$[Mo_2(gly)_4]Cl_4 \cdot nH_2O$,[8] $[Cr_2(gly)_4]X_4 \cdot nH_2O$ (X = Cl, Br),[9] and $[Rh_2(\beta\text{-ala})_4](ClO_4)_4 \cdot 2H_2O$.[10] One known exception to this "right, right, left, left" order is the compound $[Mo_2(gly)_4](SO_4)_2 \cdot 4H_2O$,[11] in which the order is "right, left, right, Left". It is notable that this compound is obtained by dissolution of the chloride salt,[8] with "right, right, left, left" arrangement, in aqueous H_2SO_4 under mild conditions.

A priori, the reaction of Mo_2^{4+} with the racemic mixture of the amino acid may yield the following isomers: Mo_2D_4, Mo_2D_3L, Mo_2DDLL, Mo_2DLDL, Mo_2DL_3, and Mo_2L_4. Provided that no steric interactions exist between the chiral centers in the complex $Mo_2D_{4-n}L_n$ (n = 0, 1, 2, 3, 4), it can be shown that the statistical distribution of these isomers in solution should be in the ratio 1:4:4:2:4:1, respectively. Preliminary kinetic results[12] show that the exchange reaction (1) reaches equilibrium rapidly at room temperature (<1 min) whereas the crystallization process is much slower (see Experimental Section). The fact that only one isomer, namely Mo_2DDLL, crystallizes from the solution may be ascribed to a low solubility product of its salts, which shifts the equilibrium in its direction. An alternative reasoning, ascribing this fact to the predominance of the Mo_2DDLL isomer in *solution*, cannot be ruled out, although no support or justification for such an assumption can be offered.

$$Mo_2[O_2CCH(NH_3^+)R]_4 + 4(^-O_2CCH(NH_3^+)R') \rightleftharpoons Mo_2[O_2CCH(NH_3^+)R']_4 + 4(^-O_2CCH(NH_3^+)R) \quad (1)$$

We intend to investigate the isomer distribution in solution by NMR and other techniques.

Registry No. **1**, 90991-54-1; **2**, 90991-55-2; **3**, 90991-58-5; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: Tables of structure factors of structures **1–3**, thermal parameters of compounds **1–3**, and non-essential bond distances and angles within the coordinated amino acids in **1–3** and in the *p*-toluenesulfonate ions in **3** (62 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, State University Leiden, 2300 RA Leiden, The Netherlands,
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Crystal Structure at 300 and 105 K, Magnetic Properties, and Mössbauer Spectra of Bis(triaquatris(4-ethyltriazole-N^1)iron(II)-$N^2,N^{2'},N^{2''}$)iron(II) Hexakis(trifluoromethanesulfonate). A Linear, Trinuclear Iron(II) Compound, Showing a Unique High-Spin–Low-Spin Transition of the Central Iron Atom

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$[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ (Ettrz = 4-ethyl-1,2,4-triazole) is a linear trinuclear coordination compound, in which the two pairs of metal centers are each linked by three 1,2-bicoordinating triazole ligands. The terminal coordination sites are occupied by H_2O molecules. Upon cooling, the central iron(II) undergoes a high-spin to low-spin transition. Mössbauer and magnetic susceptibility data show that this spin crossover gradually takes place between 230 and 190 K. The structural consequences of the spin crossover have been studied by crystal structure determinations at 300 and 105 K. The compound crystallizes in the space group $P\bar{3}1c$, with two trinuclear molecules per unit cell. The lattice constants are $a = b$ = 14.488 (5) Å and c = 19.858 (5) Å at 300 K and $a = b$ = 14.265 (7) Å and c = 19.632 (2) Å at 105 K. Fe–O(water) distances at 300 K are 2.156 (4) Å, whereas the Fe–N distances are 2.157 (4) Å (terminal Fe) and 2.174 (4) Å (central Fe). The Fe–L distances of the terminal iron hardly change (0.01–0.02 Å) upon cooling. However, the observed decrease in the Fe–N bond lengths (about 0.14 Å) upon cooling for the central Fe(II) ion reflects a clear strengthening of these bonds in the low-spin state. The low-temperature magnetic susceptibility and Mössbauer data indicate that no magnetic exchange exists between the terminal iron(II) ions.

Introduction

The spin-crossover phenomena in transition-metal chemistry have attracted much attention in recent years. A variety of iron(II) compounds are known to show a transition from the high-spin state (S = 2) to the low-spin state (S = 0) on cooling or upon increasing pressure.[2] A very strong octahedral ligand field is required to induce such a transition, and usually the transition is observed in Fe(II) compounds with chelating nitrogen donor ligands, such as phenanthroline, bipyridyl, and 2-(2-pyridyl)imidazole;[2,3] in addition, the low symmetry as in $Fe(phen)_2X_2$ might aid such a transition.

Recently, we prepared a series of isomorphous linear trinuclear coordination compounds with the composition $[M_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ (Ettrz = 4-ethyl-1,2,4-triazole) in which M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II).[4-6] The ligand field spectra of the Co and Ni compounds indicated the presence of a strong ligand field in these compounds.[4,6] Because of the asymmetric environment of the outer ions and the expected strong field affecting the central metal ion, the Fe(II) compound was studied in detail in order to investigate the possibility of high-spin–low-spin transitions. The results

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described in this paper show that the central Fe(II) ion indeed changes its spin state on cooling. The spin crossover was studied by magnetic susceptibility and Mössbauer measurements, ligand field spectroscopy, and single-crystal X-ray diffraction. Part of this work has been presented in a preliminary form.[7]

Experimental Section

Syntheses. 4-Ethyl-1,2,4-triazole (Ettrz) was prepared according to a method described by Bayer et al.[8] A solution of 1.5 mol of triethyl orthoformate and 1 mol of formylhydrazine in 400 mL of anhydrous methanol was refluxed for 3.5 h. Then 1 mol of ethylamine, mixed with N_2 gas, was passed into the solution. Finally, the solution was refluxed for 3 h. The solvent was then removed under reduced pressure. Ettrz was distilled at 2 mmHg (bp 140–160 °C) from the reaction mixture.

Iron(II) trifluoromethanesulfonate was prepared by adding trifluoromethanesulfonic acid to an excess of iron powder. Water was added and after filtration was removed under reduced pressure.

$[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ was prepared by slowly adding 2.5 mmol of Ettrz, dissolved in 10 mL of water, to a hot solution of 1.25 mmol of iron(II) trifluoromethanesulfonate in 20 mL of water. The volume of the solution was reduced by evaporating to about 15 mL. Colorless crystals formed upon standing at room temperature.

Anal. Calcd (found): Fe, 9.4 (9.6); C, 20.2 (20.6); N, 14.4 (14.4); H, 3.1 (3.1).

Measurements. The ligand field spectra were recorded on a Beckman DK-2A UV–vis spectrophotometer (350–2000 nm) by using the diffuse reflectance method with MgO as reference.

Magnetic susceptibility measurements between 80 and 300 K were carried out on an automated Faraday balance, described by Arbouw.[9]

Mössbauer spectra were obtained with a constant-acceleration spectrometer, which uses a ^{57}Co in Rh source. Isomer shifts (IS) are reported relative to the NBS standard, disodium pentacyanonitrosylferrate, at room temperature. The measured spectra were fitted by computer, with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in a nonlinear, iterative minimization routine. In the case of electric quadrupole doublets the line widths and the absorption areas of the constituent peaks were constrained to be equal.

Crystal Information. The single-crystal X-ray diffraction measurements were performed on an Enraf-Nonius CAD-4 diffractometer. All calculations were carried out on the Leiden University Amdahl V7B computer, with a set of programs written or modified by E. Rutten-Keulemans, Dr. R. A. G. de Graaff, and S. Gorter.

Two different crystals were used for the X-ray analysis at 300 and 105 K. Mo Kα radiation, monochromatized by graphite, was used to determine the unit cell parameters and the space group and to measure the reflection intensities, by using the θ–2θ scan method for all reflections. The high-temperature data were also corrected for absorption.[10] After reduction of the intensities to structure factors a Wilson plot was calculated to obtain starting values for the scale factor and the overall thermal parameter B.

Relevant crystal and diffraction data are listed in Table I. As this table shows, the number of measured reflections was about 3 times as large as the number of independent reflections. After absorption correction[10] there was good agreement between the equivalents.

Structure Determination and Refinement. The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma_F^2$. Discrepancy indices are defined as $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$. Scattering factors and anomalous dispersion corrections were taken from ref 11. No extinction correction was applied.

Table I. Relevant Crystal and Diffraction Data for $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 300 and 105 K

T, K	300	105
space group	$P\bar{3}1c$	$P\bar{3}1c$
lattice const		
a, Å	14.488 (5)	14.265 (7)
b, Å	14.488 (5)	14.265 (7)
c, Å	19.858 (5)	19.632 (2)
Z	2	2
θ range, deg	2–23	2–22
no. of measd reflcns	5533	4841
no. of indep reflcns	1811	1538
no. of signif reflcns	922	1112
final R (R_w)[a]	0.046 (0.041)	0.063 (0.075)
wavelength of X-ray, Å	0.71063	0.71063
μ, cm^{-1}	128	128

[a] Significant reflections only.

The structure at room temperature was solved by standard Patterson and Fourier techniques. Isotropic refinement of the atoms located yielded an R_w value of 0.117. After anisotropic refinement of the non-hydrogen atoms, except for the atoms of the triflate group, R_w decreased to 0.078. In the Fourier synthesis indications were found for disorder of the $CF_3SO_3^-$ group. Alternative positions were introduced for the C, F, and O atoms of the anion. Slack constraints[12] were used in the refinement. The refinement converged to an A:B occupation ratio of 0.78:0.22. The atoms of the disordered $CF_3SO_3^-$ group were refined anisotropically, and the anisotropic thermal parameters of corresponding atoms were coupled. Although this way of anisotropic refinement is not completely correct, the results were satisfactory. A number of hydrogen atoms were found from a difference Fourier synthesis. These hydrogen atoms were refined in the riding mode of their carrying atoms. The hydrogens of the CH_3 group and of the H_2O molecule could not be located. Due to the rotation of the CH_3 groups, the hydrogen atoms of these groups could not be placed at calculated positions. After anisotropic refinement of the nonhydrogen atoms, including the disorder model, a final R_w value of 0.041 (R = 0.046) was obtained.

The X-ray analysis at 105 K was carried out on the basis of the room-temperature model (without disorder). The Fourier synthesis indicated minor disorder of the triflate group, which, however, could not be interpreted in terms of a model with alternative positions. Waser constraints[12] were applied in the refinement of the anion. All hydrogen atoms could be located from a difference Fourier synthesis. The hydrogen atoms of the ethyl group were refined in the riding mode of their carrying atoms. Isotropic refinement led to an R_w value of 0.125. After several cycles of anisotropic refinement of the non-hydrogen atoms, R_w had decreased to 0.075 (R = 0.064). Although the larger number of reflections in the case of the low-temperature structure would suggest smaller R values, the present slightly larger values are due to the fact that the triflate anion disorder could not be refined at low temperature.

The fractional coordinates and isotropic thermal parameters of the atoms are listed in Table II (300 K) and Table III (105 K). Tables with anisotropic thermal parameters are included in the supplementary material, together with tables for observed and calculated structure factors.

Results and Discussion

Structural Information. The structures of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 300 and 105 K are mutually isomorphous and are also isomorphous with those of the other transition metals.[4] The structure consists of linear trinuclear units, in which the iron ions are linked by three N^1,N^2-donating triazole ligands. The terminal coordination sites are occupied by H_2O molecules. The trinuclear unit also resembles the one in the compound $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6(H_2O)_2$.[13-15]

Relevant intramolecular bond distances and angles are listed in Table IV for both studies. In Figure 1 an ORTEP drawing of the $[Fe_3(Ettrz)_6(H_2O)_6]^{6+}$ cation is shown. This drawing corresponds to the structure obtained at 300 K.

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Table II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2$) of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at Room Temperature[a]

atom	x/a	y/b	z/c	B_{iso}
Fe1	33333	66667	75000	1.63 (5)
Fe2	33333	66667	55663 (7)	2.08 (4)
N1	4555 (4)	7908 (4)	6875 (2)	2.2 (2)
N2	4515 (4)	7938 (4)	6179 (2)	2.2 (2)
C3	5337 (5)	8836 (5)	5998 (3)	2.2 (2)
N4	5899 (4)	9395 (4)	6529 (2)	2.3 (2)
C5	5379 (5)	8789 (5)	7060 (3)	2.6 (2)
C6	6868 (6)	10469 (6)	6542 (4)	3.8 (3)
C7	6657 (8)	11288 (6)	6866 (4)	6.5 (4)
Ow	4582 (3)	6826 (3)	4902 (2)	3.1 (2)
S	97961 (15)	133449 (17)	59143 (8)	3.72 (7)
O1A	1033 (2)	1380 (1)	529 (1)	5.4 (4)
O2A	8653 (4)	12860 (9)	5883 (11)	5.5 (4)
O3A	10199 (9)	14013 (10)	6504 (8)	7.1 (4)
O1B	1027 (7)	1408 (4)	536 (4)	5.0 (4)
O2B	870 (2)	1259 (3)	574 (4)	5.5 (4)
O3B	1059 (2)	1396 (4)	642 (3)	7.1 (4)
C1A	10079 (8)	12309 (5)	6090 (7)	7.7 (7)
C1B	1008 (3)	1231 (1)	576 (3)	7.7 (7)
F1A	11114 (8)	12630 (8)	6126 (8)	14.3 (8)
F2A	9647 (8)	11820 (9)	6674 (7)	12.6 (6)
F3A	9653 (9)	11538 (9)	5629 (9)	14.6 (7)
F1B	1114 (3)	1285 (3)	575 (3)	14.3 (8)
F2B	968 (4)	1150 (3)	619 (3)	12.6 (6)
F3B	971 (3)	1197 (3)	514 (2)	14.6 (7)
H3[b]	5515	9080	5531	5.0
H5	5603	8990	7528	5.0
H61	7425	10421	6793	5.0
H62	7112	10690	6079	5.0

[a] The multiplication factor is 10^5 for Fe1, Fe2, and S and 10^3 for O1A, O1B, O2B, O3B, C1B, F1B, F2B, and F3B. Standard deviations are given in parentheses. [b] The hydrogen atoms were refined in the riding mode of their carrying atoms.

Table III. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2$) of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 105 K[a]

atom	x/a	y/b	z/c	B_{iso}
Fe1	33333	66667	75000	0.70 (6)
Fe2	33333	66667	55668 (1)	0.94 (4)
N1	4491 (5)	7823 (5)	6928 (3)	0.9 (2)
N2	4517 (5)	7882 (5)	6222 (3)	0.7 (2)
C3	5376 (7)	8786 (7)	6023 (4)	1.0 (2)
N4	5924 (5)	9321 (6)	6609 (3)	0.8 (2)
C5	5336 (7)	8709 (7)	7135 (4)	1.4 (2)
C6	6906 (7)	10399 (9)	6636 (5)	1.9 (3)
C7	6683 (11)	11239 (9)	6905 (6)	3.1 (3)
Ow	4574 (5)	6816 (5)	4893 (3)	1.3 (2)
S	9799 (2)	13320 (2)	5878 (1)	1.73 (7)
O1A	10269 (5)	13677 (5)	5208 (3)	2.3 (2)
O2A	8635 (3)	12807 (5)	5911 (4)	3.3 (2)
O3A	10389 (5)	14074 (4)	6417 (3)	3.2 (2)
C1A	10026 (5)	12208 (5)	6056 (4)	3.4 (4)
F1A	11081 (4)	12529 (5)	6023 (5)	7.5 (3)
F2A	9665 (5)	11801 (6)	6677 (4)	5.8 (2)
F3A	9488 (6)	11390 (5)	5620 (4)	7.4 (3)
Hw1	444 (6)	708 (6)	459 (3)	0 (2)
Hw2	504 (8)	670 (7)	507 (4)	3 (2)
H3	564 (5)	895 (5)	560 (2)	2 (2)
H5	541 (6)	888 (6)	762 (2)	0 (2)
H61[b]	7392	10216	6899	0.5
H62	7181	10607	6175	0.5
H71	6592	11114	7405	0.5
H72	7390	11893	6813	0.5
H73	6058	11302	6714	0.5

[a] The multiplication factor is 10^5 for Fe1 and Fe2 and 10^3 for Hw1, Hw2, H3, and H5. Standard deviations are given in parentheses. [b] H61, H62, H72, and H73 were refined in the riding mode of their carrying atoms.

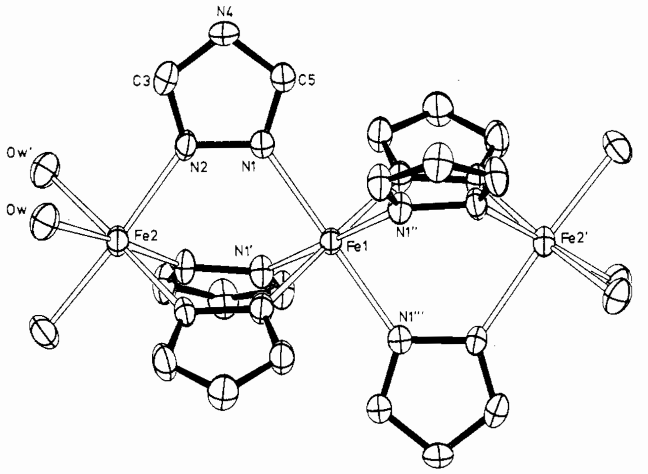

Figure 1. ORTEP drawing of the $[Fe_3(Ettrz)_6(H_2O)_6]^{6+}$ cation, showing the 50% probability ellipsoids. The structure shown is the one obtained at 300 K. Hydrogen atoms and the ethyl groups have been omitted for clarity.

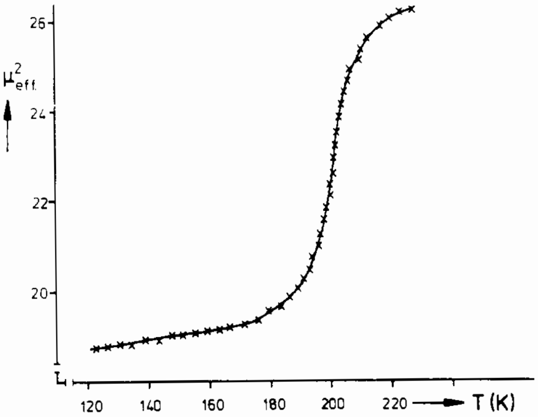

Figure 2. Plot of μ_{eff}^2 (μ in Bohr magnetons per ion of Fe) of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ as a function of temperature.

Although the structures at 300 and 105 K are essentially similar, small, but significant, differences are observed in a number of bond distances and angles. The observed decrease in the Fe–N bond lengths (see Table IV) reflects clearly the strengthening of these bonds in the low-spin state. The change of about 0.14 Å is close to the value found for the few known monomeric iron–phenanthroline compounds.[2,3] Due to the shortening of these bond lengths the orientations of the triazole ligands undergo small changes. The Ettrz groups in neighboring bridges are bent slightly toward each other, which is reflected in the decrease of the C5–C5'' distance from 3.34 (1) Å at 300 K to 3.21 (2) Å at 105 K.

The bond lengths N2–C3, N4–C5 and C5–N1 of the triazole ring show small changes, which might suggest a more delocalized π-electron density at 105 K. This, however, is very unlikely, since at low temperatures in fact a less delocalized π-system should be expected.[16,17] The differences are probably caused partly by the lower accuracy of the structure determination at 105 K.

Hydrogen bonding plays an important role in the stabilization of the structures. The coordinating H_2O molecules donate their hydrogen atoms to the oxygens of the triflate anion. The observed O–O distances are Ow–O1A = 2.70 (1) Å (300 K), 2.806 (8) Å (105 K), and Ow–O2A = 2.81 (1) Å (300 K), 2.838 (8) Å (105 K).

Physical Measurements. The ligand field spectrum recorded at room temperature shows a broad band at 11 300 cm^{-1} and a very weak band at 17 850 cm^{-1}, in agreement with high-spin

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Table IV. Bond Distances (Å) and Angles (deg) in $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 300 and 105 K[a]

	300 K	105 K		300 K	105 K
Fe1-Fe2	3.840 (1)	3.795 (2)	S-O2A	1.442 (7)	1.479 (4)
Fe1-N1	2.174 (4)	2.031 (6)	S-O3A	1.443 (7)	1.458 (4)
Fe2-N2	2.157 (4)	2.176 (6)	S-C1A	1.776 (2)	1.848 (9)
Fe2-Ow	2.156 (4)	2.166 (6)	C1A-F1A	1.331 (7)	1.371 (6)
N1-N2	1.383 (5)	1.389 (8)	C1A-F2A	1.340 (6)	1.345 (5)
N2-C3	1.300 (7)	1.33 (1)	C1A-F3A	1.334 (7)	1.358 (5)
C3-N4	1.331 (7)	1.33 (1)	C3-H3	0.98	0.97 (2)
N4-C5	1.338 (6)	1.36 (1)	C5-H5	0.98	0.98 (1)
C5-N1	1.291 (7)	1.33 (1)	C6-H61	0.98	1.02 (4)
N4-C6	1.485 (8)	1.51 (1)	C6-H62	0.98	0.98 (2)
C6-C7	1.51 (1)	1.51 (2)	Ow-Hw1		0.79 (7)
S-O1A	1.444 (9)	1.455 (4)	Ow-Hw2		0.86 (9)
N1-Fe1-N1′	90.6 (2)	92.4 (2)	C3-N4-C6	128.4 (6)	128.3 (7)
N1-Fe1-N1″	88.5 (3)	87.7 (4)	C5-N4-C6	126.9 (6)	128.4 (7)
N1-Fe1-N1‴	178.7 (3)	179.8 (4)	N4-C6-C7	112.0 (7)	112.3 (8)
N2-Fe2-Ow	89.3 (2)	89.7 (2)	F1A-C1A-F2A	106.5 (9)	108.6 (7)
N2′-Fe2-Ow	175.8 (2)	175.8 (3)	F1A-C1A-F3A	107 (1)	109.3 (8)
Ow-Fe2-Ow	86.5 (2)	86.6 (3)	F2A-C1A-F3A	104.7 (6)	104.8 (5)
Fe1-N1-N2	124.5 (4)	126.1 (5)	F1A-C1A-S	114.2 (6)	110.9 (4)
Fe1-N1-C5	128.5 (4)	128.6 (5)	F2A-C1A-S	111.9 (9)	110.9 (7)
Fe2-N2-N1	124.3 (4)	123.6 (5)	F3A-C1A-S	111.6 (8)	112.1 (6)
Fe2-N2-C3	129.6 (4)	130.1 (5)	C1A-S-O1A	104.6 (9)	103.0 (4)
N1-N2-C3	106.0 (5)	106.2 (6)	C1A-S-O2A	106.9 (7)	102.3 (3)
N2-C3-N4	111.4 (5)	112.8 (7)	C1A-S-O3A	102.7 (7)	103.3 (4)
C3-N4-C5	104.6 (5)	103.2 (7)	O1A-S-O2A	114 (2)	116.0 (4)
N4-C5-N1	111.3 (5)	112.6 (7)	O1A-S-O3A	117 (1)	116.7 (5)
C5-N1-N2	106.6 (4)	105.2 (6)	O2A-S-O3A	110 (1)	112.9 (4)

[a] A prime indicates a symmetry operation $1 - y, 1 + x - y, z$; a double prime indicates a symmetry operation $y - x, y, {}^3/_2 - z$; and a triple prime indicates a symmetry operation $1 - y, 1 - x, {}^3/_2 - z$.

Fe(II). On cooling to liquid-nitrogen temperature, the compound changes in color from white to purple and its diffuse-reflectance spectrum shows two strong bands at 11 400 cm^{-1} and 18 000 cm^{-1}, indicating the presence of both high-spin and low-spin Fe(II).[18,19]

The magnetic susceptibility measurements clearly show the HS–LS transition. In Figure 2, μ_{eff}^2 as a function of temperature is shown. The alteration in the magnetic moment near 203 K corresponds to a change to the low-spin state for one-third of the iron ions. No detectable hysteresis was observed.

The inverse magnetic susceptibility vs. temperature curve (<40 K) shows a θ value almost equal to zero, indicating the absence of a significant magnetic coupling between the terminal Fe(II) ions. The small structural change at the phase transition suggests that also at high temperature the exchange between the terminal ions is small.

For spin-crossover systems of iron, ^{57}Fe Mössbauer spectroscopy has proven to be a powerful technique. It enables one to follow directly the changes of concentrations of the coexisting spin states with temperature.[20] Therefore, Mössbauer measurements were performed from room temperature down to 2 K. Some of the spectra obtained are redrawn in Figure 3. At room temperature the resonant absorption spectrum consists of a superposition of two electric-quadrupole doublets, both of which are assigned to high-spin Fe(II) ions. At low temperatures, i.e. below 200 K, however, the spectrum has changed and consists of a superposition of one of the electric quadrupole doublets and a newly formed singlet. It is obvious that the iron site belonging to the low-intensity electric-quadrupole splitting of the spectrum at room temperature undergoes a high-spin–low-spin transition when the temperature is decreased. From the spectral contribution it follows that this Fe site has to be the central one in the trinuclear compound. As in the low-spin state, no electric-quadrupole splitting is observed; the central Fe ion must be surrounded highly symmetrically by the triazole ligands. No long-range magnetic ordering is observed at temperatures down to $T = 2$ K.

Table V. Isomer Shifts (IS) and Quadrupole Splittings (QS) of the Central and Terminal Metal Sites in $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$[a]

	site 1					site 2	
	high spin		low spin			high spin	
T, K	IS, mm/s	QS, mm/s	IS, mm/s	QS, mm/s	X_{HS}	IS, mm/s	QS, mm/s
300	1.35	2.68			1.00	1.41	1.73
228	1.37	2.96			1.00	1.47	1.97
218	1.37	2.99	0.64	0.00	0.72	1.47	1.99
208	1.38	3.03	0.76	0.00	0.59	1.47	2.01
198	1.35	2.92	0.77	0.00	0.26	1.48	1.95
195	1.36	2.99	0.77	0.00	0.16	1.47	1.93
191			0.78	0.00	0.00	1.47	1.94
162			0.79	0.00	0.00	1.45	2.08
152			0.77	0.00	0.00	1.47	2.17
77			0.80	0.00	0.00	1.52	2.51
4.2			0.78	0.00	0.00	1.54	2.62
2			0.78	0.00	0.00	1.54	2.64

[a] Site 1 = central Fe site; site 2 = terminal Fe sites.

The values of the isomer shifts (IS) and the quadrupole splitting (QS) have been deduced from the measured spectra by a computer fitting procedure and are listed in Table V. The assignment of the singlet resonant absorption line has been carried out by measurement at $T = 4.2$ K in an applied magnetic field of 5 T parallel to the γ rays. The measured spectrum is shown in Figure 4. Because of the low-spin state of the central Fe(II) ion, the hyperfine splitting of the singlet will be equal to the value of the applied field. The corresponding subspectrum of the low-spin Fe(II) ions consists of four resonant absorption lines, which are indicated in Figure 4. It follows from Table V that the IS and QS values for the

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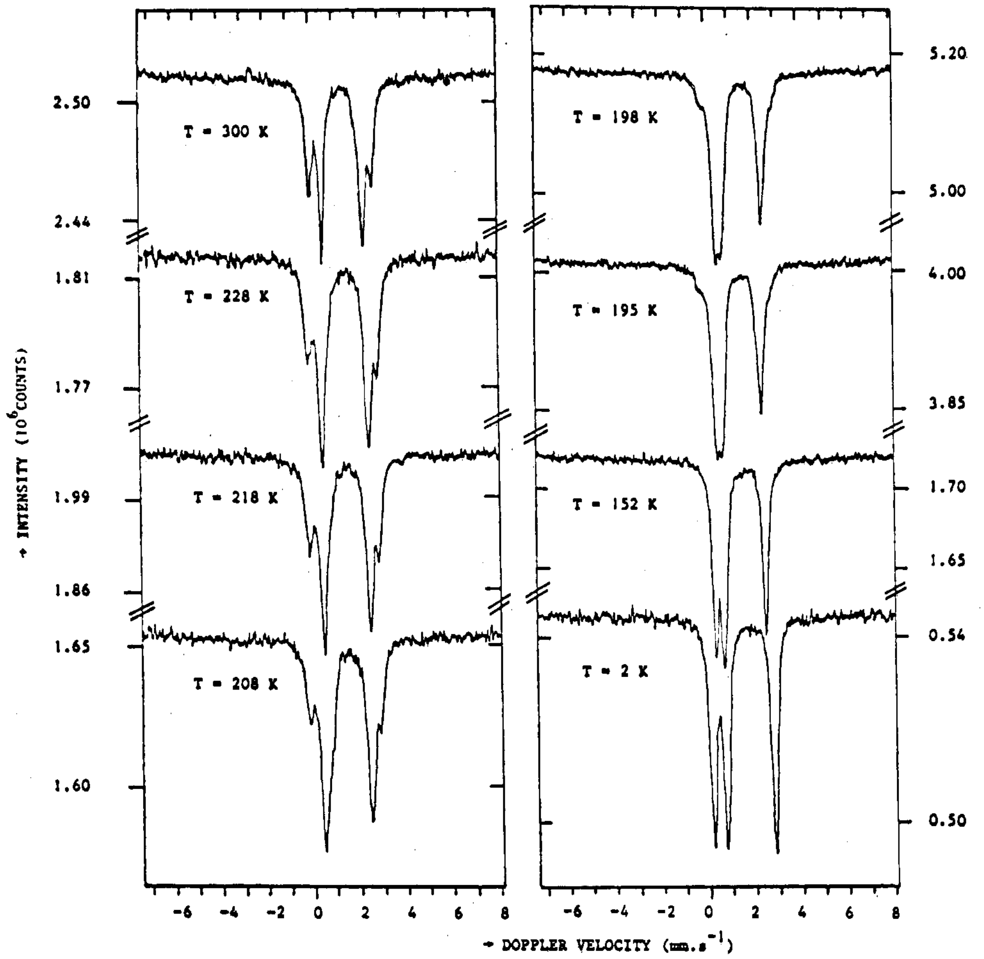

Figure 3. Mössbauer spectra of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at different temperatures.

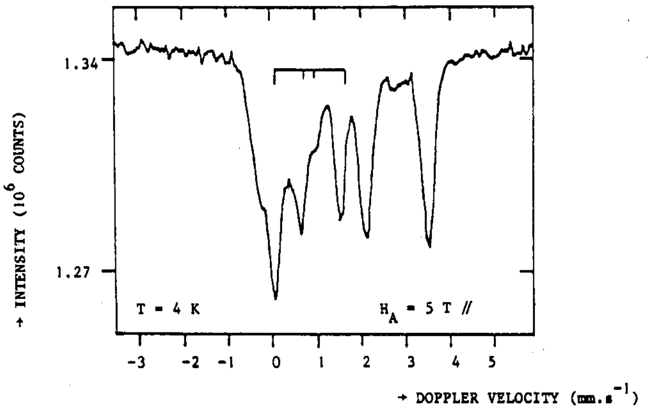

Figure 4. Mössbauer spectrum of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 4.2 K in an applied field of 5 T parallel to γ rays.

terminal Fe ions of the trimer are affected on cooling to 2 K by the high-spin transition of the central Fe(II) ion. The spin crossover is complete and takes place gradually from $T = 190$ K to $T = 230$ K, which is in agreement with the magnetic susceptibility data. No hysteresis has been detected, while also the widths of the resonant absorption lines remain essentially the same.

In order to determine the sign of the main component of the electric field gradient tensor (V_{zz}) measurements were performed in an external magnetic field parallel to the γ-ray beam up to $H = 5$ T. The measured spectra at $T = 4.2$ K and $T = 162$ K are shown in Figures 4 and 5, respectively. As the characteristic triplet, due to the magnetic perturbation of the electric-quadrupole split levels, is observed at the high-energy side of the spectrum, it is concluded that V_{zz} is negative. This agrees with the trigonal symmetry for each of the terminal iron(II) ions, since in this case the d_{xy} orbital

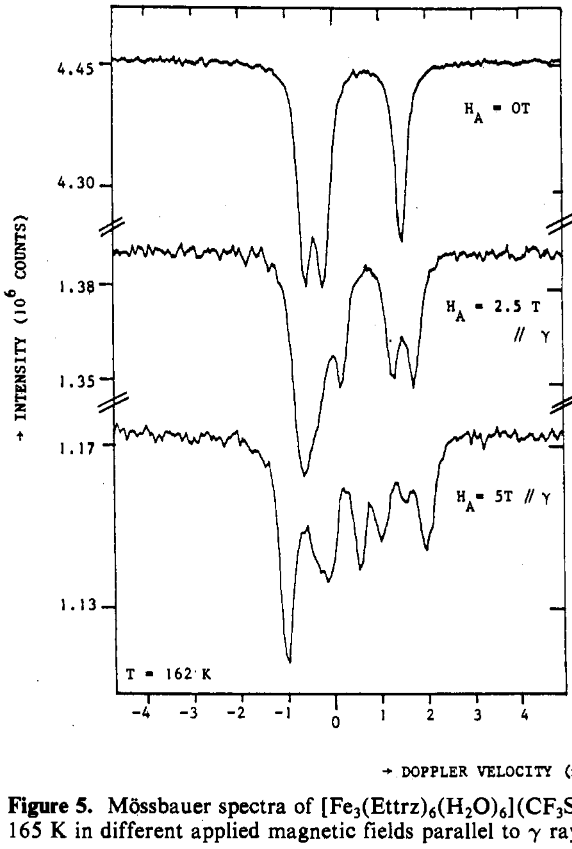

Figure 5. Mössbauer spectra of $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ at 165 K in different applied magnetic fields parallel to γ rays.

would be the ground state.[19,20]

Concluding Remarks

In this paper a unique linear trinuclear Fe(II) compound is described that can provide a suitable basis for further research, especially on the electronic properties of such a trinuclear system. The mechanism of the spin transition in the crystalline state is not yet understood. Sorai and Seki[21,22] have suggested, on the basis of precise heat capacity measurements on $[Fe(phen)_2(NCS)_2]$, that a cooperative spin transition takes place in this system through a significant coupling between the electronic state and the vibrational modes of the lattice surroundings. The suggestion of a cooperative spin transition has been well supported by the metal dilution studies on $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ by Sorai et al.[23] and Gütlich et al.[24] The different chemical environments in the outer two metal ions and in the central one allow the selective substitution of the terminal Fe atoms by for instance Mn or Zn. This may give more information on the different mechanisms of the cooperative spin transitions, as well as allowing the detailed study of the magnetic exchange through the triazole ligand. These investigations are in progress.

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Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters at 300 and 105 K (10 pages). Ordering information is given on any current masthead page.

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Notes

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Xα–SW Calculations for Naked Actinide Dimers: On the Existence of φ Bonds between Metal Atoms

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Multiple bonding in dimeric transition-metal systems involves diatomic interactions between the available d orbitals on each atom.[1] With the use of d orbitals, for which $l = 2$, these interactions can be of σ ($m_l = 0$), π ($m_l = 1$), or δ ($m_l = 2$) diatomic symmetry, leading to bond orders as high as 6 in naked metal dimers such as Mo_2.[2] It occurred to us that dimers of the actinide elements would likely involve diatomic interactions between f orbitals. As shown in Figure 1, these not only could generate bonds of σ, π, and δ symmetry but also could lead to ϕ bonds (between f orbitals with $m_l = 3$) as well. The possibility of "ϕ-back-bonding" in actinocene complexes has been successfully investigated with use of nonrelativistic and relativistic Xα–SW molecular orbital calculations,[3,4] and in this note we report preliminary Xα–SW calculations on the naked actinide dimers U_2 and Np_2 to demonstrate for the first time the existence of ϕ bonds between metal atoms.[5]

In order for ϕ bonds to exist in actinide dimers, it is apparent that two conditions must be satisfied. First, since the ϕ bond is expected to be the weakest of the f–f interactions, the 5f orbitals must be low enough in energy that the ϕ bonds are lower in energy than the 6d–6d bonding interactions. We were encouraged in this regard by our studies of organouranium(IV) complexes,[15] in which the 5f orbitals are greatly stabilized relative to the 6d and 7s orbitals. Second, the diatomic interactions must be strong enough to give an energetic separation between the ϕ bonds and antibonds. Although the 5f orbitals in higher oxidation state actinide complexes are quite contracted, it was our feeling that this might not be the case for U(0) and Np(0) and that appreciable ϕ interaction might result.

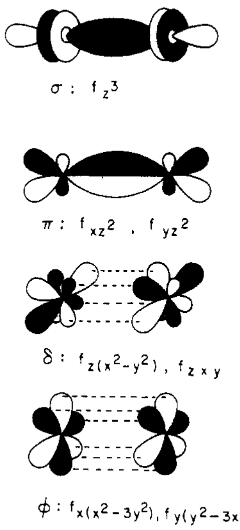

Figure 1. Qualitative diagram of f–f diatomic bonding interactions. The f orbitals that may form each type of bond are indicated below each.

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[5] Calculational details: A bond length of 2.2 Å was assumed for both U_2 and Np_2; this is ca. 0.6 and 0.4 Å shorter than the M–M distances in elemental U[6,7] and Np[8], respectively. Xα–SW calculations were performed in a fashion analogous to that for previous calculations on metal dimers[9–13] using an α value of 0.692 for both U and Np. A Watson sphere[14] with charge 2+ was used in order to stabilize unoccupied orbitals.
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