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Crystal Structure, Magnetic Properties, and ^{57}Fe Mössbauer Spectroscopy of the Two-Dimensional Coordination Polymers [M(1,2-bis(1,2,4-triazol-4-yl)ethane)$_2$(NCS)$_2$] (M^{II} = Fe, Co)

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New coordination polymers of the formula [M(btre)$_2$(NCS)$_2$] (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane; M^{II} = Fe, Co) have been synthesized, and their crystal structures have been determined at 293 K by X-ray analysis. The Fe^{II} compound ($C_7H_8FeN_7S_2$) crystallizes in the monoclinic space group $P2_1/n$, $a = 12.439(5)$ Å, $b = 8.941(2)$ Å, $c = 9.321(3)$ Å, $\beta = 90.88(2)°$, $V = 1036.6(6)$ Å^3, $Z = 2$, 3791 reflections [$I > 3\sigma(I)$], $R_F = 0.036$, wR2 = 0.123. The Co^{II} compound is isostructural to the Fe^{II} compound. The crystal structure consists of a 2D sheet in which the metal ions are linked by bis monodentate (*N1*, *N1′*) 1,2,4-triazole ligands. The structure is stabilized by π-bond interactions between two adjacent sheets and by S···S interactions. Temperature-dependent SQUID, ^{57}Fe Mössbauer, and X-ray diffraction measurements indicate that [Fe(btre)$_2$(NCS)$_2$] retains a HS ground state upon cooling from 293 K down to 8 K. The surprising absence of spin-crossover behavior for this Fe(II)–1,2,4-triazole polymeric coordination compound that has been confirmed by pressure experiments up to ~12 kbar and by light irradiation experiments at 10 K is discussed on the basis of its structural features. Insight into the origin of the cooperative effects of the spin transition in [Fe(btr)$_2$(NCS)$_2$]·H$_2$O (btr = 4,4′-bis-1,2,4-triazole) is also given thanks to a re-evaluation of its distortion parameters in the high- and low-spin states.

Introduction

There is a growing interest in the design and crystal engineering of new coordination polymers because these attractive materials can exhibit many interesting catalytic, electrical, magnetic, optical, and porous properties.[1] Many synthetic efforts have been devoted to the increase and control of the lattice dimensionality working with bis (monodentate) ligands with nitrogen donor atoms, such as pyridine, pyrazine, etc, leading to extended coordination networks with various topologies.[2−4]

Working with bis(polydentate) ligands with azole units leads to Fe^{II} coordination polymers with cooperative spin-crossover (SCO) properties.[5,6] Indeed, linking metal centers with bridging ligands can allow the molecular distortions associated with the spin-state change of the isolated ions to be self-propagated throughout the crystal lattice,[7] provided these ligands act as efficient elastic information transmitters. Along this line, the study of the mechanical character of the

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(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.

(2) Batten, S. R.; Robson, R. In *Molecular Catenanes, Rotaxanes and Knots: A Journey Through the World of Molecular Topology*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, Germany,1999; p 77.

(3) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91.

(4) Yaghi, O. M.; O'Keefe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(5) (a) Haasnoot, J. G. In *Magnetism: A Supramolecular Function*; Kahn O., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; p 299. (b) Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *200/202*, 131.

(6) Garcia, Y.; Niel, V.; Muñoz, M. C.; Real, J. A. *Top. Curr. Chem.* **2004**, *233*, 229.

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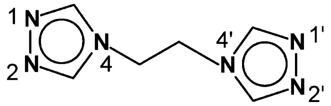
Scheme 1. 1,2-bis(1,2,4-triazol-4-yl)ethane) (btre)



active sites spacer is of particular interest for controlling cooperative effects in these materials. The coordination polymer *trans*-[Fe(btr)$_2$(NCS)$_2$]$\cdot$H$_2$O (btr = 4,4′-bis-1,2,4-triazole) exhibits exceptional spin transition properties[8] that were attributed to its 2D character[7] since no crystallographic phase transition was identified in the high-spin (HS) and low-spin (LS) states.[9] The introduction of an ethane spacer between the 1,2,4-triazole subunits should provide a more flexible link between the Fe^{II} ions while the 2D structural character is maintained. Indeed, a flexible network was revealed in the crystal structure of the 3D Cu^{II} coordination polymer, [Cu$_3$(btre)$_5$(H$_2$O)$_2$](ClO$_4$)$_6\cdot$H$_2$O, made of trinuclear metallic units interconnected by btre ligands. The flexibility of btre (1,2-bis(1,2,4-triazol-4-yl)ethane, Scheme 1) allowed the tridentate and tetradentate coordination mode to be observed, for the first time, for a bis-1,2,4-triazole coordination compound.[10]

We report here on the crystal structure of the new compounds [M(btre)$_2$(NCS)$_2$] with M^{II} = Fe (**1**), Co (**2**) and compare the spectroscopic, structural, and magnetic properties of compound **1** under several perturbations (temperature, pressure, and light irradiation) in the light of the ones of [M(btr)$_2$(NCS)$_2$]$\cdot$H$_2$O with M^{II} = Fe (**3**)[8] and Co (**4**)[11] and [Fe(btr)$_2$(NCS)$_2$] (**5**).[8]

Experimental Section

Physical Measurements. Elemental analyses were performed by the Service Central d'Analyse (CNRS) in Vernaison, France. Melting point determinations were done on a Kolfer bench. Infrared spectra were collected on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer using KBr pellets. UV−vis spectra were recorded with a CARY 5E spectrophotometer using the diffuse reflectance technique with poly(tetrafluoroethylene) as a reference. Magnetic susceptibilities were measured in the temperature range of 2−300 K using a Quantum design MPMS-5S SQUID magnetometer and on the temperature range of 5−300 K under hydrostatic pressure using a Foner-type magnetometer (Princeton Applied Research 151) equipped with a Bruker electromagnet operating at 1 T and a CryoVac liquid helium cryostat. A prototype of the actual construction of the hydrostatic high-pressure cell made of hardened beryllium bronze with silicon oil as a pressure transmitting medium operating in a range of pressure up to 13 kbar was described elsewhere.[12] The accuracy of the pressure cell is 0.25 kbar, and the nonhydrostaticity of pressure is less than 0.5 kbar.[13] The dimensions of the cylindrically shaped powder sample holder are 1 mm in diameter and 5−7 mm in length. The pressure was calibrated using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of 99.99% tin. Magnetic data were corrected for diamagnetic contributions, which were estimated from Pascal's constants. ^{57}Fe Mössbauer spectra were recorded in transmission geometry with a constant-acceleration conventional spectrometer. The samples were sealed in a Plexiglas sample holder and mounted in a helium-bath cryostat. The ^{57}Co(Rh) source was kept at 4.2 K. The spectra were fitted using Recoil 1.03a Mössbauer Analysis Software.[14]

Materials for Syntheses. Monoformylhydrazine, triethyl orthoformate, ethylenediamine, Co(SO$_4$)$\cdot$7H$_2$O, Fe(NH$_4$)$_2$(SO$_4$)$_2\cdot$6H$_2$O, and NH$_4$NCS were used as received without further purification. Methanol was dried with Mg(OMe)$_2$ prior to distillation.

Synthesis of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre). The btre ligand was prepared according to the general method adapted from Bayer.[15] Monoformyl hydrazine (6 g, 0.1 mol, 1 equiv) was dissolved in 200 mL of dried methanol together with 33 mL of triethyl orthoformate (0.2 mol, 2 equiv). The mixture was refluxed under constant stirring for 2 h before the dropwise addition of 3.34 mL of ethylenediamine (0.05 mol, 0.05 equiv). The reaction mixture was then refluxed for 4 additional hours. A white-pink milky residue was obtained after solvent evaporation; the residue was dissolved in methanol (40 mL) and extracted with ether (145 mL). A white solid was filtered off, washed with acetonitrile, and recrystallized in MeOH to produce colorless crystals. Yield: 3.7 g (30%). mp > 260 °C. IR (KBr): ν 3439 (s), 3097 (s), 1574 (w), 1525 (s), 1459 (m), 1384 (m), 1322 (w), 1263 (w), 1219 (w), 1191 (s), 1160 (w), 1065 (s), 968 (m), 949 (w), 887 (m), 675 (m), 642 (s) cm^{-1}. ^{1}H NMR (200 MHz, D$_2$O): δ 2.67 (s, 2 H, CH$_2$), 6.40 (s, 2 H, trz-H). Anal. Calcd for C$_6$H$_8$N$_6$: C, 43.90; H, 4.91; N, 51.19. Found: C, 44.07; H, 4.39; N, 50.00.

Synthesis of [Fe(btre)$_2$(NCS)$_2$] (1). An aqueous solution (5 mL) containing 0.91 mmol (0.36 g) of Fe(NH$_4$)$_2$(SO$_4$)$_2\cdot$6H$_2$O and ~200 mg of ascorbic acid to prevent oxidation of the iron(II) ions was quickly added to a boiling solution containing 1.84 mmol (0.14 g) of NH$_4$NCS. A boiling aqueous solution (20 mL) containing 1.83 mmol (0.30 g) of btre was added dropwise to this warm solution and left to stand at room temperature. Transparent colorless single crystals crystallized overnight upon cooling. The crystals were filtered, washed with water, and dried under ambient air. Anal. Calcd for C$_{14}$H$_{16}$N$_7$S$_2$Fe: C, 33.61; H, 3.22; N, 39.19; S, 12.82; Fe, 11.16. Found: C, 33.37; H, 3.30; N, 39.22; S, 12.71; Fe, 11.06. IR data (KBr): ν 3120 (m), 3093 (s), 2999 (vw), 2952 (vw), 2860 (w), 2551 (w), 2360 (w), 2063 (vs), 1539 (s), 1522 (s), 1462 (m), 1433 (m), 1388 (s), 1370 (m), 1346 (w), 1249 (vw), 1189 (s), 1165 (s), 1069 (s), 1046 (s), 1002 (s), 964 (m), 929 (m), 895 (m), 863 (m), 796 (w), 683 (vw) 649 (m), 634 (vs), 488 (w), 477 cm^{-1} (w).

Synthesis of [Co(btre)$_2$(NCS)$_2$] (2). Ligand btre (1.40 mmol, 0.23 g) in 10 mL of water was boiled, and the mixture was added to a boiling aqueous solution (10 mL) containing 0.57 mmol (0.19

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(7) Kahn, O.; Codjovi, E.; Garcia, Y.; van Koningsbruggen, P. J.; Lapouyade, R.; Sommier, L. In *Molecule-Based Magnetic Materials*; Turnbull, M. M., Sugimoto, T., Thompson, L. K., Eds.; ACS Symposium Series 644; American Chemical Society: Washington, DC, 1996; p 298.

(8) Vreugdenhil, W.; van Diemen, J. H.; De Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; van der Kraan, A. M.; Kahn, O.; Zarembowitch, J. *Polyhedron* **1990**, *9*, 2971.

(9) (a) Garcia, Y.; Gieck, C.; Stauf, S.; Tremel, W.; Gütlich P. 4th TMR-TOSS-Meeting, Bordeaux, France, 2001. (b) Pillet, S.; Hubsch, J.; Lecomte, C. *Eur. Phys. J. B* **2004**, *38*, 541.

(10) Garcia, Y.; van Koningsbruggen, P. J.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Kahn, O. *Eur. J. Inorg. Chem.* **2000**, 307 and 575.

(11) Vreugdenhil, W.; Gorter, S.; Haasnoot, J. G.; Reedijk, J. *Polyhedron* **1985**, *10*, 1769.

(12) (a) Dyakonov, V. P.; Levchenko, G. *Prib. Tekh. Eksper.* **1983**, *5*, 236. (b) Baran, M.; Dyakonov, V.; Gladczuk, L.; Levchenko, G.; Piechota, S.; Szymczak, H. *Physica C* **1995**, *241*, 383.

(13) Gaspar, A. B.; Muñoz, M. C.; Moliner, N.; Ksenofontov, V.; Levchenko, G.; Gütlich, P. *Monatsh. Chem.* **2003**, *134*, 285.

(14) Lagarec, K.; Rancourt, D. G. *Recoil, Mössbauer Spectral Analysis Software for Windows*, version 1.0; Department of Physics, University of Ottawa: Ottawa, Canada, 1998.

(15) Bayer, H. O.; Cook, R. S.; von Meyer, W. C. US Patent 3,821,376, 1974.

Table 1. Crystallographic and Refinement Data for [M(btre)$_2$(NCS)$_2$] (M^{II} = Fe, Co)

	1	**2**
formula	$C_{14}H_{16}SFeN_{14}$	$C_{14}H_{16}SCoN_{14}$
mol wt	500.4	503.46
cryst syst	monoclinic	monoclinic
space group	*P*21/*n* (No. 14)	*P*21/*n* (No. 14)
a (Å)	12.439(5)	12.444(3)
b (Å)	8.941(2)	8.9060(18)
c (Å)	9.321(3)	9.3133(19)
β (deg)	90.88(4)	90.26(3)
V (Å^3)	1036.5(1)	1032.1(4)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.603	1.620
temp (K)	295(1)	293(2)
μ (Mo Kα) (mm^{-1})	0.978	1.07
θ range (deg)	2.7−38	2.73−28.31
index ranges	$-21 \le h \le 21$, $0 \le k \le 15$, $-1 \le l \le 16$	$-14 \le h \le 16$ $-11 \le k \le 9$ $-8 \le l \le 12$
measured reflns	6528	6593
independent reflns	5635	2561
R_{int}	0.009	0.0466
params	143	142
GOF on F^2	0.918	0.971
R values^a ($I > 3\sigma(I)$)	R1 = 0.036 wR2 = 0.097	R1 = 0.0418 wR2 = 0.0812
R values^a (for all data)	R1 = 0.066 wR2 = 0.123	R1 = 0.0933 wR2 = 0.0948

^{a} $R1 = \Sigma||F_{obsd}| - |F_{calcd}||/\Sigma|F_{obsd}|$ for observed reflections, $wR2 = [\Sigma\ wF_{obsd}^2 - F_{calcd}^2)^2/\Sigma wF_{obs}^2]^{1/2}$, $w = 1/(\sigma^2(F_{obs}^2) + 0.03F^2)$, $F = (2F_{obs} + F_{calc})/3$.

g) of $Co(SO_4)_2 \cdot 7H_2O$ and 1.31 mmol (0.10 g) of NH_4NCS. An orange-pink precipitate, which appeared immediately, was filtered off and discarded. Small orange single crystals appeared in the filtrate solution when it had stood at room temperature for ~3 weeks. These were filtered and dried under ambient air.

X-ray Crystallography. The crystal data and the details of data collection and refinement for compounds **1** and **2** are given in Table 1.

[Fe(btre)$_2$(NCS)$_2$] (1). A colorless crystal 0.65 × 0.45 × 0.20 mm was mounted on an ENRAF-NONIUS CAD4 diffractometer and analyzed at 295(1) K using the monochromated Mo Kα X-ray radiation (λ = 0.7069 Å). The unit-cell parameters were obtained by least-squares refinement from 25 centered reflections in the range of $11.5° \le \theta \le 16.0°$. The intensities of three standard reflections monitored every 2 h revealed no significant decay over the course of data collection. A semi-empiric correction of absorption, based on ψ scans of three axial reflections, was applied.[16] The structure was solved by direct methods with the program MITHRIL.[17] Structure refinement based on F^2 was carried out by the full-matrix method. The locations of hydrogen atoms were generated geometrically (C−H = 1.0 Å) and included in the refinement with an isotropic fixed thermal parameter. All non-hydrogen atoms were refined with anisotropic thermal parameters. Neutral atom scattering factors were taken from the International Tables for Crystallography.[18] A final difference Fourier map showed a residual density of 1.69 e Å^{-3}. Calculations were carried out using programs written or modified locally.

A single crystal of [Fe(btre)$_2$(NCS)$_2$] was also investigated in the temperature range between 10 and 300 K with a four-circle Huber diffractometer using a two-stage closed-cycle helium low-temperature attachment (CTI-Cryogenics) with a beryllium cap. The temperature was controlled to within 0.1 K. For measurements of the lattice parameters a Schneider rotating anode with Cu Kα radiation monochromatized with a "side-by-side" confocal OSMIC multilayer monochromator,[19] which is a modification of the classical Kirkpatrick−Baer focusing optics, has been used. The Huber diffractometer was controlled by a PC computer using STOE STADI4 software. Precise lattice parameters were obtained by measuring about 60 strong reflections with high 2θ values on both sides of the primary beam. The ω scans were carried out for $+2\theta$ and -2θ. From the center of gravity of both scans, the $+2\theta$ values were determined to be the difference of the two ω centers. These results are free of zero-offset errors.[20] The absorption effects are the same for both ω scans. The use of Friedel pairs (*hkl* and $-h$ $-k$ $-l$) also eliminates systematic errors, which stem from miscentering of the crystal. Red-light irradiation was carried out with a He−Ne laser (~2 mW).

[Co(btre)$_2$(NCS)$_2$] (2). An orange crystal (0.10 × 0.20 × 0.001 mm) was embedded in a thin film of epoxy glue and fixed at the tip of a glass fiber on a Bruker SMART CCD diffractometer equipped with a monochromated Mo Kα source (λ = 0.71073 Å) and a graphite monochromator. The crystal to detector distance was 5 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in ω in groups of 600 frames at φ settings of 0, 120, and 240°. The exposure time was 30 s/frame. The collection of the intensity data was carried out with the program SMART.[21] Cell parameters were initially calculated from reflections taken from approximately 30 frames of reflections. The final lattice parameters were calculated from all reflections observed in the actual data collection. These data were processed using the SAINT program[22] and corrected for absorption using SADABS.[23] The structure was solved using direct methods, which revealed the atomic positions, and refined using the SHELXTL 5.1 program package.[24] The positions of the H atoms were generated geometrically and included in the refinement with an isotropic fixed thermal parameter. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinements were carried out on F_o^2. Atomic scattering factors for spherical neutral free atoms were taken from standard sources, and anomalous dispersion corrections were applied.[18] Calculations performed at an intermediate stage, in which the relative positional occupancies were refined, did not indicate any nonstoichiometry.

Results

Description of the Crystal Structure of [M(btre)$_2$(NCS)$_2$] (M^{II} = Fe, Co). An ORTEP plot of the asymmetric unit is represented in Figure 1, and relevant information on the bond lengths and angles is given in Table 2. [M(btre)$_2$(NCS)$_2$] (M^{II} = Fe (**1**), Co (**2**)) crystallizes in the space group $P2_1/n$. The asymmetric unit contains one NCS^- anion, one

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(16) North, A. C. T.; Phillips, D. C.; Mathew, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(17) Gilmore, C. J.; Brown, S. R. *J. Appl. Cryst.* **1988**, *21*, 571.

(18) *International Tables for Crystallography*; Wilson, A. J. C., Prince, E., Eds.; Kluwer Academic Publishers: Norwell, MA, 1999; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(19) *Max-Flux Beam-Conditioning Optics Assembly*; Osmic, Inc.: Troy, MI, 1997.

(20) *STADI4 Software Manual*; Stoe and Cie: Darmstadt, Germany, 1995.

(21) *SMART*, 5th ed.; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(22) *SAINT*, 4th ed.; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(23) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1997.

(24) Sheldrick, G. M. *SHELXTL*, version 5.1; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1998.

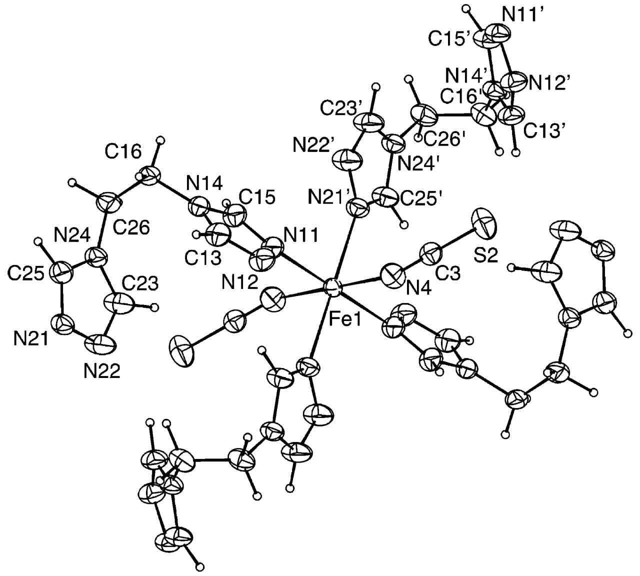

Figure 1. ORTEP view of the asymmetric unit of [Fe(btre)$_2$(NCS)$_2$] with 50% probability ellipsoids. Atoms marked with a quote are generated by the $-1/2 + x$, $3/2 - y$, $1/2 + z$ *n*-glide symmetry. No labeled atoms are generated by the center of symmetry at 1/2, 1/2, 1/2 from the first ones.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [Fe(btre)$_2$(NCS)$_2$] [a]

Fe(1)−N(4)	2.1116(9)	C(15)−N(11)	1.304(1)
Fe(1)−N(11)	2.1910(7)	N(14)−C(16)	1.462(1)
Fe(1)−N(21)#1	2.2467(7)	C(16)−C(26)	1.515(1)
N(4)−C(3)	1.161(1)	C(26)−N(24)	1.460(1)
C(3)−S(2)	1.6210(9)	N(21)−N(22)	1.378(1)
N(11)−N(12)	1.379(1)	N(22)−C(23)	1.310(2)
N(12)−C(13)	1.304(1)	C(23)−N(24)	1.353(1)
C(13)−N(14)	1.352(1)	N(24)−C(25)	1.349(1)
N(14)−C(15)	1.354(1)	C(25)−N(21)	1.307(1)
Fe(1)−Fe(1)#1	9.015(3)		
N(4)−Fe(1)−N(11)	91.83(3)	Fe(1)−N(4)−C(3)	151.05(8)
N(4)−Fe(1)−N(21)#1	86.68(3)	N(4)−C(3)−S(2)	179.37(9)
N(21)#1−Fe(1)−N(11)	90.17(3)		
Fe(1)−N(11)−N(12)	124.83(6)		
Fe(1)−N(11)−C(15)	126.46(6)		
C(15)−N(11)−N(12)	107.88(7)	C(25)−N(21)−N(22)	107.61(8)
N(11)−N(12)−C(13)	106.03(8)	N(21)−N(22)−C(23)	106.12(9)
N(12)−C(13)−N(14)	111.38(8)	N(22)−C(23)−N(24)	111.2(1)
C(13)−N(14)−C(15)	104.54(7)	C(23)−N(24)−C(25)	104.61(8)
N(14)−C(15)−N(11)	110.16(8)	N(24)−C(25)−N(21)	110.48(8)
C(13)−N(14)−C(16)	127.84(7)	C(23)−N(24)−C(26)	127.58(8)
C(15)−N(14)−C(16)	127.51(7)	C(25)−N(24)−C(26)	127.74(7)
N(14)−C(16)−C(26)	111.52(7)	C(16)−C(26)−N(24)	112.16(7)

[a] Estimated standard deviations are given in parentheses. Labeled atoms are generated by the following symmetry operation: #1 $-1/2 + x$, $3/2 - y$, $1/2 + z$.

Table 3. Bond Distances (Å) and Distortion Parameters (deg) for Compounds **1**−**4**

	T (K)	M−N (Å)	M−N(CS) (Å)	M···M (Å)	Σ (deg)	Θ (deg)	ref
1	295(1)	2.223(3)	2.11	8.94−9.01	21.2	70.2	*a*
2	293(2)	2.17(3)	2.089(3)	8.94−8.97	19.2	60.6	*a*
3	293	2.184(3)	2.125(3)	9.30(2)	14.8	40.8[a]	8
3	104.0(5)	1.971(2)	1.950(2)	8.962(5)	14.9[a]	42.3[a]	9
4	295	2.135(1)	2.098(2)	9.207(2)	16.4[a]	40.8[a]	25

[a] This work.

btre ligand, and a M^{II} cation located on the symmetry center. M^{II} (M = Fe, Co) is coordinated to two nitrogen atoms, N(11) and N(21), which belong to the two triazole groups (tr1 and tr2) of btre. The Fe−N bond lengths are ∼2.22(3) Å for **1**, and the Co−N bond lengths are ∼ 2.17(3) Å for **2**; their directions are nearly perpendicular. These M−N distances correspond to typical values for M^{II} ions in the HS state. In particular, the Fe−N distances are longer than the ones found for [Fe(btr)$_2$(NCS)$_2$]·H$_2$O (**3**) in the HS state with Fe−N = 2.184(3) Å or for the 2D HS compound [Fe(Htrz)$_2$(NCS)$_2$] (Htrz = 4-H-1,2,4-triazole) with Fe−N ≈ 2.19(2) Å.[25] The metal centers are also bound to two isothiocyanato anions located in trans to each other at distances of ∼2.11 and 2.089(3) Å for the Fe^{II} and Co^{II} complexes, respectively. These M−NCS distances are slightly lower than those for **3** and **4** in the HS state (2.125(3) and 2.098(2) Å,[8,11] respectively). The Fe−N bond makes an angle of 3.8° with the normal to the N(11)−Fe−N(21) plane and an angle of 151.05(8)° with the NCS$^-$ anion that is almost linear (179.37(9)°). Thus, because of centrosymmetry, the environment of the M^{II} cation is octahedral but slightly distorted as revealed by the HS Σ parameter[26] which is 21.2 and 19.2° for **1** and **2**, respectively. This structural parameter, defined as the sum of the deviations from 90° of the 12 *cis*-N−M−N angles, is useful to accurately evaluate the octahedral distortion of the MN$_6$ coordination sphere.[26] Interestingly, this distortion is found to be higher than it is for the relative Fe^{II} and Co^{II} 2D btr polymers with 14.8° for **3**[9b] and 16.4° for **4**. These observations are confirmed by looking at the HS Θ parameter[27] with 70.2° for **1** and 60.6 ° for **2** which are are much higher than the value found for **3** and **4** in the HS state (40.8°) (Table 3). The Θ parameter was recently introduced to account for the trigonal distortion of a MN$_6$ octahedron.[27] It is defined as the sum of the deviations from 60° of the 24 angles formed by the projections of the N−M−N angles on the octahedron faces. Pillet et al. concluded that the octahedron of the spin transition compound (**3**) is more regular in the LS state as shown by the decrease of the Σ parameter from 14.84 (HS) to 13.24° (LS).[9b] Using the published data,[9b] we found a Σ^{LS} parameter of 14.9(3)°, comparable with the reported Σ^{HS} parameter. Thus, a weak angular distortion is associated with the thermal spin state switching in **3** as confirmed by the Θ^{LS} parameter of 42.3° (Table 3) leading to an unprecedented $\Delta\Theta$ value of −1.5°.

The btre ligand presents a folded conformation around the C(16)−C(26) central bond with a torsion angle around this bond of 57.32(7)° for **1** (Figure 1) and 57.5(3)° for **2**. The tr1 [N(11)···C(15)] and tr2 [N(21)···C(25)] triazole groups make an angle of 47.90° for **1** and of 49.6° for **2**; for each ring, the deviations of the atoms to the mean planes are nearly the same. The M^{II} cations and their ligands show a 2D packing. As a result of the presence of the 2$_1$ screw axes, the [111] polymeric chains form sheets parallel to the (101) planes (Figure 2). Within a sheet, the distances between M^{II} cations are 8.94 and 9.01 Å for **1**, and 8.94 and 8.97 Å for **2**, values which are well below the intramolecular M···M

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(25) Engelfriet, D. W.; Verschoor, G. C. *Acta Crystallogr.* **1981**, *B37*, 237.

(26) Guionneau, P.; Brigouleix, C.; Barrans, Y.; Goeta, A. E; Létard, J.-F.; Howard, J. A. K.; Gaultier, J.; Chasseau, D. *C. R. Acad. Sci. Paris* **2001**, *4*, 161.

(27) Marchivie, M.; Guionneau, P.; Létard, J.-F.; Chasseau, D. *Acta Crystallogr.* **2005**, *B61*, 25.

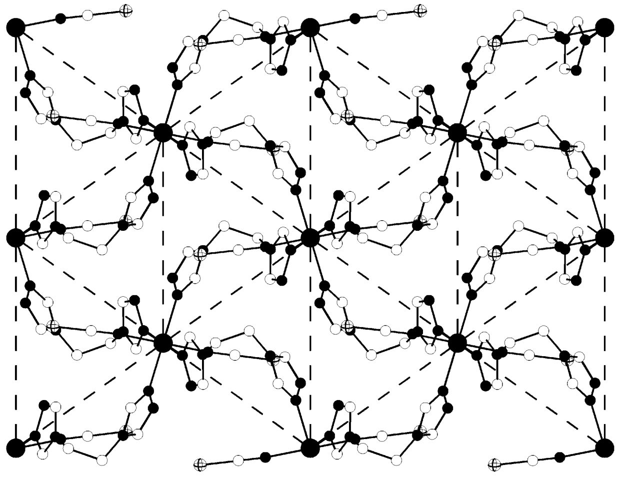

Figure 2. View of a single layer of [Fe(btre)$_2$(NCS)$_2$] along the *c* axis. Black, white, and ellipsoid-filled small spheres correspond to nitrogen, carbon, and sulfur atoms, respectively. The larger black spheres correspond to Fe^{II} ions.

distances of 9.30(2) and 9.207(2) Å found for **3** and **4**, respectively. The shortest intersheet M···M distance is 8.91 Å for [M(btre)$_2$(NCS)$_2$] (M^{II} = Co, Fe). Tiny channels are found between the layers as shown in Figure 3.

The nearest MN$_6$ coordination octahedra are tilted by 21.5 and 23.7° for **1** and **2**, respectively. It is important to stress that no short intermolecular contact is observed between the different parts of a single sheet. There are, however, π-bond interactions between two adjacent sheets by overlap of their (1/2, 0, 1/2) centrosymmetric tr1 triazole groups at a distance of 3.27 Å for both compounds. The triazole groups are arranged in a parallel fashion (the dihedral angle between their plane being zero) at this distance and are displaced with respect to each other with an offset of 1.43 and 1.46 Å for **1** and **2**, respectively. The angle between the normal to a ring and the centroid−centroid vector is 23.6 and 22.9° for **1** and **2**, respectively.[28] The shortest distances between the triazole rings are found for C(13)−N(14)* (3.303 Å) and C(13)−C(15)* (3.383 Å) for **1** and **2** (Figure 4). A short S···S distance of 3.567 Å for **1** and 3.61 Å for **2**, caused by the (0, 1/2, 1/2) centrosymmetry, may also be pointed out. The angles between the direction of this intermolecular interaction, S···S, and the NCS axis are 147.13 and 147.42° for **1** and **2**, respectively.

Spectroscopic Properties. The solid-state UV−vis spectrum for **1** at 293 K consists of one broad band in the near-infrared region which is assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition of the HS Fe^{II} species.[29] The $10Dq^{HS}$ value, which is directly taken from the UV−vis spectrum, is 10 610 cm^{-1}. This ligand field value is just below the limit of 11 000 cm^{-1} suggesting a HS Fe^{II} compound without expected thermal SCO behavior.[29] The IR spectrum of **1** shows a strong singlet at 2063 cm^{-1}, which is characteristic of the C−N stretching vibration of a N-bonded isothiocyanato complex.[30] A medium singlet for the CS stretching vibration is found at 863 cm^{-1}, which lies in the expected range for a N-bonded complex.[31]

Magnetic Properties and ^{57}Fe Mössbauer Measurements. The magnetic properties of **1** which have been studied in the temperature range of 2−300 K with a SQUID magnetometer are presented in Figure 5 in the form of a $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility. At 300 K, $\chi_M T$ equals 3.35 cm^3 mol^{-1} K which corresponds to the expected value for a HS Fe^{II} ion. When the temperature is lowered, $\chi_M T$ remains constant down to ~50 K. Below this temperature, $\chi_M T$ smoothly decreases and drops rapidly below ~14 K reaching a value of 1.50 cm^3 mol^{-1} K at 2 K. The magnetic curve was fitted with the Curie−Weiss expression ($C = 3.395(4)$ cm^3 mol^{-1} K and $\theta = -2.35(3)$ K). The decrease below 50 K can be attributed to very weak antiferromagnetic interactions as indicated by large metal−metal distances and the low value of the Weiss constant.

^{57}Fe Mössbauer spectra of **1** were recorded down to 8 K to clarify the nature of the fall of $\chi_M T$ below ~14 K in the SQUID measurement. The spectrum at 8 K displayed in Figure S1 shows a quadrupole doublet with isomer shift and quadrupole splitting values of $\delta = 1.086(2)$ mm s^{-1} and $\Delta E_Q = 3.223(4)$ mm s^{-1} (relative to α iron), respectively. The half-width of the lines, $\Gamma/2$, is 0.13(1) mm s^{-1}. These Mössbauer parameters are characteristics of a HS Fe^{II} compound with an FeN$_6$ octahedral core.[8] The FeN$_6$ chromophore is tetragonally distorted and has quasi D_{4h} symmetry (or even lower) in this network. In view of the relatively large quadrupole splitting, $\Delta E_Q > 3$ mm s^{-1},[32] it is clear that the doubly occupied $|xy\rangle$ orbital lies lowest and is the origin of the dominating valence electron contribution to the electric-field gradient (EFG). The lattice contribution to the EFG resulting from the distortion of the FeN$_6$ core is expected to have a sign opposite of the one for the valence electron contribution to EFG. The isomer shift value corresponds well with the one obtained for [Fe(btr)$_2$(NCS)$_2$] (**5**) at 85 K, $\delta^{HS} = 1.183$ mm s^{-1}.[8] No Fe^{II} LS species were detected at low temperatures, confirming that the fall of $\chi_M T$ below ~14 K cannot be assigned to a thermally induced spin-state transition, which is hardly to be expected at such low temperatures. Instead, this behavior could be attributed to the zero-field splitting of HS Fe^{II} ions favored by the distortions of the octahedral coordination sphere as shown in the X-ray study. The magnetic properties of **1** were also investigated under hydrostatic pressure at ~12 kbar in the temperature range of 20−300 K to track a possible pressure-induced SCO from the HS to LS states, but no noticeable change was observed in the $\chi_M T$ data.

X-ray Measurements upon Cooling and under Light Irradiation. A single crystal of **1** was selected and mounted on a CCD diffractometer equipped with a cryogenic system

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[28] Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.

[29] (a) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024. (b) Gütlich, P.; Garcia, Y.; Goodwin, H. A. *Chem. Soc. Rev.* **2000**, *29*, 419. (c) Gütlich, P.; Garcia, Y.; Spiering, H. In *Magnetism: From Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2003; Vol. IV, p 271.

[30] Clark, R. J. H.; Williams, C. S. *Spectrosc. Acta* **1966**, *22*, 1081.

[31] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1997.

[32] Gütlich, P.; Link, R.; Trautwein, A. In *Mössbauer Spectroscopy and Transition Metal Chemistry*; Springer: Berlin, 1978.

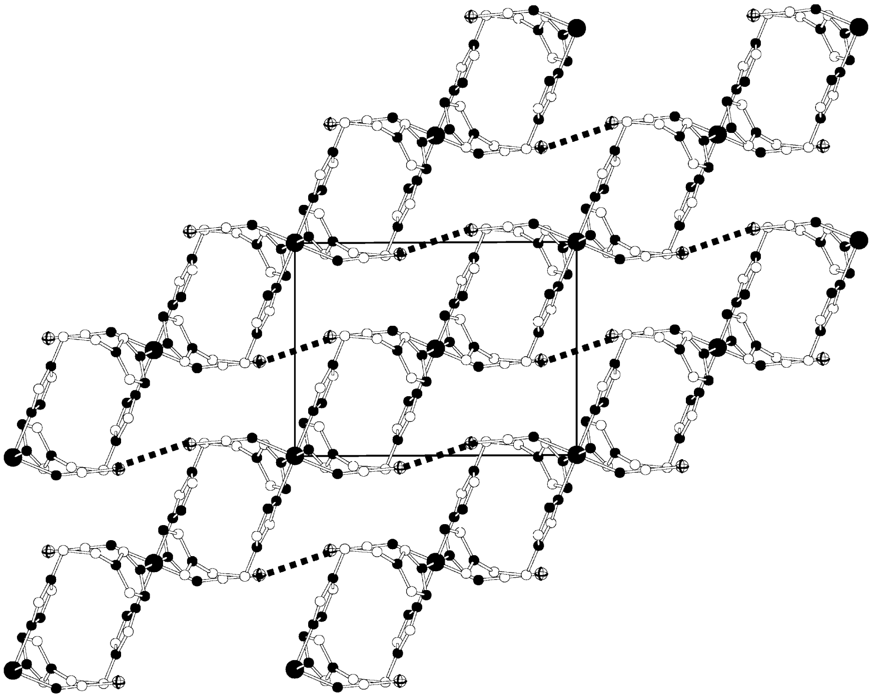

Figure 3. View of the structure of [Fe(btre)$_2$(NCS)$_2$] along the *b* axis, showing the channels between the layers. Black, white, and ellipsoid-filled small spheres correspond to nitrogen, carbon, and sulfur atoms, respectively. The larger black spheres correspond to Fe^{II} ions. The dotted lines refer to the S···S intermolecular interactions.

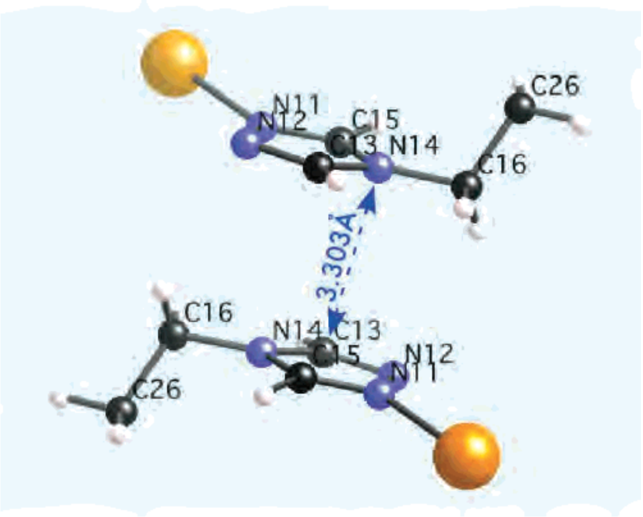

Figure 4. Overlapping of adjacent triazole groups by the symmetry operation: 1 − *x*, 2 −*y*, 1 − *z*. The short distance between C(13) and N(14)* is evidence of a $\pi-\pi$ interaction in [Fe(btre)$_2$(NCS)$_2$].

and a diode laser guide. Cell parameters were precisely measured from 300 K down to 25 K. No drastic variation of the cell parameters except the expected thermal contraction was observed. The thermal expansion coefficients of the lattice parameters at 300 K were determined: $\alpha_a = 7.02(5) \times 10^{-4}$ K^{-1}, $\alpha_b = 2.26(11) \times 10^{-4}$ K^{-1}, $\alpha_c = 3.53(5) \times 10^{-4}$ K^{-1}, and $\alpha_\beta = 10.2(1) \times 10^{-3}$ K^{-1}. The volume expansion coefficient, α_V, is equal to $12.7(2) \times 10^{-2}$ K^{-1}. A single crystal of **1** was cooled to 10 K and subsequently irradiated with red light (λ = 820 nm) with the aim of observing a photoinduced HS to LS transition from the stable HS state to a metastable LS state (LIESST);[28] however, no effect could be observed.

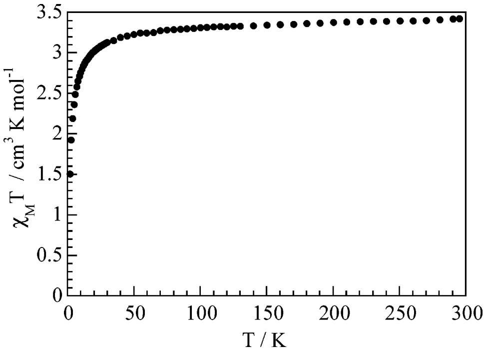

Figure 5. $\chi_M T$ vs *T* curve for [Fe(btre)$_2$(NCS)$_2$] in the temperature range of 2−300 K.

Discussion and Conclusions

A few polymeric complexes with pseudohalogenide ions and flexible bis-azole ligands have been recently described. [Mn(bim)$_2$(N$_3$)$_2$] (bim = 1,2-bis(imidazol-1-yl)ethane) presents a 2D (4,4)-network with bim ligands in an anti conformation.[33] This contrasts with the 1D character of [Co(btp)$_2$(NCS)$_2$] (btp = 1,3-bis(1,2,4-triazol-1-yl)propane) favored by doubly bridged btp ligands in a trans-gauche conformation.[34] [M(btre)$_2$(NCS)$_2$] complexes represent rare examples of structurally characterized 2D coordination networks with bis-4-R-1,2,4-triazole ligands. In particular, [Fe(btre)$_2$(NCS)$_2$] is the second example of an Fe^{II} compound with such ligands after [Fe(btr)$_2$(NCS)$_2$]·H$_2$O [8] and [Fe(btr)$_3$](ClO$_4$)$_2$.[35] M^{II} ions are coordinated to both linear trans-oriented isothiocyanato anions and bis-monodentate 1,2,4-

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(33) Li, B.-L.; Zhu, X.; Zhou, J.-H.; Zhang, Y. *Acta Crystallogr*. **2004**, *C60*, m373.

(34) Zhao, Q.; Li, H.; Wang, X.; Chen, Z. *New. J. Chem*. **2002**, *26*, 1709.

(35) Garcia, Y.; Kahn, O.; Rabardel, L.; Chansou, B.; Salmon, L.; Tuchagues, J.-P. *Inorg. Chem.* **1999**, *38*, 4663.

triazole in a N1,N1′ fashion despite the use of the flexible btre ligand that could potentially lead to multidentate coordination as found for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$.[10] The same coordination mode was found in $[M(btr)_2(NCS)_2] \cdot H_2O$ (M^{II} = Fe(HS), Fe(LS), Co(HS)),[8,9,25] but the supramolecular organization is different. In $[M(btr)_2(NCS)_2] \cdot H_2O$, the layers are connected by van der Waals forces and weak hydrogen bonds through noncoordinated water molecules.[8,9,25] In $[M(btre)_2(NCS)_2]$, there are neither water molecules nor hydrogen-bonding contacts. The layers are, however, strongly connected by $\pi-\pi$ and S···S interactions. Interestingly, the interlayer distance of 8.91 Å for **1** and **2** is much larger than the one found for $[M(btr)_2(NCS)_2] \cdot H_2O$ (8.58 Å).[11] In **3**, the increase of the interlayer spacing on going from the HS to the LS state has been attributed to the reorientation of the NCS anion toward a more linear Fe−NCS geometry.[9] In **1**, the interlayer spacing is as large as for **3** in the LS state,[9] but the Fe−NCS configuration is not linear and does not point toward the neighboring layer like in **3**. The Fe−N bond lengths in **1** are longer than those in **3** and are typical for a HS state. This rigid and dense structure type may well explain the fact that the Fe^{II} ions in **1** could not be switched either by hydrostatic pressure (~12 kbar) or thermally over the range of 300−2 K since they are, at 295 K, already much closer within a layer (by ~0.3 Å in comparison to **3**) and, in addition, the layers stand at a distance corresponding to the LS structure for **3**. This result is in good agreement with the fact that the isostructural compound to **1** and **2**, $[Fe(btre)_2(NCSe)_2]$, is HS at room temperature and does not exhibit any spin-state switching upon cooling.[36] Indeed, the internal electrostatic pressure caused by the anion−cation interaction created by the replacement of isothiocyanato groups with isoselecyanato anions, which are known to set a somewhat stronger field, was insufficient to have an effect on the spin state.

Interestingly, **1** could not be switched by a light irradiation since the LIESST effect was absent at 10 K. The fact that **1** has a HS ground state may seem surprising since its homologue (**3**) is a spin transition compound that is switchable by temperature, pressure, and light irradiation.[8,37] The FeN_6 octahedron in **3** becomes more compact in the LS state with shorter bond lengths and a reduced volume.[9] However, very weak and comparable angular variations are found in the HS and LS states thanks to the weak variation of the dihedral angle[9] between the 1,2,4-triazole units that are linked to the Fe(II) centers. The fact that the local symmetry around the Fe(II) ion and the space group are not affected by the important volume change (4.8%)[9b] associated with the spin-state switching contributes to the very cooperative spin transition in this material. Indeed, we recall that **3** presents, on cooling, a very abrupt spin transition with a square-shaped hysteresis of width of 21 K.[8] The presence of guest water molecules in the crystal lattice of **3** is also known to play a key role in the observation of SCO behavior, since $[Fe(btr)_2(NCS)_2]$ (**5**) was found to be HS upon cooling to 85 K,[8] like **1**. Such loss of SCO properties upon desolvatation was observed for a few other polymeric spin transition complexes (e.g., for the linear chain $[Fe(hyptrz)_3]$(4-chloro-3-nitrophenylsulfonate)$_2 \cdot 2H_2O$ (hyptrz = 4-3′-hydroxypropyl-1,2,4-triazole),[38] the 2D grid $[Fe(azpy)_2(NCS)_2] \cdot MeOH$ (azpy = *trans*-4,4′-azopyridine),[39] the 3D catenane $[Fe(btzb)_3](ClO_4)_2$ (btzb = 1,4-bis(tetrazol-1-yl)butane) for which aged samples were found to be HS,[40] and the 3D bimetallic coordination polymer $[Fe(pmd)(H_2O)\{Au(CN)_2\}_2] \cdot H_2O$).[41] Crystals of compound **1** were exposed to saturated vapors of H_2O, MeOH, and EtOH, but no inclusion of guest solvent molecules was effective, confirming the nonporous character of the network in **1** and precluding the observation of SCO behavior.

In summary, we have structurally characterized a novel Fe^{II} 1,2,4-triazole 2D coordination polymer whose lattice is stabilized by aromatic and inter-chalcogen atom interactions.[42−44] Such a lattice, built on coordinative bonds and supramolecular interactions, was designed to favor a cooperative SCO behavior.[7] However, despite the fact that a favorable FeN_6 1,2,4-triazole core for SCO observation has been obtained, surprisingly $[Fe(btre)_2(NCS)_2]$ could not be switched by any kind of perturbation (temperature, pressure, or light irradiation). The stiffness of the crystal lattice of this compound, despite the use of a flexible ligand, as well as its nonsolvated character, play a crucial role in the absence of the spin-state switching since Fe^{II} btre coordination compounds incorporating noncoordinated anions (ClO_4^- or BF_4^-) and noncoordinated water molecules were found to exhibit gradual and incomplete spin conversion on cooling with an associated thermochromic effect. Such a behavior presumably results from the presence of oligomeric species, as detected in the crystal structure of $[Cu_3(btre)_5(H_2O)_2]$-

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(36) Rudolf, M. F.; Ciunik, Z.; Sachañbiñska, A. 2nd TMR-TOSS Meeting, Seeheim, Germany, 1999.

(37) (a) Zilverentant, C. L.; van Albada, G. A.; Bousseksou, A.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chim. Acta* **2000**, *287*, 303. (b) Garcia, Y.; Ksenofontov, V.; Levchenko, G.; Schmitt, G.; Gütlich, P. *J. Phys. Chem. B* **2000**, *104*, 5045. (c) Codjovi, E.; Jeftic, J.; Menendez, N.; Varret, F. *C. R. Acad. Sci. IIc* **2001**, *4*, 181. (d) Boillot, M.-L.; Zarembowitch, J.; Itie, J.-P.; Polian, A.; Bourdet, E.; Haasnoot, J. G. *New. J. Chem.* **2002**, *26*, 313. (e) Roubeau, O.; Gubbens, P. C. M.; Visser, D.; Blaauw, M.; Dalmas de Réotier, P.; Yaouanc, A.; Haasnoot, J. G.; Reedijk, J.; Sakarya, S.; Jayasooriya, U. A.; Cottrell, S. P.; King, P. J. C. *Chem. Phys. Lett.* **2004**, *395*, 177.

(38) Garcia, Y.; Moscovici, J.; Michalowicz, A.; Ksenofontov, V.; Levchenko, G.; Bravic, G.; Chasseau, D.; Gütlich, P. *Chem.−Eur. J.* **2002**, *8*, 4992.

(39) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762.

(40) van Koningsbruggen, P. J.; Garcia, Y.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Kahn, O.; Linares, J.; Codjovi, E.; Varret, F. *J. Chem. Soc., Dalton Trans.* **2001**, *4*, 466.

(41) Niel, V.; Thompson, A. L.; Galet, A.; Muñoz, M. C.; Goeta, A. E., Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3759.

(42) Zhong, Z. J.; Tao, J.-Q.; Yu, Z.; Dun, C.-Y.; Liu, Y.-J.; You, X.-Z. *J. Chem. Soc., Dalton Trans.* **1998**, 327.

(43) Takahashi, K.; Kawakami, T.; Gu, Z.-Z.; Einaga, Y.; Fujishima, A.; Sato, O. *Chem. Commun.* **2003**, 2374.

(44) Dorbes, S.; Valade, L.; Real, J. A.; Faulmann, C. *Chem. Commun.* **2005**, 69.

(45) (a) Vos, G.; Le Fêbre, R. A.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *J. Am. Chem. Soc.* **1983**, *105*, 1682. (b) Vos, G.; de Graaff, R. A. G.; Haasnoot, J. G.; van der Kraan A. M.; de Vaal, P.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 2905. (c) Thomann, M.; Kahn, O.; Guilhem, J.; Varret, F. *Inorg. Chem.* **1994**, *33*, 6029. (d) Kolnaar, J. J. A.; van Dijk, G.; Kooijman, H.; Spek, A. L.; Ksenofontov, V. G.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 2433. (e) Garcia, Y.; Guionneau, P.; Bravic, G.; Chasseau, D.; Howard, J. A. K.; Kahn, O.; Ksenofontov, V.; Reiman, S.; Gütlich P. *Eur. J. Inorg. Chem.* **2000**, *7*, 1531.

$(ClO_4)_6 \cdot H_2O$, whose Fe^{II} derivatives are known to lead to spin-state crossover with 4R-1,2,4-triazole ligands.[45]

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Note Added after ASAP Publication. This article was released ASAP on November 19, 2005, with an error in the chemical name in the title. The correct version was posted on December 19, 2005.

Supporting Information Available: CIF files for complexes **1** and **2** and a ^{57}Fe Mössbauer spectrum of $[Fe(btre)_2(NCS)_2]$ recorded at 8 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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