

Synthesis, Structure, Magnetic Behavior, and Mössbauer Spectroscopy of Two New Iron(II) Spin-Transition Compounds with the Ligand 4-Isopropyl-1,2,4-triazole. X-ray Structure of $[\text{Fe}_3(4\text{-isopropyl-1,2,4-triazole})_6(\text{H}_2\text{O})_6](\text{tosylate})_6 \cdot 2\text{H}_2\text{O}$

Jeroen J. A. Kolnaar,[†] Gytha van Dijk,[†] Huub Kooijman,[‡] Anthony L. Spek,[‡]
Vadim G. Ksenofontov,[§] Philipp Gütlich,[§] Jaap G. Haasnoot,^{*,†} and Jan Reedijk[†]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands, Bijvoet Centre for Biomolecular Research,
Crystal and Structural Chemistry, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands, and Institut für Anorganische und Analytische Chemie,
Universität Mainz, Staudingerweg 9, D-55099 Mainz, Germany

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Two new iron(II) compounds with the formula $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6]\text{X}_6 \cdot x\text{H}_2\text{O}$ (with iptrz = 4-isopropyl-1,2,4-triazole and X = *p*-toluenesulfonate (Tos) or trifluoromethanesulfonate (Trifl)) were synthesized. The crystal structure of $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{Tos})_6 \cdot 2\text{H}_2\text{O}$ (**I**) has been solved at room temperature. Crystals of **I** are triclinic, space group *P*1 with $a = 12.8820(11)$ Å, $b = 15.580(2)$ Å, $c = 24.445(4)$ Å, $\alpha = 79.270(12)^\circ$, $\beta = 86.688(11)^\circ$, $\gamma = 83.007(8)^\circ$, $Z = 2$. The structure of **I** consists of linear trinuclear cations with a +6 charge and noncoordinated anions and lattice water molecules. The central iron ion is located on an inversion center and is coordinated by 6 nitrogen atoms of 6 iptrz molecules bridging via the nitrogen atoms in the 1,2-positions. Each external iron atom completes its coordination sphere with three coordinated water molecules. The temperature dependent magnetic measurements of compound **I** and $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{Trifl})_6$ (**II**) show that both compounds exhibit a gradual spin conversion of the central iron ion centered at $T_{1/2} = 242$ K for **I** and 187 K for **II**. Temperature dependent Mössbauer spectroscopy measurements on **I** show the behavior expected for a compound of this nature. The measurements on **II** indicate a strong influence of the spin conversion of the central iron ion on both external iron ions. The nature of this phenomenon is proposed to be connected to a very rigid lattice structure (ionic, H-bonding) connecting the trinuclear units.

Introduction

Transition metal ions with an electronic configuration $3d^4$ to $3d^7$ in an octahedral environment have two possible spin states, a high spin (HS) and a low spin (LS) state. Only in some cases is a transition between these spin states possible. This phenomenon, known as spin transition (ST), can be induced by light, either light induced excited spin state trapping (LIESST)¹ or ligand driven light induced spin crossover (LD-LISC),² pressure,⁵ as in most cases, temperature.^{1,2,4–10} Though ST was described first in 1931³ for iron(III), research into this phenomenon has increased over the last 20 years and focuses on iron(II) ST compounds with an octahedral N6 chromophore. In fact, iron(II) spin crossover compounds are now by far the best studied spin-transition systems.

Soon after Haasnoot et al.¹¹ found thermochromism above room temperature in an iron(II) compound with the ligand 1*H*-1,2,4-triazole (Htrz), several research groups started to investigate iron(II) compounds with (substituted)-1,2,4-triazoles ((*R*)-trz).^{12–21} Of special interest are the 4-*R*-1,2,4-triazoles, for these are known to give polynuclear linear products with a triple bridge.^{13,16,18} The length of these products varies from dinuclear compounds with one triple bridge,²² via trinuclear com-

* Author to whom correspondence should be addressed.

[†] Leiden University.

[‡] Utrecht University.

[§] Universität Mainz.

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pounds,^{13,18} to polynuclear, linear-chain products.^{4,11,12,20,21} A two-dimensional compound with 4,4'-bis(1,2,4-triazole) was also obtained.^{15,17} A large number of these compounds show ST behavior with a variety of transition temperatures (80 K < $T_{1/2}$ < 420 K) and transition curve shapes.

A problem attracting much attention is the question of what properties influence the $T_{1/2}$ and the transition trajectory.^{16,20} To answer this question research is needed into well-described systems, preferably in series with only a single change in chemical components. One promising system in this field is a growing series of trinuclear compounds with two triple triazole bridges of which crystal structures are available.^{13,18}

In these trinuclear compounds only the central iron may have a strong enough ligand field to allow a ST. It is thus reasonable to assume that the cooperativity between the ST iron ions is small. This assumption is backed by the transitions found, which all are gradual. This property adds to the suitability of these compounds for the proposed line of research because cooperativity, which has a major influence on the transition trajectory,^{1,23} is hard to describe and to control.

Until now most attention has been given to substituents (ethyl¹³ and *p*-methoxyphenyl¹⁸) and anions. In the present research a new substituent, isopropyl, is considered in combination with anions introduced in earlier publications, namely, triflate (Trifl)¹³ and tosylate (Tos).¹⁸ Two new compounds and their properties are described in detail.

Experimental Section

Synthesis. The ligand 4-(isopropyl)-1,2,4-triazole (iptrz) was synthesized using the method described by Bayer *et al.*²⁴ A solution of 0.75 mol of triethyl orthoformate and 0.5 mol of monoformylhydrazine in 200 mL HPLC grade methanol was refluxed for 1 h. Then 0.5 mol of isopropylamine was added to the solution. Finally the solution was refluxed for 5 h. The solvent was removed under reduced pressure. The ligand was distilled from the reaction mixture at a reduced pressure of 2 mm Hg (temperature \approx 140 °C).

[Fe₃(iptrz)₆(H₂O)₆]X₆ (with X = Tos or Trifl) was prepared by adding a hot solution of 12.5 mmol of iptrz (1.39 g) in 10 mL of ethanol to a hot solution of 5 mmol of FeX₂ in 20 mL of water; a small amount of ascorbic acid was added to prevent oxidation of the Fe(II). The compounds precipitated upon standing at room temperature. [Fe₃(iptrz)₆(H₂O)₆](Tos)₆ (**I**) was obtained as a bluish crystalline material, from which a single crystal, suitable for X-ray structure analysis, could be isolated. [Fe₃(iptrz)₆(H₂O)₆](Trifl)₆ (**II**) was obtained as a white microcrystalline material. Anal. [Fe₃(iptrz)₆(H₂O)₆](Tos)₆·2H₂O. Calcd for C₇₂H₁₁₂N₁₈S₆O₂₆Fe₃ (found): Fe, 8.35 (8.18); C, 43.12 (42.81); H, 5.63 (5.65); N, 12.57 (12.60); S, 9.59 (9.49). Anal. [Fe₃(iptrz)₆(H₂O)₆](Trifl)₆ (**II**). Calcd for C₃₆H₆₆N₁₈F₁₈Fe₃S₆O₂₄ (found): Fe, 9.12 (9.34); C, 23.54 (23.63); H, 3.62 (3.71); N, 13.73 (13.88); S, 10.47 (10.31); F, 18.62 (18.96).

Physical Measurements. The magnetic susceptibility of **I** was measured in the temperature range 4.2–300 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Magnetization of **II** was measured with a Faraday-type magnetometer equipped with a He continuous-flow cryostat working in the 4.2–450 K temperature range. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Mössbauer spectra were measured with a ⁵⁷Co(Rh) source on a constant acceleration spectrometer in a cryostat with exchange gas. The spectra obtained of polycrystalline samples were fitted with Lorentzian-

Table 1. Crystallographic Details for **I**

empirical formula	C ₃₀ H ₆₆ Fe ₃ N ₁₈ O ₆ ·6C ₇ H ₇ O ₃ S·2H ₂ O
fw	2005.73
space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.8820(11)
<i>b</i> (Å)	15.580(2)
<i>c</i> (Å)	24.445(4)
α (deg)	79.270(12)
β (deg)	86.688(11)
γ (deg)	83.007(8)
<i>V</i> (Å ³)	4781.4(11)
<i>Z</i>	2
ρ_{calc} (g cm ⁻³)	1.3932(3)
ρ_{obs} (g cm ⁻³)	1.35(4)
μ (Mo K α) (cm ⁻¹)	6.6
<i>R</i> ^a	0.096
<i>R</i> _w ^b	0.238
λ (Å)	0.710 73 (Mo K α , Zr-fitted)

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

shaped lines using a nonlinear iterative minimization routine (MOS-FUN).

Elemental analyses were performed at the Microanalytical Laboratory, University College Dublin, Ireland.

Crystal Structure Determination of I. A pale blue, plate-shaped crystal of approximate dimensions 0.1 × 0.3 × 0.4 mm, suitable for X-ray structure determination, was mounted on a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4-F sealed tube diffractometer at room temperature. Broad, highly-structured reflection profiles of varying width were observed, which is indicative of a crystal consisting of several slightly misaligned individuals. The *A*-vector method²⁵ was used to calculate for each reflection the ψ angle for which the minimal profile width can be expected. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 24 well-centered reflections (SET4²⁶) in the range 10.05° < θ < 13.70°. Reduced-cell calculations did not indicate higher lattice symmetry.²⁷ Crystal data and details on data collection are given in Table 1. Data were collected at the calculated minimum profile width ψ -angle in the $\omega/2\theta$ scan mode with a scan angle of $\Delta\omega = 0.67 + 0.35 \tan \theta^\circ$. Intensity data of 24 370 reflections were measured ($\theta_{\text{max}} = 27.5^\circ$), of which 21 861 were independent ($R_{\text{int}} = 0.055$). Data were corrected for L_p effects, but not for absorption. Three periodically measured reference reflections ($\bar{2}16$, 324 , $\bar{1}42$) showed no significant decay during 326 h of X-ray exposure time. The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92²⁸). Refinement on F^2 was carried out using full-matrix least-squares techniques (SHELXL-93²⁹); no observance criterion was applied during refinement; 136 reflections with uneven background were omitted from refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms; the coordinates of the water hydrogen atoms were refined. Mild distance restraints were included on O–H bonds and H···H distances within each water molecule in order to maintain a reasonable geometry within the water molecule. The methyl hydrogen atoms were refined in a rigid group. All non-hydrogen atoms were refined with anisotropic thermal parameters. The relatively high anisotropy of the carbon atoms in the isopropyl moiety containing C(136) is indicative of small conformational disorder in this group. No reasonable model could be refined. The hydrogen atoms were included in the refinement with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameters of their carrier atoms by a factor of 1.5 for the methyl and water hydrogens and 1.2 for the other hydrogen atoms. Convergence was

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Table 2. Fractional Coordinates (x, y, z) of Compound I

atom	x	y	z	atom	x	y	z
Fe(11)	0.77087(7)	1.02231(6)	-0.09675(4)	C(118)a	1.0991(10)	1.3885(7)	0.0019(6)
Fe(12)	1	1	0	C(123)a	1.3233(5)	0.9100(4)	-0.0121(3)
O(101)	0.7806(4)	0.9786(4)	-0.1731(2)	C(125)a	1.1924(5)	0.9186(4)	-0.0633(3)
O(102)	0.6212(4)	0.9681(3)	-0.0828(2)	C(126)a	1.3659(5)	0.8593(5)	-0.1043(3)
O(103)	0.6869(4)	1.1431(3)	-0.1329(2)	C(127)a	1.3685(7)	0.9321(5)	-0.1565(3)
N(111)	0.9390(4)	0.8894(3)	-0.0259(2)	C(128)a	1.3293(7)	0.7783(5)	-0.1168(4)
N(112)	0.8546(4)	0.8980(3)	-0.0593(2)	C(133)a	0.9394(5)	1.1267(5)	-0.1673(3)
N(114)	0.9239(5)	0.7610(4)	-0.0445(3)	C(135)a	1.0672(5)	1.1189(5)	-0.1138(3)
N(121)	0.8415(4)	1.0542(3)	0.0180(2)	C(136)a	1.0950(8)	1.2067(10)	-0.2100(5)
N(122)	0.7574(4)	1.0599(3)	-0.0157(2)	C(137)a	1.0344(10)	1.2684(10)	-0.2447(7)
N(124)	0.7032(4)	1.1061(3)	0.0603(2)	C(138)a	1.1962(9)	1.1572(9)	-0.2224(5)
N(131)	1.0043(4)	0.9258(3)	0.0849(2)	Fe(21)	0.73469(7)	0.02879(6)	0.39699(4)
N(132)	1.0868(4)	0.9195(3)	0.1194(2)	Fe(22)	1/2	0	1/2
N(134)	0.9644(5)	0.8481(4)	0.1658(3)	O(201)	0.8833(4)	0.0686(4)	0.4096(2)
C(113)	0.8492(5)	0.8196(5)	-0.0699(3)	O(202)	0.7257(5)	0.1156(5)	0.3192(2)
C(115)	0.9775(5)	0.8074(5)	-0.0172(3)	O(203)	0.8157(5)	-0.0732(4)	0.3607(3)
C(116)	0.9440(7)	0.6660(5)	-0.0491(5)	N(211)	0.3460(4)	0.0614(4)	0.4847(2)
C(117)	1.0577(7)	0.6439(6)	-0.0662(4)	N(212)	0.2608(4)	0.0510(4)	0.5203(2)
C(118)	0.9009(10)	0.6115(7)	-0.0019(6)	N(214)	0.2094(4)	0.1364(4)	0.4427(3)
C(123)	0.6767(5)	1.0900(4)	0.0121(3)	N(221)	0.5587(4)	0.1242(4)	0.4670(2)
C(125)	0.8076(5)	1.0814(4)	0.0633(3)	N(222)	0.6431(4)	0.1350(4)	0.4298(2)
C(126)	0.6341(5)	1.1407(5)	0.1043(3)	N(224)	0.5737(5)	0.2640(4)	0.4442(3)
C(127)	0.6315(7)	1.0679(5)	0.1565(3)	N(231)	0.4911(4)	0.0344(4)	0.5806(2)
C(128)	0.6707(7)	1.2217(5)	0.1168(4)	N(232)	0.4075(4)	0.0208(4)	0.6186(2)
C(133)	1.0606(5)	0.8733(5)	0.1673(3)	N(234)	0.5248(5)	0.0788(5)	0.6558(3)
C(135)	0.9328(5)	0.8811(5)	0.1138(3)	C(213)	0.1805(5)	0.0949(5)	0.4941(3)
C(136)	0.9050(8)	0.7933(10)	0.2100(5)	C(215)	0.3141(5)	0.1126(5)	0.4388(3)
C(137)	0.9656(10)	0.7316(10)	0.2447(7)	C(216)	0.1428(7)	0.1911(6)	0.4001(4)
C(138)	0.8038(9)	0.8428(9)	0.2224(5)	C(217)	0.1420(9)	0.1479(8)	0.3507(4)
Fe(11)a	1.22913(7)	0.97769(6)	0.09675(4)	C(218)	0.1796(8)	0.2804(6)	0.3851(5)
O(101)a	1.2194(4)	1.0214(4)	0.1731(2)	C(223)	0.6497(6)	0.2176(5)	0.4176(3)
O(102)a	1.3788(4)	1.0319(3)	0.0828(2)	C(225)	0.5193(6)	0.2021(5)	0.4739(3)
O(103)a	1.3131(4)	0.8569(3)	0.1329(2)	C(226)	0.5522(8)	0.3613(5)	0.4388(4)
N(111)a	1.0610(4)	1.1106(3)	0.0259(2)	C(227)	0.4403(8)	0.3920(6)	0.4268(4)
N(112)a	1.1454(4)	1.1020(3)	0.0593(2)	C(228)	0.5901(9)	0.3885(6)	0.4881(5)
N(114)a	1.0761(5)	1.2390(4)	0.0445(3)	C(233)	0.4308(6)	0.0487(5)	0.6623(3)
N(121)a	1.1585(4)	0.9458(3)	-0.0180(2)	C(235)	0.5587(6)	0.0687(5)	0.6048(3)
N(122)a	1.2426(4)	0.9401(3)	0.0157(2)	C(236)	0.5791(8)	0.1200(8)	0.6950(4)
N(124)a	1.2968(4)	0.8939(3)	-0.0603(2)	C(237)	0.5174(10)	0.1252(10)	0.7454(5)
N(131)a	0.9957(4)	1.0742(3)	-0.0849(2)	C(238)	0.6893(9)	0.0817(10)	0.7000(5)
N(132)a	0.9132(4)	1.0805(3)	-0.1194(2)	O(1)	0.0098(6)	0.9224(4)	0.3065(3)
N(134)a	1.0356(5)	1.1519(4)	-0.1658(3)	H(1A)	-0.0031(10)	0.9749(10)	0.2891(10)
C(113)a	1.1508(5)	1.1804(5)	0.0699(3)	H(1B)	0.0240(10)	0.9375(10)	0.3373(10)
C(115)a	1.0225(5)	1.1926(5)	0.0172(3)	O(2)	0.1337(6)	0.1553(7)	0.1684(4)
C(116)a	1.0560(7)	1.3340(5)	0.0491(5)	H(2A)	0.3535(10)	0.1463(10)	0.2022(10)
C(117)a	0.9423(7)	1.3561(6)	0.0662(4)	H(2B)	0.3869(10)	0.1213(10)	0.1573(10)

reached at $R_w = 0.238$, $w^{-1} = \sigma^2(F^2) + (0.0559P)^2 + 25.6P$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, $R = 0.096$ for 12 111 $F_o > 4\sigma(F_o)$, $S = 1.05$ for 1178 parameters. The residual density was in the range -0.48 to $1.06 \text{ e } \text{\AA}^{-3}$. Positional parameters are listed in Table 2 (coordinates of the noncoordinating counterions are given in the Supporting Information); selected bond distances and angles are given in Table 3. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*.³⁰ Geometrical calculations and illustrations were performed with PLATON.³¹ All calculations were performed on a DEC5000 cluster.

Results

Description of the Structure of Compound I. The structure of the cation of compound I (see Figure 1) was found to be comparable to the other trinuclear iron 4-R-1,2,4-triazole structures found until now.^{13,18} The asymmetric unit contains two half-molecules, each having a central iron ion located on an inversion center and coordinated by 6 triazole nitrogen atoms. The coordination sphere is a distorted octahedron with Fe-N distances of 2.166(5), 2.180(5), and 2.187(5) Å for one independent unit and 2.177(5), 2.129(5), and 2.161(6) Å for

the second independent unit. The sharper angles around the iron atom are found to be 88.71(18)° to 91.29(18)° for the first independent unit and 88.7(2)° to 91.3(2)° for the second independent unit. The outer iron ions are coordinated in a distorted octahedral fashion by three triazole nitrogen atoms at 2.143(5), 2.160(5), and 2.167(5) Å and three water oxygen atoms at 2.095(5), 2.119(5), and 2.182(5) Å with typical sharp angles ranging from 86.2(2)° to 93.5(2)°. In the second unit the nitrogen atoms are at 2.164(6), 2.167(5), and 2.152(5) Å and the water oxygen atoms at 2.138(5), 2.119(6), and 2.101- (7) Å with sharp angles from 85.3(2)° to 95.4(2)°. The second independent unit is found to be more distorted, especially around the outer iron ions. This distortion might be caused by differences in crystal packing. There are five sulfonate moieties within 5.5 Å of Fe(21), compared to four such moieties for Fe(11). The independent trinuclear units are linked by an extensive two-dimensional network of hydrogen bonds in the *ac*-plane, involving the toluenesulfonate groups and two independent noncoordinated water molecules (see Table 4, Figure 2).

Magnetic Measurements. Compound I shows a gradual transition from $\chi T = 8.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 380 K, indicating the presence of three HS iron(II) ions (theoretical spin-only value $10.9 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), to $6.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 180 K, indicating

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Table 3. Selected Distances and Angles for Structure I^a

		Distances (Å)	
Fe(11)–O(101)	2.095(5)	Fe(21)–O(201)	2.138(5)
Fe(11)–O(102)	2.182(5)	Fe(21)–O(202)	2.119(6)
Fe(11)–O(103)	2.119(5)	Fe(21)–O(203)	2.101(7)
Fe(11)–N(112)	2.167(5)	Fe(21)–N(212)b	2.167(5)
Fe(11)–N(122)	2.160(5)	Fe(21)–N(222)	2.164(6)
Fe(11)–N(132)a	2.143(5)	Fe(21)–N(232)b	2.152(5)
Fe(12)–N(111)	2.187(5)	Fe(22)–N(211)	2.177(5)
Fe(12)–N(121)	2.166(5)	Fe(22)–N(221)	2.161(6)
Fe(12)–N(131)	2.180(5)	Fe(22)–N(231)	2.129(5)
		Angles (deg)	
O(101)–Fe(11)–O(102)	86.2(2)	O(201)–Fe(21)–O(202)	90.2(2)
O(101)–Fe(11)–O(103)	91.0(2)	O(201)–Fe(21)–O(203)	87.8(2)
O(101)–Fe(11)–N(112)	89.1(2)	O(201)–Fe(21)–N(222)	95.4(2)
O(101)–Fe(11)–N(122)	176.5(2)	O(201)–Fe(21)–N(212)b	89.2(2)
O(101)–Fe(11)–N(132)a	89.2(2)	O(201)–Fe(21)–N(232)b	175.0(2)
N(112)–Fe(11)–N(122)	88.66(18)	N(222)–Fe(21)–N(212)b	90.1(2)
N(112)–Fe(11)–N(132)a	92.24(19)	N(222)–Fe(21)–N(232)b	89.7(2)
N(122)–Fe(11)–N(132)a	93.51(19)	N(212)b–Fe(21)–N(232)b	90.8(2)
N(111)–Fe(12)–N(121)	89.61(18)	N(211)–Fe(22)–N(221)	89.1(2)
N(111)–Fe(12)–N(131)	88.71(18)	N(211)–Fe(22)–N(231)	90.6(2)
N(111)–Fe(12)–N(121)a	90.39(19)	N(211)–Fe(22)–N(221)b	90.9(2)
N(121)–Fe(12)–N(131)	88.72(18)	N(221)–Fe(22)–N(231)	88.7(2)

^a Suffix a denotes the symmetry operation $2 - x, 2 - y, -z$; suffix b denotes the symmetry operation $1 - x, -y, 1 - z$.

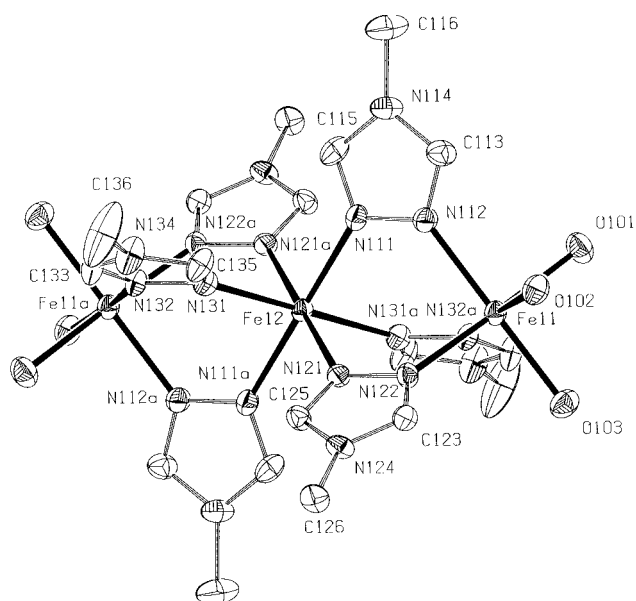


Figure 1. Atomic displacement ellipsoid plot³¹ of one of the trinuclear units of **I** drawn at the 30% probability level. Hydrogen atoms (and the methyl groups of the *i*-Pr moieties) have been omitted for clarity. Fe(12) is located on a crystallographic inversion center. The suffix a denotes the symmetry operation $2 - x, 2 - y, -z$.

two HS iron(II) ions (theoretical spin-only value $7.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). The transition trajectory can be described as quite gradual, with a ΔT_{80} (the temperature range in which 80% of the iron cores change spin) of approximately 120 K. This value for ΔT_{80} is the highest value observed in this type of compound, indicating a very small interaction between the central iron cores of the trinuclear units. $T_{1/2}$ was estimated to be 242 K from the magnetic measurement (see Figure 3). The obtained value is comparable to the values found in other research on 4-R-1,2,4-triazole trinuclear compounds with tosylate anions.

Compound **II** was found to have $\chi T \approx 10.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K; this indicates the presence of three HS iron(II) ions per unit (Figure 4). The magnetization gradually decreases to $\chi T \approx 6.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 120 K. At lower temperatures the magnetic behavior is of a weak antiferromagnetic nature, comparable to the results found by Thomann et al.¹⁸ $T_{1/2}$ could be estimated

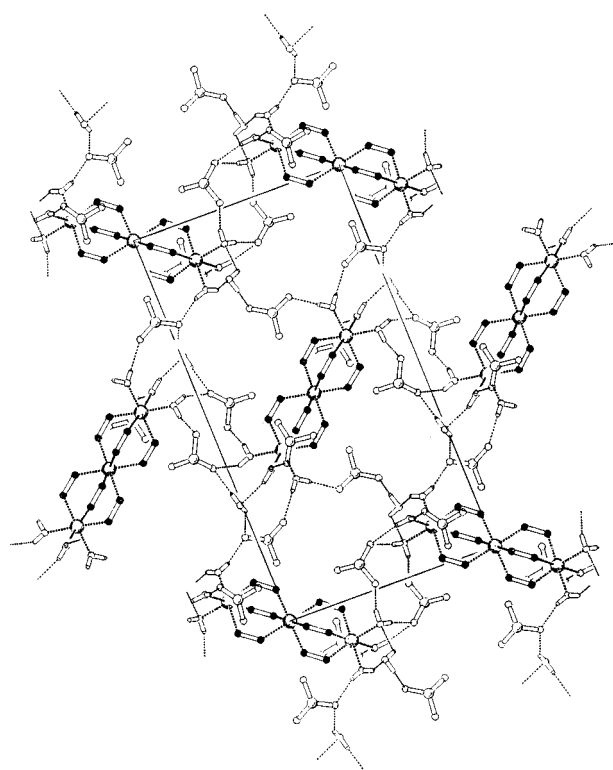


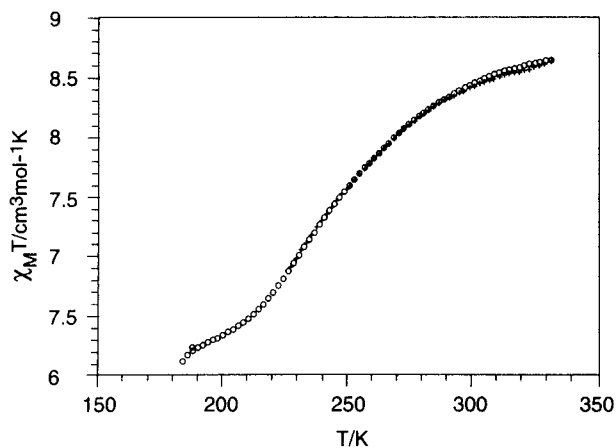
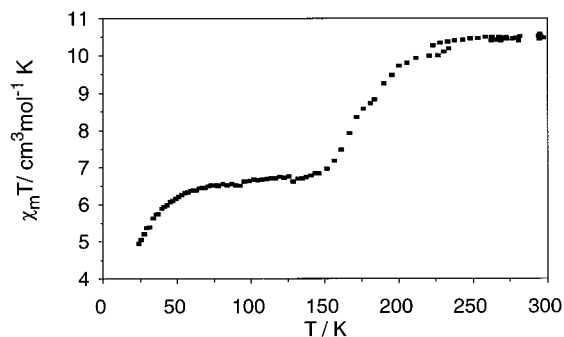
Figure 2. Hydrogen bridging network for **I** viewed along the *b*-axis with $-1/2 < y < 1/2$; only relevant atoms and the trinuclear units are shown.

to be 185 K, in good agreement with the $T_{1/2}$ of 187 K found from the Mössbauer measurements. Eighty percent of the transition was found to occur in a temperature window of 40 K. This can still be considered as a gradual transition though indicative of a greater interaction between the central iron cores of the trinuclear units when compared to compound **I**.

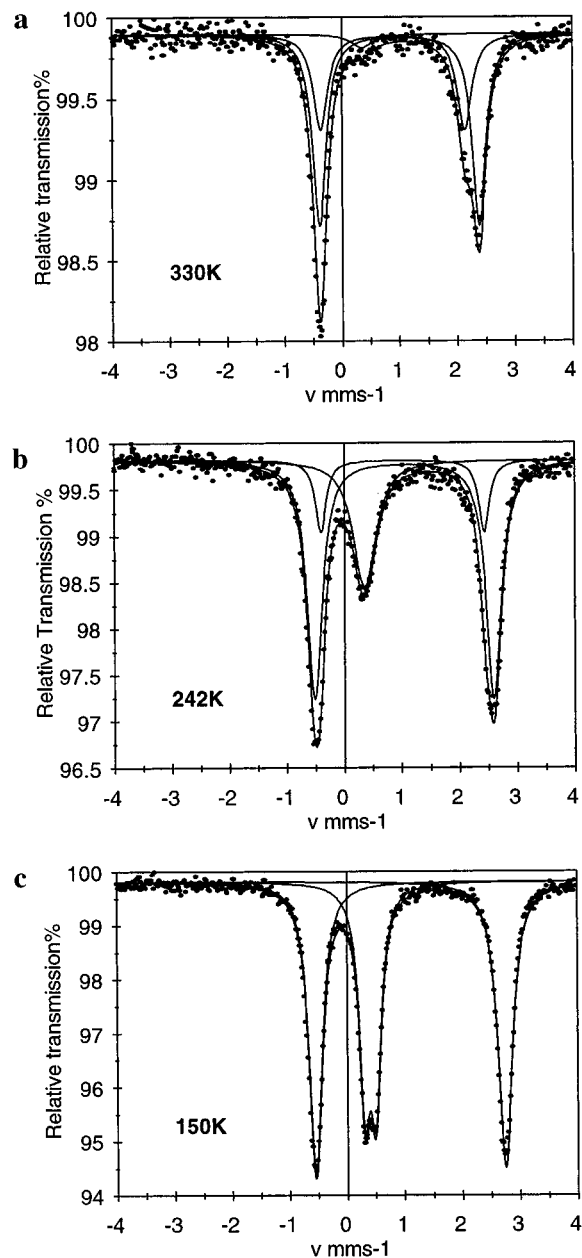
Mössbauer Measurements. ⁵⁷Fe Mössbauer spectra of **I** were recorded from 330 K down to 150 K. As can be seen from Figure 5a, the spectrum taken at 330 K shows the expected pattern for a trinuclear iron-1,2,4-triazole compound with all three iron(II) ions in the HS state.^{13,18} Least-squares-fitted parameters are listed in Table 5. The observed asymmetric doublet can be fitted using two HS sites in a 1:2 ratio of the

Table 4. Hydrogen Bond Geometries for **I**

	D...A (Å)	D-H (Å)	H...A (Å)	D-H...A (deg)
O(101)-H(11A)...O(2) [1 - x, 1 - y, -z]	2.706(11)	0.78(6)	2.03(7)	145(8)
O(101)-H(11B)...O(23) [2 - x, 1 - y, -z]	2.689(7)	0.80(6)	1.91(7)	163(9)
O(102)-H(12A)...O(11)	2.701(7)	0.81(4)	1.97(6)	150(7)
O(102)-H(12B)...O(12) [1 - x, 2 - y, -z]	2.786(7)	0.82(6)	1.97(6)	173(7)
O(103)-H(13A)...O(43) [1 - x, 2 - y, -z]	2.713(8)	0.81(5)	1.92(5)	168(9)
O(103)-H(13B)...O(12) [1 - x, 2 - y, -z]	2.814(7)	0.82(4)	2.04(5)	157(8)
O(201)-H(21A)...O(32) [1 - x, 1 - y, 1 - z]	2.711(9)	0.82(6)	1.93(7)	159(8)
O(201)-H(21B)...O(33) [1 + x, -1 + y, z]	2.875(9)	0.80(6)	2.26(8)	135(8)
O(202)-H(22A)...O(21)	2.697(8)	0.80(9)	1.95(8)	155(10)
O(202)-H(22B)...O(62)	2.763(11)	0.82(8)	1.95(9)	174(10)
O(203)-H(23A)...O(53) [1 - x, -y, 1 - z]	2.682(10)	0.82(5)	1.93(7)	153(9)
O(203)-H(23B)...O(1) [1 + x, -1 + y, z]	2.761(10)	0.81(9)	1.97(8)	166(9)
O(1)-H(1A)...O(23) [-1 + x, 1 + y, z]	2.772(9)	0.85(7)	2.02(9)	147(10)
O(1)-H(1B)...O(33)	2.791(10)	0.86(8)	1.95(8)	163(9)
O(2)-H(2A)...O(61)	2.640(15)	0.84(6)	2.02(13)	130(13)
O(1)-H(2B)...O(102) [1 - x, 1 - y, -z]	3.079(11)	0.85(12)	2.49(13)	126(9)

**Figure 3.** Magnetic measurement χT vs T for compound **I**.**Figure 4.** Magnetic measurement χT vs T for compound **II**.

relative areas. The area fractions of the resonance signals do not necessarily reflect the actual concentrations of the different iron sites. Different bond properties, or rather bond strengths, of the Mössbauer nuclide in its lattice position lead to different Mössbauer-Lamb factors (MLF), which give rise to different intensities of the Mössbauer resonance signals. Particularly if spin transitions occur in a lattice site, the MLF cannot *a priori* be considered the same for both spin states. In iron(II) spin-crossover compounds with strong cooperative interactions, the MLF for the LS state turns out to be larger (roughly up to 20%) than for the HS state. In the present study the area fractions derived from the Mössbauer spectra are taken as a direct measure for the concentrations. Deviations from expected straight ratios are due to the fact that the MLF for the LS state appears indeed to be somewhat larger than for the HS state. A minor amount of LS iron is present, as can be observed from a small "singlet". At 242 K (Figure 5b), the $T_{1/2}$ estimated from magnetic measurements, one of the high-spin doublets decreases in intensity, while the corresponding low-spin signal increases. The

**Figure 5.** Mössbauer spectra of **I** at three selected temperatures.

second high-spin doublet remains unchanged as does roughly the ratio of the inner and outer iron signals (sum of intensities of HS_c and LS_c versus intensity of HS_c). At 150 K (Figure 5c) two doublets are visible, one with a large quadrupole splitting

Table 5. Isomer Shift (IS), Half-Height Width (Γ), Quadrupole Splitting (QS), Relative Area, and Spin State for $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{Tos})_6 \cdot 2\text{H}_2\text{O}$ (**I**) at Selected Temperatures^a

<i>T</i> (K)	IS (mm s ⁻¹)	Γ (mm s ⁻¹)	QS (mm s ⁻¹)	rel area (%)	spin state
330	0.88(3)	0.15(2)	2.50(7)	33.8	HS _c
	1.00(1)	0.14(1)	2.77(3)	62.6	HS _e
	0.36(9)	0.2(1)		3.7	LS
242	1.014(6)	0.108(9)	2.83(2)	13.2	HS _c
	1.040(2)	0.155(5)	3.11(1)	62.3	HS _e
	0.357(7)	0.21(2)	0.12(6)	24.5	LS
150	1.100(1)	0.137(3)	3.288(3)	64.5	HS _e
	0.406(2)	0.148(3)	0.197(3)	35.5	LS

^a Mean-square deviations of statistical origin are given in parentheses. Isomer shifts are referred to metallic iron at room temperature. HS refers to the high-spin state for the two iron sites; HS_c refers to the high-spin state for the central iron site, and HS_e refers to the outer iron site. LS refers to the low-spin state.

(QS), indicating a high-spin iron(II), and one with a small QS, typical for a low-spin iron(II). The relative areas of the integrals of both doublets indicate approximately a 2:1 ratio of HS to LS, which is in good agreement with the expected behavior.

⁵⁷Fe Mössbauer spectra of **II** were recorded from 300 K down to 8 K (Figure 6a–e). Least-squares-fitted parameters are listed in Table 6. The spectrum at 300 K was found to be comparable to the spectrum of compound **I** though the difference between the QS of the inner and outer iron cores is larger, such that the two HS quadrupole doublets are now well resolved. At 200 K the spectrum had to be fitted using four doublets, one LS and one HS doublet arising from the central iron ion; the relative intensities indicate $x_{\text{HS}} = 0.8$ (x_{HS} is defined as the molar fraction of HS molecules). Contrary to what was known from the literature and the tosylate compound, two doublets with different splitting energies had to be used for the outer two iron ions as well. The ratio of these two doublets (HS_{is} and HS_{hs}) was found to be 1:4 at 200 K. Approximately the same intensity ratio of ca. 1:4 is observed for LS_c:HS_e (at 200 K). Furthermore, the new doublet HS_{is} shows twice as large an intensity as compared to the LS_c resonance at all temperatures. This undoubtedly indicates that the HS_{is} and LS signals are related to each other. This means that the outer two iron centers, which remain in the HS state at all temperatures, “feel” the occurrence of a thermal spin transition in the central iron core via perturbation of the quadrupolar interaction in the outer iron sites. The new HS_{is} state is induced by the LS state of the central iron ion.

When the temperature is lowered further, the residual HS_c signal decreases in intensity with decreasing x_{HS} . The HS_{hs} signal decreases with a similar rate, as might be expected from the observed behavior at higher temperatures. The spectrum taken at 8 K shows no residual HS state for the central iron ion and no residual intensity for the HS_{hs} state of the outer iron ions. The spectrum could again be fitted with two doublets, referring to LS_c and HS_{is}, respectively. The temperature dependence of the integrals of the Mössbauer signals is shown in Figure 7.

Discussion

In this paper two new compounds are presented with the formula $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{anion})_6$ (anion = tosylate, triflate). Both compounds exhibit thermochromism upon cooling to liquid nitrogen temperatures, changing from pale blue at room temperature to a clear red at low temperatures. The structure of the tosylate compound was found to be comparable to the known structures of the same iron to ligand ratio.^{13,18} As this result in a series of compounds with different anions and or different

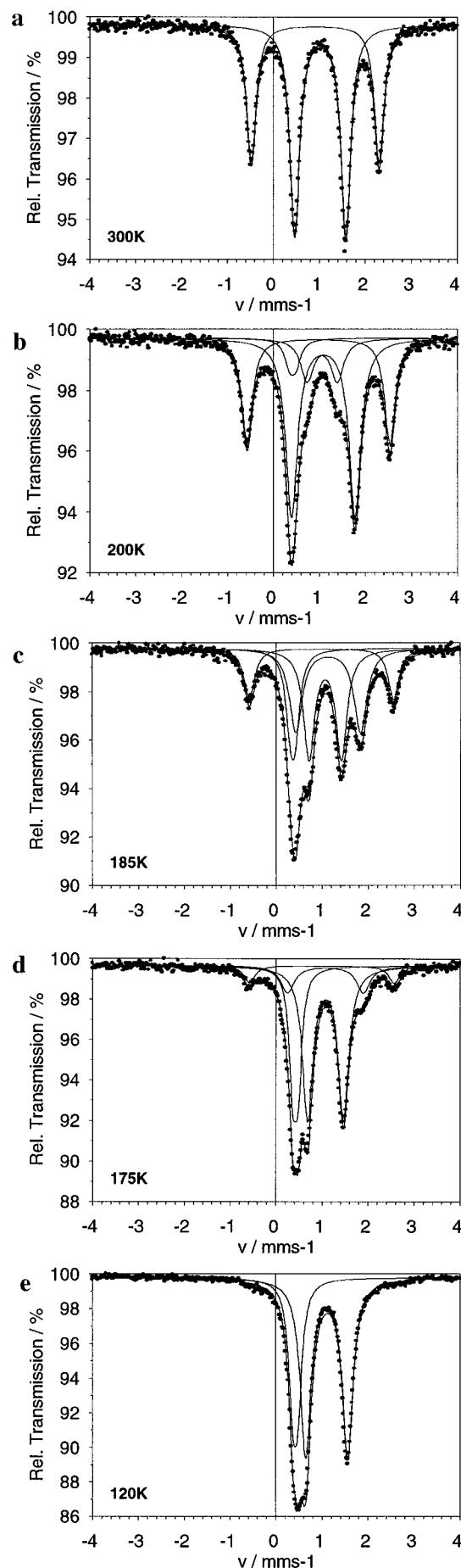
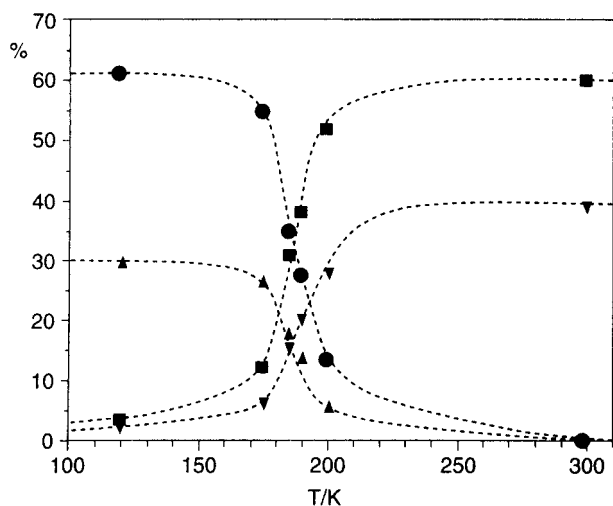
**Figure 6.** Mössbauer spectra of **II** at five selected temperatures.

Table 6. Isomer Shift (IS), Half-Height Width (Γ), Quadrupole Splitting (QS), Relative Area, and Spin State for $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{Trifl})_6 \cdot 2\text{H}_2\text{O}$ (**II**) at Selected Temperatures^a

T (K)	IS (mm s ⁻¹)	Γ (mm s ⁻¹)	QS (mm s ⁻¹)	rel area (%)	spin state
300	0.914(2)	0.125(3)	2.778(4)	39.5	HS _c
	1.024(1)	0.126(2)	1.109(3)	60.4	HS _e
200	0.981(2)	0.140(4)	3.102(5)	28.3	HS _c
	0.42(3)	0.13(2)	0.14(4)	5.7	LS _c
	1.087(4)	0.154(4)	1.377(7)	52.5	HS _{hs}
190	1.064(9)	0.17(1)	0.65(2)	13.5	HS _{ls}
	0.987(3)	0.140(5)	3.122(6)	20.8	HS _c
	0.341(4)	0.124(10)	0.05(3)	37.9	LS _c
	1.130(3)	0.152(5)	1.375(6)	27.3	HS _{hs}
185	1.075(3)	0.150(4)	0.674(6)	13.9	HS _{ls}
	0.990(5)	0.137(8)	3.13(1)	15.8	HS _c
	0.37(1)	0.122(9)	0.10(2)	18.0	LS _c
	1.14(1)	0.167(9)	1.40(2)	31.1	HS _{hs}
175	1.073(3)	0.144(4)	0.701(6)	35.1	HS _{ls}
	0.99(1)	0.14(2)	3.14(2)	6.3	HS _c
	0.424(2)	0.18(2)	0.118(4)	26.5	LS _c
	1.07(1)	0.18(2)	1.65(2)	12.4	HS _{hs}
120	1.079(1)	0.137(2)	0.777(3)	54.7	HS _{ls}
	1.00	0.2(1)	3.20	2.2	HS _c
	0.427(1)	0.130(2)	0.111(3)	29.7	LS _c
	1.10	0.2(1)	1.85	3.8	HS _{hs}
	1.106(1)	0.137(1)	0.906(2)	64.4	HS _{ls}

^a Mean-square deviations of statistical origin are given in parentheses. Isomer shifts are referred to metallic iron at room temperature. HS refers to the high-spin state for the two iron sites; HS_c refers to the high-spin state for the central iron site, and HS_e refers to the high-spin state of the two external iron sites; HS_{hs} and HS_{ls} refer to the outer iron site when the central iron is high-spin and low-spin, respectively. LS refers to the low-spin state. The values given in italics were fixed during the fitting.

**Figure 7.** Fractions of the different spin states in **II** as derived from Mössbauer spectroscopy. The dashed lines are used as a guide to the eye: ■, HS_{hs}; ▼, HS_c; ●, HS_{ls}; ▲, LS_c.

ligands, but with comparable structures, the influences of both factors on the spin-transition behavior can be discussed.

As can be seen from Table 7, the average influence of the ligand system on the transition temperature is rather small; compounds containing isopropyl, *p*-tolyl, and *p*-methoxyphenyl substituents yield tosylate systems with $T_{1/2}$ being 242, 240, and 245 K, respectively. The differences in ΔT_{80} can probably be attributed to the differences in intermolecular distance and intermolecular contacts. The different $T_{1/2}$ found for the *m*-tolyl-1,2,4-triazole compound might be explained by assuming a more pronounced influence of the sterically interfering meta substituent. This assumption is based on related research on the influence of the anions.³² This indicates a pronounced

Table 7. Influences of Ligand and Anion in Compounds of the Type $[\text{Fe}_3(\mu\text{-}1,2\text{-}(4\text{-R-}1,2,4\text{-triazole})_6(\text{H}_2\text{O})_6)(\text{anion})_6] \cdot x\text{H}_2\text{O}$

substituent R	x	anion	$T_{1/2}$ (K)	ΔT_{80} (K)	ref
ethyl	0	triflate	202	40	13
isopropyl	0	triflate	187	60	<i>a</i>
isopropyl	2	tosylate	242	120	<i>a</i>
<i>p</i> -tolyl	4	tosylate	240		<i>b</i>
<i>m</i> -tolyl	2	tosylate	200		18
<i>p</i> -methoxyphenyl	8	tosylate	245	65	18

^a This work. ^b Unpublished results; ΔT_{80} is the temperature range in which 80% of the transition takes place.

sterical influence of the anion on the transition temperature in this type of compound. The same research indicates that the influence of the substituent used is of minor importance when compared to the anion effect. An electronic effect of the substituent is thus expected to be minor but cannot be excluded. The transition temperatures of the triflate-containing compounds show a less constant behavior. The observed differences in the Mössbauer behavior can be used to explain this difference from the tosylate compounds.

The Mössbauer data obtained from **II** can be explained by assuming that the change in QS originates from a change in the geometry around the central iron ion. This change is expected because of the difference in size of the HS and the LS iron ion. The fact that the behavior of **II** is not observed in any other compound might be explained by assuming a more rigid crystal structure for this compound, not allowing very much movement in the structure, implying more extensive deformation in the iron coordination spheres.

Mössbauer spectroscopy proves to be very sensitive in probing not only the valence state (oxidation as well as spin state) but also minute changes in the nearby geometry of the Mössbauer probe. For instance, the spectrum of compound **II** recorded at 300 K exhibits two quadrupole doublets, both having the same isomer shifts of ca. 1 mm/s, which are typical for iron(II) in the HS state.^{33,34} The quadrupole splitting, however, is entirely different for the two doublets. The outer two lines refer to the doublet denoted as HS_c, which arises from the central iron ion. The inner two lines constitute the doublet denoted as HS_e, which refers to the two external HS iron(II) sites of the trinuclear assembly. The intensity ratio of 1:2 reflects well the relative concentrations of the two different sites. The large difference in the quadrupole splitting is due to the following factor. The electric field gradient (EFG), which causes quadrupolar interaction at the iron site, is composed of two contributions, the valence electron contribution, which arises from the noncubic population of the valence electrons, the molecular orbitals of the metal centers, and the lattice contribution of the EFG, which arises from a noncubic lattice surrounding. In iron(II) HS compounds the valence electron contribution generally dominates, but will be reduced by an existing lattice contribution because of the opposite signs of the two contributions.³³ The fact that the external iron positions in the present compounds are surrounded by three nitrogen atoms and three oxygen atoms points to a considerably larger lattice contribution to the EFG than in case of the central iron site which is coordinated to six nitrogen atoms and thus causing a much smaller deviation from cubic symmetry. This is the reason for the much larger quadrupole splitting observed for the HS_c

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doublet. All HS quadrupole doublets observed in the present study undergo an increase in their splitting energy with decreasing temperature. This phenomenon is well-known as being caused by a temperature dependent population of the valence orbitals; low-lying excited levels depopulate on lowering of the temperature, thereby enforcing the deviation of the charge distribution from cubic symmetry.

The structure of **I** has a strong H-bonding network linking the trinuclear units via the coordinated water molecules to the toluenesulfonate groups and noncoordinating water molecules. This most likely leads to more uniform bond strengths around the external iron sites and therefore a smaller lattice contribution to the EFG, which in turn causes less reduction of the valence contribution to the EFG. As a result, the HS quadrupole doublets arising from the central and the external iron sites are similar in their splitting energies. On the basis of the composition and the ST behavior, the structure of **II** is expected to be comparable to the structure previously found for the 4-ethyl-1,2,4-triazole triflate compound.¹³ The difference between the Mössbauer data of **II** and the 4-ethyl-1,2,4-triazole triflate compound, however, indicates a more rigid nature for the structure of **II**, probably due to the larger isopropyl substituent. The larger substituent might cause a decrease in the ability to accommodate change in iron–ligand distance accompanying a spin transition.

Conclusion

The main objective of the work presented in this paper was to gain more insight into the factors that determine the spin-transition behavior of iron(II) compounds with 4-substituted 1,2,4-triazoles. The influence of the substituent is studied by comparing the results obtained for compound **I** with literature data for a series of comparable, trinuclear tosylate compounds. The transition temperatures of the compounds with isopropyl-, *p*-tolyl-, and (*p*-methoxyphenyl)-1,2,4-triazole are not significantly different, though the electronic properties of the substituents are expected to differ. The significantly different $T_{1/2}$ found for the *m*-tolyl-1,2,4-triazole compound is attributed to a sterical effect of the substituent, though electronic effects cannot be completely excluded. This explanation can be supported with the transition temperatures observed for the triflate compounds. Though the difference between the $T_{1/2}$ values of these compounds is more pronounced, $\Delta T = 15$ K for the triflate

compounds, compared to only 5 K for the three tosylate compounds, the tendency is significant, $T_{1/2}$ for triflate-containing compounds being ca. 195 K, for tosylate compounds ca. 240 K.

The effect of the noncoordinated water molecules on the transition temperature of the compounds described is not entirely clear. The presence of a strong hydrogen-bonding network in the triflate compounds, where only triflate anions and coordinated water molecules are part of the network, is a possible reason for the more abrupt nature of the spin transition in these compounds. The less abrupt spin transition in the tosylate compounds might be attributed to the more extended and probably also more flexible hydrogen-bonding network observed for these compounds. This difference might be caused by a change in the cooperativity due to the hydrogen-bonding network.

The Mössbauer spectra obtained for the 4-isopropyl-1,2,4-triazole compound with triflate anions are the first empirical data showing a definite influence of the spin-transition phenomenon on another iron(II) in a compound. The observed change in the Mössbauer signal from the outer iron ions is probably visible due to the rigidity of the structure. This structure is expected to be comparable to the structure of the 4-ethyl-1,2,4-triazole compound described by Vos et al.¹³

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Supporting Information Available: Further details on the structure determinations including tables of atomic coordinates, bond lengths and angles, and thermal parameters (16 pages). Ordering information is given on any current masthead page. For details of the crystallography the reader is referred to one of the authors (A.L.S.).

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