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An Unprecedented Trinuclear Structure Involving Two High-Spin and One Spin-Crossover Iron(II) Centers

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Anaerobic reaction of ferrous thiocyanate with the deprotonated form of the pentadentate dinucleating Schiff base 1,3-bis[(2-pyridylmethyl)imino]propan-2-ol (LH) yields the novel trinuclear $[Fe_3L_2(NCS)_4(H_2O)]$ species **1**. LH results from the bis-condensation of 2-acetyl-pyridine with 1,3-diaminopropan-2-ol and includes an N_4O donor set. The X-ray crystal structure of **1** [$C_{38}H_{40}N_{12}O_3S_4Fe_3$, triclinic, space group *P*-1; $a = 10.7730(10)$ Å, $b = 12.2048(14)$ Å, $c = 19.0559(19)$ Å, $\alpha = 76.908(12)°$, $\beta = 89.106(12)°$, $\gamma = 79.637(12)°$, $V = 2399.8(4)$ Å^3] can be described either as a bent linear arrangement of ferrous centers pairwise bridged through the alkoxo oxygen atom of L^- or as a triangular Fe^{II}_3 core with an Fe2–SCN–Fe3 bridge as the longer side of the Fe1–Fe2–Fe3 triangle. The metric parameters characterizing the ligand environments of the three ferrous centers in **1** and its Mössbauer spectra show that this unprecedented trinuclear structure involves two high-spin (Fe2 and Fe3) and one spin-crossover (Fe1) Fe^{II} centers. The donor set to the spin-crossover center (Fe1) is unprecedented: two $N_{pyridine}$, two N_{imine}, and two O_{alkoxo}. Weak antiferromagnetic interactions transmitted through the *end-to-end* NCS bridge and/or through the O1–Fe1–O2 bridge operate between Fe2 and Fe3.

Introduction

The recent impetus in the search for new spin-crossover (SCO) materials stems from the potential interest of such bistable molecular species (molecular switches) in further miniaturization of electronic devices, i.e., molecular electronics and spintronics.[1] SCO materials based on discrete polynuclear ferrous complexes are scarce and most often limited to dinuclear[2] or trinuclear[3] species, although a tetranuclear SCO compound has recently been reported.[4] The iron ligand environment of Fe^{II} SCO materials is overwhelmingly of the N_6 type.[5] However, very few exceptions have been reported that deserve an extensive exploration of the ability of different types of donor sets to generate SCO materials with remarkable properties: five-coordinate Fe^{II} compounds with NP_2I_2 and NP_2IN_{NCS} donor sets exhibit unusual spin transitions,[6] one six-coordinate Fe^{II} compound with a P_4Cl_2 donor set also exhibits SCO,[7] and one six-coordinate Fe^{II} compound with a N_4O_2 donor set (two N_{amine}, two N_{imine}, and two $O_{phenoxo}$) exhibits a two-step spin transition with hysteresis.[8] In this article, we report on an

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unprecedented trinuclear structure involving two high-spin (HS) and one SCO iron(II) centers; the ligand environment of the latter is of N_4O_2 type: two $N_{pyridine}$, two N_{imine}, and two O_{alkoxo}.

Experimental Section

Materials. All chemicals, unless otherwise stated, were commercially available and were used as received. Ferrous thiocyanate was prepared in methanol with a method adapted from Erickson et al.[9] Solvents were analytically pure and were deoxygenated prior to use.

Synthesis. $Fe_3L_2(SCN)_4(H_2O)$, 1. 2-Acetylpyridine (484 mg, 4 mmol) was slowly added under stirring to a methanolic solution (30 mL) of 1,3-diaminopropan-2-ol (180 mg, 2 mmol). The resulting colorless solution was stirred for 1 h, and 108 mg (2 mmol) of freshly prepared sodium methanolate were added to deprotonate the central alcoholic function of 1,3-bis[(2-pyridylmethyl)imino]-propan-2-ol (LH). The reaction mixture was stirred for an additional 1 h. To the resulting light brown LNa solution was slowly added a methanolic solution (30 mL) of ferrous thiocyanate (3 mmol). The reaction mixture, which immediately turned deep blue, was stirred for an additional 1 h, was then allowed to stand for 2 days, and was finally filtered. Deep blue crystals were obtained after allowing slow evaporation of the filtrate for a few days. Yield: 400 mg, 39%. Anal. Calcd for $Fe_3L_2(SCN)_4(H_2O)$ ($C_{38}H_{40}N_{12}O_3S_4Fe_3$): C, 45.25; H, 4.00; N 16.67; S, 12.71; Fe, 16.61. Found: C, 45.37; H, 3.71; N, 16.02; S, 12.55; Fe, 16.54. IR (KBr pellet, cm^{-1}): ν(O−H), 3435 (m, br); $\nu(C{\equiv}N)_{NCS}$, 2052(vs); $\nu(C{=}N)_{imine}$, 1647(s), 1595 (s); $\nu(C{=}S)_{NCS}$, 745 (m); π(C−H), 778 (s); δ(NCS), 480 (w).

Crystallographic Data Collection and Structure Determination of 1. Single-crystal X-ray data collection was carried out at 180(2) K on a Stoe Imaging Plate Diffraction System (IPDS) using graphite-monochromated Mo Kα radiation and equipped with an Oxford Cryostream Cooler Device. Final unit cell parameters were obtained by least-squares refinement of the setting angles of a set of 5000 reflections [$I > 10\sigma(I)$]. The crystal decay was monitored by measuring 200 reflections per image. No significant fluctuations of diffracted intensities were observed during the measurements. A total of 22941 reflections (8635 independent) were collected; 5257 observed reflections ($R_{int} = 0.0673$) were used in the refinements. The structure was solved by direct methods using the SHELXS-97 program[10] and refined by least-squares procedures on F_o^2 with SHELXL-97[11] by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are, respectively, the observed and calculated structure factors. The atomic scattering factors were taken from the standard compilation.[12] All atoms were located on difference Fourier maps. All non-hydrogen atoms were refined anisotropically; H atoms (riding model) were refined isotropically. Weighted R factors, wR, and goodness of fit, S, are based on F_o^2; conventional R factors, R, are based on F_o, with F_o set to zero for negative F_o^2. Drawings of the molecule were performed with the program ZORTEP[13] with 50% of probability displacement ellipsoids for non-hydrogen atoms. Crystal data collection and refinement parameters are reported in Table 1, and selected bond distances are gathered in Table 2.

Table 1. Crystallographic Data for $[Fe_3L_2(NCS)_4(H_2O)]$, **1**

formula	$C_{38}H_{40}N_{12}O_3S_4Fe_3$	fw	1026.65
space group	$P\bar{1}$ (No. 2)	temp, K	180(2)
a, Å	10.7730(10)	α, deg	76.908(12)
b, Å	12.2048(14)	β, deg	89.106(12)
c, Å	19.0559(19)	γ, deg	79.637(12)
V, Å^3	2399.8(4)	Z	2
λ, Å	0.71073	ρ_{calcd}, g cm^{-3}	1.421
μ(Mo Kα), cm^{-1}	1.075	$R_{(obs,all)}{}^a$	0.0584, 0.0761
$wR_{(obs,all)}{}^b$	0.1225, 0.1283		

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

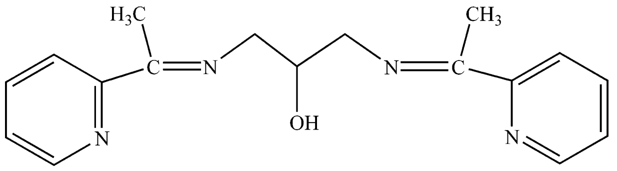
Physical Measurements. Microanalyses for C, H, N, and S were performed by the Microanalytical Laboratory of the Laboratoire de Chimie de Coordination at Toulouse and at the Service Central de Microanalyses du CNRS in Vernaison, France, for Fe. Infrared spectra (4000−400 cm^{-1}) were recorded as KBr disks on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Mössbauer measurements were recorded on a constant-acceleration conventional spectrometer with a 50 mCi source of ^{57}Co (Rh matrix). The absorber was a powdered sample enclosed in a 20-mm-diameter cylindrical, plastic sample holder, the size of which had been determined to optimize the absorption. Variable-temperature spectra were obtained in the 80−300 K range, by using a MD 306 Oxford cryostat, the thermal scanning being monitored by an Oxford ITC4 servocontrol device (±0.1 K accuracy). A least-squares computer program[14] was used to fit the Mössbauer parameters and determine their standard deviations of statistical origin (given in parentheses). Isomer shift values (δ) are relative to iron foil at 293 K. Variable-temperature (2−300 K) magnetic susceptibility data were collected on a powdered microcrystalline sample with a Quantum Design MPMS SQUID susceptometer. Data were corrected with the standard procedure for the contribution of the sample holder and for diamagnetism of the sample.

Results and Discussion

Synthesis. $[Fe_3L_2(NCS)_4(H_2O)]$, **1**, results from the anaerobic reaction of ferrous thiocyanate with the deprotonated form of the pentadentate dinucleating Schiff base 1,3-bis-[(2-pyridylmethyl)imino]propan-2-ol (LH, Chart 1) including a N_4O donor set and resulting from the bis-condensation of 2-acetyl-pyridine with 1,3-diaminopropan-2-ol.

The adjacent five-membered −Fe−N−C−C−O− metallacycles resulting from the bridging of two Fe^{II} cations by the binucleating L^- ligand preclude the presence of an additional monatomic bridge, and the absence of potential triatomic bridge such as carboxylate does not allow formation of dinuclear species similar to those previously described for related pentadentate Schiff bases with N_4O donor sets (1,4-bis{[2-pyridyl(1-ethyl)imino]}butane-2-ol and 1,5-bis-{[2-pyridyl(1-ethyl)imino]}pentane-3-ol).[15] The 3:2 Fe/L^-

Chart 1. Pentadentate Dinucleating Schiff Base 1,3-Bis[(2-pyridylmethyl)imino]propan-2-ol (LH)



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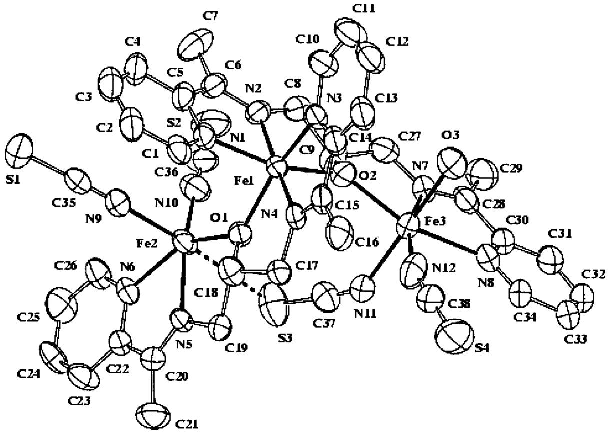

Figure 1. ORTEP view of $[Fe_3L_2(NCS)_4(H_2O)]$, **1** with atom numbering scheme showing 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) for $[Fe_3L_2(NCS)_4(H_2O)]$, **1**

bond	length (Å)	bond	length (Å)
Fe1−N1	2.054(4)	Fe1−N2	1.991(3)
Fe1−N3	2.046(4)	Fe1−N4	1.977(4)
Fe1−O1	2.022(3)	Fe1−O2	1.992(3)
Fe2−N5	2.108(3)	Fe2−N6	2.215(3)
Fe2−N9	2.106(5)	Fe2−N10	2.031(4)
Fe2−O1	2.022(3)	Fe2−S3	3.063(2)
Fe3−N7	2.123(5)	Fe3−N8	2.244(4)
Fe3−N11	2.161(4)	Fe3−N12	2.074(5)
Fe3−O2	2.044(3)	Fe3−O3	2.210(4)

stoichiometry then allows better satisfaction of the iron coordinative requirement, and the resulting trinuclear species is further stabilized through pseudo-cyclization involving an *end-to-end* NCS^- anion.

Molecular Structure of 1. The X-ray crystal structure of $[Fe_3L_2(NCS)_4(H_2O)]$ at 180 K (Figure 1) can be described either as a bent linear arrangement of ferrous centers pairwise bridged through the alkoxo oxygen atom of L^- (Fe1−O1−Fe2, 129.7°; Fe1···Fe2, 3.660 Å; Fe1−O2−Fe3, 130.4°; Fe1···Fe3, 3.665 Å) or as a triangular Fe^{II}_3 core, provided that the Fe2···S3 interaction (3.063 Å, N9−Fe2−S3 = 174.4°) can be regarded as a weak bond yielding an Fe2−SCN−Fe3 bridge as the longer side (5.642 Å) of the Fe1−Fe2−Fe3 triangle (Figure 1).

This *end-to-end* thiocyanato bridging mode has already been observed, with corresponding M−S distances either in the 2.6−2.9 Å range[16] or in the longer 3.11−3.18 Å range,[15] the latter suggesting weak Fe···S interactions rather than the covalent bonding suggested by the former. The intermediate 3.063 Å value observed for $[Fe_3L_2(NCS)_4(H_2O)]$ is close to the lower limit for weak Fe···S interactions, preventing us from qualifying this Fe2···S3 interaction as a covalent bonding.

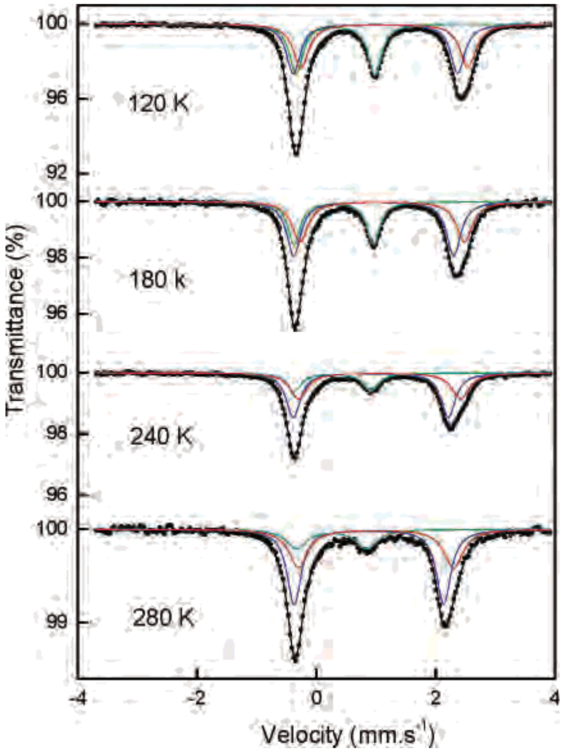

Figure 2. Representative least-squares-fitted Mössbauer spectra of $[Fe_3L_2(NCS)_4(H_2O)]$, **1**.

The three coordination polyhedra have distinct and unique features: the distorted octahedron around Fe1 involves two $N_{pyridine}$, two N_{imine}, and two O_{alkoxo}, one of each from each L^- ligand; the distorted pseudo-octahedron around Fe2 involves one $N_{pyridine}$, one N_{imine}, two $N_{thiocyanato}$, one O_{alkoxo}, and one $S_{thiocyanato}$; the distorted octahedron around Fe3 involves one $N_{pyridine}$, one N_{imine}, two $N_{thiocyanato}$, one O_{alkoxo}, and one O_{aquo}. Whereas the donor sets to Fe1 and Fe3 are of the N_4O_2 type, although different, the donor set to Fe2 is of the uncommon $N_4O(S)$ type. All Fe-donor atom distances around Fe1 are in the 1.977(4)−2.054(4) Å range (average 2.014 Å), indicating a prevailing LS state for this Fe^{II} ion at 180 K, the temperature at which the single-crystal X-ray data were collected. The larger Fe-donor atom distances around Fe2 (average for N_4O donor set, 2.096 Å; average for $N_4O(S)$ donor set, 2.258 Å) and Fe3 (average 2.143 Å) are indicative of HS states for these two Fe^{II} ions at 180 K.

Mössbauer Spectroscopy. The Mössbauer spectra of ground crystals of **1** (80−300 K) were unambiguously fitted to two staggered HS and one LS quadrupole split doublets (Figure 2), provided that the area ratio of the HS doublet corresponding to the Fe2 site [$N_4O(S)$ donor set, isomer shift $\delta = 1.160(3)$ mm/s, quadrupole splitting $\Delta E_Q = 2.808(6)$ mm/s at 80 K] was set to one-third at all temperatures. Although the molecular structure evidences different donor sets for the three Fe^{II} centers, the Mössbauer spectra could not be fitted to three HS and one LS doublets. Actually, the minute difference in nature of the donor atoms, and in symmetry of their arrangement, between the N_4O_2 donor sets to Fe1 and Fe3 (see Molecular Structure subsection) does not allow Mössbauer spectroscopy to distinguish HS Fe1 from Fe3. At 80 K, the parameters of the LS site are δ(LS)

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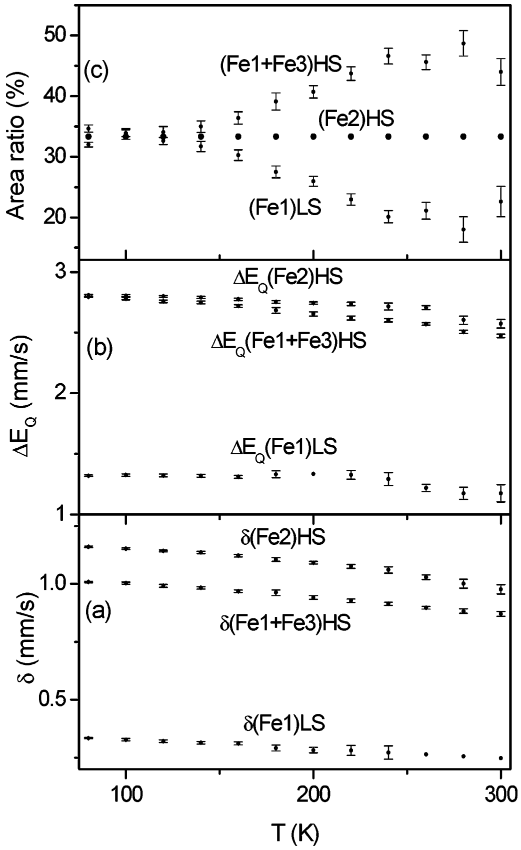

Figure 3. Temperature dependence of (a) the isomer shift, (b) the quadrupole splitting, and (c) the area ratio of the Fe^{II} sites of complex **1**.

$= 0.334(3)$ mm/s and $\Delta E_Q(LS) = 1.320(7)$ mm/s, and the parameters of the HS site corresponding to Fe1 and Fe3 are $\delta(HS) = 1.008(4)$ mm/s and $\Delta E_Q(HS) = 2.795(6)$ mm/s.

The mirror variations in area ratios (toward one-third) of the two latter Fe^{II} sites between values close to 33% LS and 33% HS in the 80−120 K range and values close to 20% LS and 47% HS in the 240−300 K range clearly indicate that an incomplete SCO occurred in the 120−240 K range at either Fe1 or Fe3 (Figure 3). In view of the structural information gained at 180 K, it was then obvious that Fe1 is the SCO site in this trinuclear ferrous species. It is worth noting that the donor set to Fe1 (two $N_{pyridine}$, two N_{imine}, two O_{alkoxo}) is quite similar to that evidenced in the previously reported SCO compound with a N_4O_2 donor set[8] (two N_{amine}, two N_{imine}, two $O_{phenoxo}$): indeed, the increase in ligand field strength expected for the change from two N_{amine} to two $N_{pyridine}$ is approximately compensated by the decrease in ligand field strength expected for the change from two $O_{phenoxo}$ to two O_{alkoxo}.

Taking into account all observed iron sites, the overall HS area ratio is included between ∼66% (below 120 K) and ∼80% (above 240 K). The ∼33% contribution for LS Fe^{II} in the range 80−120 K is remarkable, given that the Lamb−Mössbauer factor for LS Fe^{II} is usually larger than that for HS Fe^{II} {the Lamb−Mössbauer factor depends on the product $(m_{eff})^{1/2}\Theta_D$, i.e., it involves both the lattice [$\Theta_D(LS) > \Theta_D(HS)$] and the bond strength [$m_{eff}(LS) > m_{eff}(HS)$] effects}.[17] The SCO of Fe1 is thus most probably incomplete not only at high temperature, but also at low temperature. On the other hand, at high temperature, the SCO goes further than the ∼80% indicated by the nonweighted Mössbauer intensities.

Magnetic Properties. Magnetic susceptibility measurements were carried out on ground crystals of **1** (2−300 K) in an applied field of 1 T. The product $\chi_M T$ of **1** decreases smoothly from 8.7 $cm^3\ mol^{-1}$ K at 300 K to 4.0 $cm^3\ mol^{-1}$ K at 12 K. Below 12 K, it decreases rapidly to 2.2 $cm^3\ mol^{-1}$ K at 2 K as a result of zero-field splitting effects. As expected from the Mössbauer study, the 8.7 $cm^3\ mol^{-1}$ K value at 300 K is below the spin-only value for three noninteracting $S = 2$ metal centers (9.0 $cm^3\ mol^{-1}$ K), but accounts for less than ∼20% of the value for $S = 0$ centers: (i) the $^5T_2$ ground state of HS Fe^{II} is split by the ligand field and spin−orbit coupling, yielding levels separated by energies on the order of kT (thermally populated in the high-temperature range), which result in larger and slightly temperature-dependent magnetic moments in the high-temperature range,[18] and (ii) at high temperature, the SCO goes further than the ∼80% indicated by the nonweighted Mössbauer intensities (see Mössbauer Spectroscopy subsection). With 33% of LS Fe^{II} centers below 120 K, a $\chi_M T$ value of 6.0 $cm^3\ mol^{-1}$ K would be expected for two noninteracting $S = 2$ metal centers. For the reasons mentioned above in i and ii, the 6.6 $cm^3\ mol^{-1}$ K value measured at 120 K is in slight excess of this spin-only value. However, the continuous smooth decrease below 120 K, leading to 4.0 $cm^3\ mol^{-1}$ K at 12 K, indicates operation of antiferromagnetic interactions between the Fe^{II} centers of this trinuclear species. Considering the molecular structure of **1**, this observation made between 120 and 12 K, the temperature range in which Fe1 is essentially in the $S = 0$ (LS) state, implies that the magnetic interactions involve almost exclusively Fe2 and Fe3 and that they are transmitted by the *end-to-end* NCS bridging anion and/or through the O1−Fe1−O2 bridge.

Conclusions

The X-ray crystal structure of $[Fe_3L_2(NCS)_4(H_2O)]$, **1**, is better described as a triangular Fe^{II}_3 core with an Fe2−SCN−Fe3 bridge as the longer side of the Fe1−Fe2−Fe3 triangle. This novel asymmetrical trinuclear ferrous structure includes two high-spin centers, Fe2 [$N_4O(S)$ donor set] and Fe3 (N_4O_2 donor set), and one spin-crossover center, Fe1, with an unprecedented donor set: two $N_{pyridine}$, two N_{imine}, and two O_{alkoxo}. Although Mössbauer spectroscopy does not distinguish HS Fe1 from Fe3, because of their similar N_4O_2 donor sets, the ligand field generated by the donor set to Fe1 (see

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above) is large enough to locate Fe1 in the SCO range, whereas the ligand field generated by the donor set to Fe3 ($N_{pyridine}$, N_{imine}, two $N_{thiocyanato}$, O_{alkoxo}, and O_{aquo}) is lower, because of the thiocyanato ligands, and stabilizes the HS state of Fe3. The variation in LS area ratio from ∼33% in the 80−120 K range to ∼20% in the 240−300 K range clearly indicates occurrence of a smooth and incomplete SCO at Fe1 in the 120−240 K range. A likely explanation to this smooth and incomplete SCO is that the Fe1 SCO sites are isolated from each other: indeed, not only do they constitute solely one-third of the overall Fe^{II} sites, but also no significant intermolecular interactions were observed between the trinuclear species in this material. The magnetic study shows that, in addition to the $Fe1_{HS}\cdots Fe2$ and $Fe3\cdots Fe1_{HS}$ superexchange interactions operating only at temperatures where the percentage of HS Fe1 is not negligible, weak antiferromagnetic interactions operate between Fe2 and Fe3 through the *end-to-end* NCS bridging anion and/or the O1−Fe1−O2 bridge.

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Supporting Information Available: Mössbauer parameters obtained from fitting the Mössbauer spectra (80−300 K) of complex **1** (Table SI-1). Magnetic data (Table SI-2) and temperature dependence of the $\chi_M T$ product (Figure SI-1). X-ray crystallographic file of $[Fe_3L_2(SCN)_4(H_2O)]$, **1**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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