The geometry of the ligand is similar, with Fe(1)–O(11) 1.911(2) Å, Fe(1)–N(19) 2.109(2) Å, and Fe(1)–N(22) 2.240(2) Å, but the bonds to the bridging nitrogen atoms are significantly longer at 2.088(2) and 2.137(2) Å than those to the bridging methoxy oxygen atoms in **1**. The equatorial plane is far more distorted than

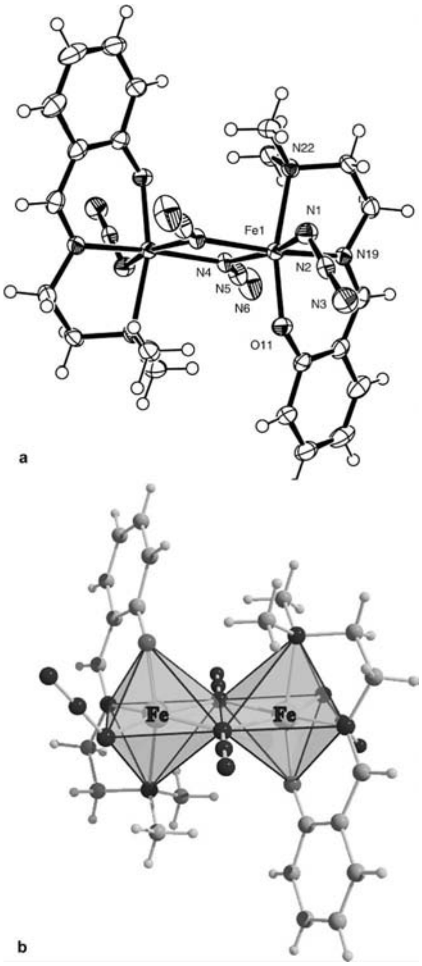


Figure 2. Structure of complex **2**. (**a**) The centrosymmetric structure with ellipsoids drawn at 50% probability. (**b**) Edge-sharing dimeric structure of **2**.

in **1** with an r.m.s. deviation for the four donor atoms of 0.123 Å. The iron atom is 0.130(1) Å from the mean plane in the direction of the terminal N(1) azido group. Two azido ions bridge the Fe^{III} ions in a μ-1,1 (end-on) fashion. Like complex **1** two Fe^{III} octahedrals are joined together by two bridging azido groups sharing an edge as shown in Figure 2 (b). The bond length involving the axial bridging azido is 2.137(2) Å, much longer than that of the equatorial bridging azido [2.088(2) Å]. The Fe_2N_2 ring is perfectly planar as the dimer sits on a crystallographic inversion center. The intradimer metal···metal separation is 3.413(1) Å, and the $N_{(bridging)}$–Fe–$N_{(bridging)}$ and Fe–N–Fe bond angles are 72.21(9)° and 107.79(9)°, respectively. These values are close to those reported for other high-spin dinuclear bis(μ-end-on-azido)iron(III) complexes.[12–13] The dihedral angle between the phenyl rings and the Fe_2N_2 core (75.159°) is slightly less than that in complex **1**, where the distance between the two bridging nitrogen atoms [2.49(1) Å] is slightly greater than that in **1**. Both the bridging and terminal azido ligands are quasi-linear, and the value of the N–N–N angle varies between 178.2(3)° and 179.4(3)°.

In this compound, there is a weak intramolecular H-bonding interaction between the H22A and O11 atoms (2 – *x*, 2 – *y*, 1 – *z*) with dimensions C221···O11 3.411(3) Å, H22A···O11 2.48 Å, and C221···H22A···O11 162°. There are also two other very weak interdimer interactions: one between the N6 atom of one molecule and the H20A atom of a neighboring molecule (3/2 –*x*, –1/2 + *y*, 1/2 – *z*) and the other between the N6 atom and H22D atom of another neighboring molecule (1/2 + *x*, 3/2 – *y*, 1/2 + *z*) with dimensions C20···N6 3.273(4) Å, H20A···N6 2.54 Å, C20···H20A···N6 133°, C222···N6 3.206(4) Å, H22D···N6 2.59 Å, and C222···H22D···N6 122°. These noncovalent interactions are likely to control the packing of the molecules (Figure S2).

It is worth noting that most of the previously reported Fe^{III} complexes of tridentate N,N,O-donor Schiff base ligands are bis(Schiff base) complexes with non-coordinating counter anions such as ClO_4^-, NO_3^-, PF_6^-, etc.[8] Only a few mono(Schiff base) complexes are reported and among them two are methoxido-,[9a,9b] one ethoxido-,[9b] one hydroxido-,[9d] and two are oxido-bridged diferric compounds.[9c–9d] Therefore, the methoxy-bridged diferric compound **1** is rather uncommon with tridentate Schiff bases although commonplace with other types of ligands. On the other hand, μ-1,1-azido bridged iron(III) complexes are very rare with any type of coligands. To the best of our knowledge, only two such examples are reported to date. One is a double μ-1,1-azido-bridged diiron(III) complex derived from a tetradentate N_2O_2 donor Schiff base, *N,N′*-bis(salicylidene)-1,3-diaminopropane, while the other is a dinuclear μ-1,1-azido-bridged anionic species, $[Fe_2^{III}(N_3)_{10}]^{4-}$, isolated with the help of a cationic species, $[Fe^{II}(bpym)]^{2+}$ (bpym = 2,2′-bipyrimidine). Thus compound **2** is the first example of a double 1,1-azido-bridged dimer of Fe^{III} with a tridentate N,N,O-donor Schiff base ligand, whereas more than thirty similar Cu^{II} and at least five Ni^{II} complexes are known with this type of ligands.

Magnetic Properties

The variable-temperature magnetic susceptibility of complexes **1** and **2** has been recorded in the region 2–300 K, under an applied field of 5000 G in all ranges of temperature and 300 G only at low temperatures. A plot of $\chi_M T$ vs. T for complex **1** is shown in Figure 3. The $\chi_M T$ value at 300 K (5.62 $cm^3 mol^{-1} K$) is well below the expected value for two high-spin Fe^{3+} ions (8.75 $cm^3 mol^{-1} K$ assuming g = 2). Upon cooling, the $\chi_M T$ product decreases continuously to 0 $cm^3 mol^{-1} K$ at 2 K, indicating the occurrence of an antiferromagnetic intramolecular interaction between the two Fe^{3+} ions. The $\chi_M T$ vs. T data were fitted to the theoretical equation[14] derived for a Heisenberg exchange model, $(H = -JS_1S_2)$ with $S_1 = S_2 = 5/2$. The best fit gave $J = -29.45\ cm^{-1}$, $g = 2.03$ and $R = 4.8 \times 10^{-5}$. The agreement factor R is defined as $R = \Sigma_i[(\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2/\Sigma_i[(\chi_M T)_{obsd}]$. It is to be emphasized that the magniude of the J value must be taken with a certain amount of caution because we have not considered the possible D value or the $z'J'$ value (antiferromagnetic) resulting from the molecular packing. This consideration is made for antiferromagnetic systems because their effect on the curve, at low temperatures, is the same as J_{AF} and, thus, their inclusion only overparametrizes the fit. However, the D and/or $z'J'$ values must be considered when the coupling is ferromagnetic (see below for complex **2**). Indeed, the value of the exchange coupling constant of complex **1** is perfectly in line with the values reported for other dimethoxido-bridged iron(III) complexes with similar structural features: Fe···Fe distances, Fe–O–Fe angles, and Fe···O distances.[9a,11,15–20] In Table 2 we list the examples of dimethoxido-bridged iron(III) complexes upon which both structures and magnetic studies have been performed, including J values and the three structural parameters. Although it is clear that the above geometrical parameters play a role in their contribution to the coupling constant J, the trend of the J parameter in systems with analogous geometrical parameters and similar J values is still largely unexplained.

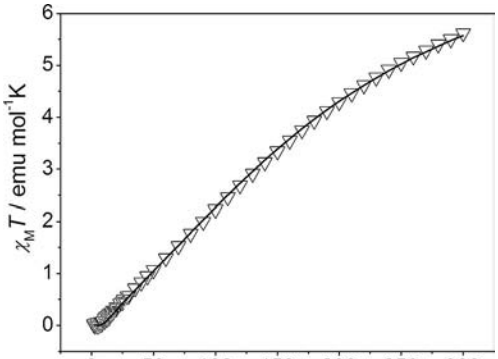


Figure 3. Plot of $\chi_M T$ vs. T of compound **1**. The solid line is the best fit to the experimental data.

A plot of $\chi_M T$ vs. T, for complex **2**, where χ_M is the magnetic susceptibility per formula unit, in the temperature range 2–300 K is shown in Figure 4. The $\chi_M T$ value is

Table 2. Relative bond angles and bond lengths of other reported dimethoxido-bridged iron(III) complexes.

	Fe···Fe [Å]	Fe–O–Fe [°]	Fe···O [Å]	J [cm^{-1}]
Complex **1**[a]	3.178	105.8	1.993	–29.35
$[Fe_2(H_3L^3)_2(OMe)_2]\cdot 8MeOH$[b]	3.145	104.2	1.992	–24.2
$[Fe_2(mxba)_2(OMe)_2]\cdot CH_2Cl_2$[c]	3.164	104.97	1.994	–27
$[Fe_2(HL)_4(OMe)_2]$[d]	3.085	102.73	1.967	–27.4
$[Fe_2Cl_4(amp)_4(OMe)_2]$[e]	3.18	104.44	1.955	–29.4
$[Fe_2(Cl)_2(salEen)_2(OMe)_2]$[f]	3.11	104.35	2.00	–27.3
$[Fe_2(dbm)_4(OMe)_2]$[g]	3.087	102.0	1.987	–15.4
$[Fe_2(dpm)_4(OMe)_2]$[g]	3.105	103.7	1.974	–19.0
$[Fe_2(chp)_4(dmbipy)_2(OMe)_2]\cdot 2MeOH$[h]	3.194	104.7	1.987	–26.8
$[Fe_2(chp)_4(phen)_2(OMe)_2]\cdot 2MeOH$[h]	3.153	104.3	1.948	–28.6
$[Fe_2Cl_2L(OMe)_2]$[i]	3.106 / average	103	1.920	–16.3

[a] This work. [b] H_5L^3 = 2-hydroxy-*N*-{3-hydroxy-5-[(2-hydroxybenzoyl)amino]pentyl} benzamide, ref.[15] [c] mxba = *m*-xylylenebis(acetylacetone), ref.[16] [d] H_2L = 2-salicyloylhydrazono-1,3-dithiolate, ref.[17] [e] amp = 2-(aminomethyl)pyridine, ref.[18] [f] HsalEen = *N*-ethyl-*N*-(2-aminoethyl)salicylaldimine, ref.[9a] [g] dbm = dibenzoylmethane, dpm = dipivaloylmethanate, ref.[19] [h] Hchp = 6-chloro-2-pyridone, dmbipy = 4,4′-dimethyl-2,2′-bipyridine, phen = 1,10-phenanthroline, ref.[20] [i] L = 1,4-piperazinebis(*N*-ethylenesalicylaldimine), ref.[11]

8.36 cm^3 mol^{-1} K at 300 K. This value agrees well with that expected for the two spin-only Fe^{III} ion (S = 5/2) values of 8.75 cm^3 mol^{-1} K. Upon cooling the $\chi_M T$ value increases smoothly to a maximum of 9.48 cm^3 mol^{-1} K at 12 K, which suggests the presence of ferromagnetic coupling between the Fe^{III} ions. Below 12 K, $\chi_M T$ drops down, reaching 5.50 cm^3 mol^{-1} K at 2 K. Considering the rhombicity of the iron sides (see structural part), and the drastic decrease of the susceptibility data at low temperature, the experimental data was fitted using the following Hamiltonian in which single-ion anisotropy is assumed:

$$H = -J(S_1S_2) + \Sigma_{i=1-2}\,(g_{Fe}\mu_B S_i\cdot H_i + S_i\cdot D_i\cdot S_i)$$

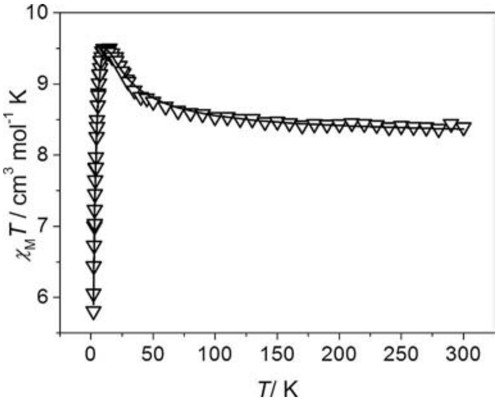


Figure 4. Plot of $\chi_M T$ vs. T of compound **2**. The solid line is the best fit to the experimental data.

The single-ion anisotropy parameters, D and E, are assumed to be the same for the two iron ions. The best fit was found with J = 1.1(1) cm^{-1}, g = 2.02, $|D|$ = 6.4(2) cm^{-1}and $|E|$ = 0.31(2) cm^{-1}. However, the $\chi_M T$ decrease at very low temperatures could also be due to intermolecular interactions (generally antiferromagnetic). For this reason we have also fitted the experimental curve by means of the mean-field approach, assuming (in an artificial manner) that D = 0. With this approach the best fit parameters were J = 1.08(1) cm^{-1}, g = 2.02, $z'J'$ = –0.19(3) cm^{-1}. As a consequence, we can state that the decreasing $\chi_M T$ has a combination of the two parameters, D and $z'J'$, and the contributions from both are impossible to separate. As a conclusion, it is important to underline that $|D|$ is not necessarily 6.8 cm^{-1}; this value is simply the limit when $z'J'$ is (artificially) assumed to be 0.

The magnetic susceptibility data treatment for complex **2** was made using the MAGPAK program[21] employed with a nonlinear least-squares curve-fitting program DSTEPIT.[22]

The above results are in accordance with the literature data since azido ligands are known to generally propagate ferromagnetic coupling interactions between nickel(II), manganese(II), or copper(II) centers when bound in a μ-1,1 end-on mode. Correlations between structural parameters that exert the largest influence, in particular the M–N–M angle, and the energy gap between the magnetic orbitals has been well-established experimentally for μ-1,1-N_3-bridged Cu^{II} dinuclear complexes.[7] In the case of iron(III) dinuclear complexes, this structure relationship has not been tested to date since only two such compounds have been reported.[12–13] The value of the exchange coupling constant of complex **2** (Fe···$N_{av.dist.}$ 2.112 Å, Fe–N–Fe_{angle} 107.78°, and J = 1.08 cm^{-1}) is perfectly in line with the previously reported complexes: $[Fe(bpym)_3]_2[Fe_2(N_3)_{10}]\cdot 2H_2O$ (Fe···$N_{av.dist.}$ 2.179 Å, Fe–N–Fe 106.0°, and J = 4.80 cm^{-1}),[13] and $[Fe_2(N_3)_2(salpn)_2]$ (Fe···$N_{av.dist.}$ 2.118 Å, Fe–N–Fe 107.1°, and J = 1.05 cm^{-1}).[12] The D value of the Fe^{III} ion is of the same order as that reported by Boca for high-spin Fe^{III} mononuclear complexes.[23]

Further examples of Fe^{III} complexes with this structural type are needed to characterize the influence of the angle at the azido bridge on the nature and magnitude of the magnetic coupling.

Conclusions

The tridentate Schiff base ligand 2-[(2-dimethylaminoethylimino)methyl]phenol produces two new dinuclear complexes, $[Fe_2L_2(\mu\text{-}OMe)_2(NCS)_2]$ (**1**) and $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$ (**2**), with pseudohalide coligands, thiocyanato and azido, respectively. In **1**, two Fe^{III} centers are joined together by methoxy bridges and the thiocyanato ions remain terminally coordinated. This is to be expected because of the high oxophilicity of Fe^{III}. On the other hand, a double μ-1,1-azido bridge, which has rarely been found in Fe^{III} complexes, holds the two iron centers in **2**. It is therefore apparent that under suitable conditions the azido-bridged complexes of Fe^{III} can also be formed with tridentate N,N,O-donor Schiff base ligands as is the case for other metal ions e.g. Cu^{II}, Ni^{II}, etc. The moderate intradimer coupling in **1** with $J = -29.45$ cm^{-1} is in good agreement with that found in similar methoxy-bridged complexes. The weak ferromagnetic coupling in **2** corroborates with that in Fe^{III}, also the μ-1,1-azido bridge mediates ferromagnetic coupling with an Fe–N–Fe angle as high as 107.78°, like in the other first transition metal ions.

Experimental Section

Materials: The reagents and solvents used were of commercially available reagent quality.

Caution: Azide salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Physical Measurements: Elemental analyses (C, H, and N) were performed using a Perkin–Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1000–200 nm for complexes **1**) and acetonitritile (1000–200 nm for complex **2**) were recorded with a Hitachi U-3501 spectrophotometer. Magnetic measurements were carried out with the "Unitat de Mesures Magnètiques (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The diamagnetic corrections were evaluated from Pascal's constants.

Synthesis of the Schiff Base Ligand 2-[(2-Dimethylaminoethylimino)-methyl]phenol (HL): The ligand (HL) (Scheme 1) has been synthesized in two different solvents: methanol and acetonitrile. For the first set: A solution of salicylaldehyde (10 mmol, 1.05 mL) and 1,2-bis(dimethylamino)ethane (10 mmol, 1.10 mL) in methanol (40 mL) was refluxed for 1 h. For the second set: A solution of salicylaldehyde (10 mmol, 1.05 mL) and 1,2-bis(dimethylamino)-ethane (10 mmol, 1.10 mL) in acetonitrile (40 mL) was refluxed for 1 h. The resulting dark yellow solutions were then used directly for complex formation.

Synthesis of [Fe$_2$L$_2$(OMe)$_2$(SCN)$_2$] (1): FeCl$_3$ (0.810 g, 5 mmol), dissolved in methanol (10 mL), was added to a methanolic solution of the ligand (HL) (5 mmol) with constant stirring. After 5 min, a methanol/water solution (9:1, v/v) of NaSCN (0.56 g, 10 mmol) was added. The color of the solution turned to reddish-black. By slow evaporation of the resulting solution at room temperature, black-colored X-ray-quality, plate-shaped single crystals were obtained in 2 d; yield 1.26 g; (75%). $C_{26}H_{36}Fe_2N_6O_4S_2$ (**1**, 672.42): calcd. C 44.46, H 5.40, N 12.50; found C 44.47, H 5.35, N 12.54. IR (KBr pellet): $\tilde{\nu}$ = 3181 ν(NH), 2079 ν(SCN), 1616 ν(C=N) cm^{-1}. λ_{max} (methanol) = 433 and 330 nm.

Synthesis of [Fe$_2$L$_2$(N$_3$)$_2$(N$_3$)$_2$] (2): The procedure was the same as that for complex **1**, except that FeCl$_3$ (0.810 g, 5 mmol), dissolved in acetonitrile (10 mL), was added to an acetonitrilic solution of the ligand (HL) (5 mmol) with constant stirring and after 5 min an acetonitrile/water solution (9:1, v/v) of NaN$_3$ (0.650 g, 10 mmol) was added. By slow evaporation of the solution, needle-shaped, black-colored X-ray-quality, single crystals were obtained overnight; yield 1.29 g; (78%). $C_{22}H_{30}Fe_2N_{16}O_2$ (**2,** 662.28): calcd. C 39.90, H 4.57, N 33.84; found C 39.95, H 4.54, N 33.81. IR (KBr pellet): $\tilde{\nu}$ = 2063 ν(N=N) (bridging), 2051 ν(N=N) (terminal), 1616 ν(C=N) cm^{-1}. λ_{max} (acetonitrile) = 325 and 425 nm.

Crystal Data Collection and Refinement: Crystal data for the two crystals are given in Table 3. 4080 and 4289 independent reflections were collected for Compound **2** and **1**, respectively, with Mo-K_α radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CrysAlis program.[24] The structures were solved by direct methods with the Shelxs97 program.[25] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times (1.5 times for methyl groups) those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program.[26] The structures were refined on F^2 using Shelxl97[25] to R_1 0.0333, 0.0414; wR_2 0.0835, 0.0941 for 3102, 2478 reflections with $I > 2\sigma(I)$.

Table 3. Crystal data and structure refinement of complexes **1** and **2**.

	1	2
Empirical formula	$C_{26}H_{36}Fe_2N_6O_4S_2$	$C_{22}H_{30}Fe_2N_{16}O_2$
M_r [g mol^{-1}]	672.42	662.32
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	13.1267(2)	11.0863(9)
b [Å]	9.3627(8)	10.9650(14)
c [Å]	13.6752(2)	12.1782(17)
β [°]	118.602(8)	107.868(11)
V [Å^3]	1475.6(3)	1409.0(3)
Z	2	2
D_c [g cm^{-3}]	1.513	1.561
μ [mm^{-1}]	1.167	1.083
F(000)	700	684
R(int)	0.0516	0.0501
Total reflections	9960	9647
Unique reflections	4289	4080
$I > 2\sigma(I)$	3102	2478
R1, wR2	0.0333, 0.0835	0.0414, 0.0941
T [K]	150(2)	150(2)

CCDC-819886 (for **1**) and -819887 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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