dinitrogen complex is not recovered on treatment with base, and (3) a halide anion of AlX_3 is transferred to the tungsten metal.

On treatment of complex **4** with 1 mol equiv of HCl gas in benzene, an aluminum hydrazido(2−) complex $[WCl(py)(NN(H)AlCl_2)(PMe_2Ph)_3]Cl$, **6**, is isolated as crystals in moderate yield. The complex shows a broad and strong band at 3050 cm^{-1} assigned to $\nu(NH)$ in the IR spectrum, suggesting hydrogen bonding between the N–H group and Cl anion.

Further studies are now in progress to develop the idea of activation of dinitrogen on multimetallic centers.

Supplementary Material Available: Tables of atomic positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

Unique High-Spin–Low-Spin Transition of the Central Ion in a Linear, Trinuclear Iron(II) Triazole Compound

Ger Vos, Rob A. le Fêbre, Rudolf A. G. de Graaff,
Jaap G. Haasnoot, and Jan Reedijk*

Department of Chemistry, Gorlaeus Laboratories
State University Leiden, 2300 RA Leiden, The Netherlands

Received November 24, 1982

A variety of iron(II) compounds is known to show transitions from the high-spin ($S = 2$) state to the low-spin ($S = 0$) state upon cooling or upon increasing pressure.[1] A very strong 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, dipyridyl, and 2,2′-pyridylimidazole.[1-3] In only a few cases such HS–LS transitions[4] have been observed with monodentate ligands in compounds $Fe(L)_6(anion)_2$, i.e., in isoxazole[5] and tetrazole[6] coordination compounds. Dinuclear and polynuclear Fe(II) compounds with strong-field ligands have not yet been reported to exhibit such transitions.

We recently prepared[7] a series of new trinuclear triazole compounds of the general formula $M_3(Rtr)_6(H_2O)_6(CF_3SO_3)_6$ (M = Mn, Fe, Co, Ni, or Zn, R is an alkyl group, and tr is 1,2,4-triazole). The structure of these compounds consists of linear trinuclear cations $[(H_2O)_3M(Rtr)_3M(Rtr)_3M(OH_2)_3]^{6+}$ and the triflate counterions.[7] The ligand-field spectra of the Co(II) and Ni(II) compounds indicate the presence of a strong ligand field in these compounds. Because of the asymmetric environment of the terminal metal ions and the expected strong ligand field, which affects the central ion, we have studied the iron compounds in detail to investigate the possibilities of HS–LS transitions. The results described below show that the central iron ion indeed changes its spin state upon cooling.

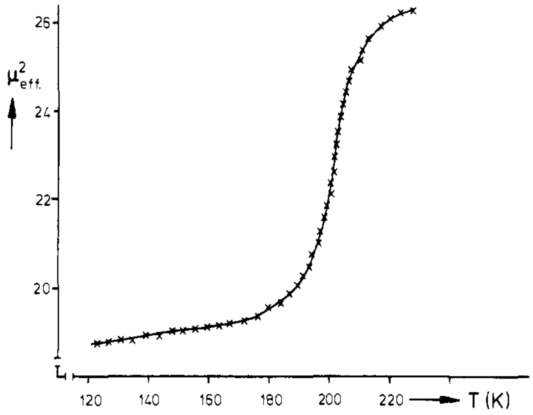


Figure 1. Plot of μ_{eff}^2 (μ in μ_B/mol of Fe) of $[Fe_3(4\text{-}Ettr)_6(H_2O)_6](CF_3SO_3)_6$ as a function of temperature.

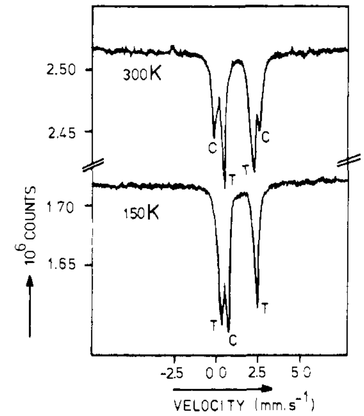


Figure 2. Mössbauer spectra at 300 and 150 K of $[Fe_3(4\text{-}Ettr)_6(H_2O)_6](CF_3SO_3)_6$; T refers to terminal iron; C refers to central iron.

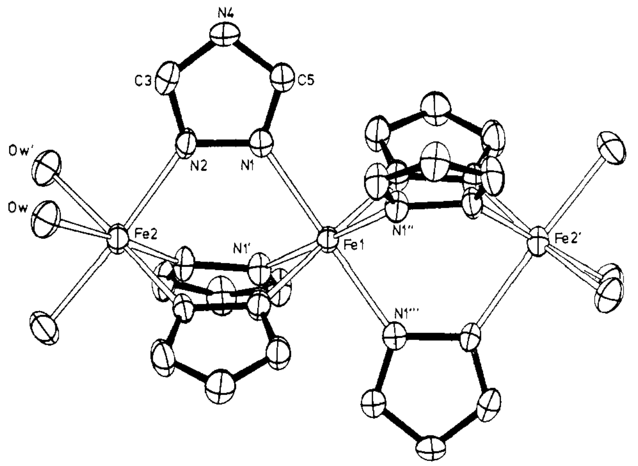


Figure 3. ORTEP drawing of the $[Fe_3(4\text{-}Ettr)_6(H_2O)_6]^{6+}$ cation showing the 50% probability ellipsoids. Hydrogen atoms and the ethyl groups have been omitted for clarity. Selected distances and angles are given in the table. The structure shown is the one obtained at 300 K; the low-temperature structure is essentially similar, apart from changes in bond lengths and angles. The triflate anions are hydrogen bonded to the water molecules (not shown in the figure).

The compound $[Fe(4\text{-}Ettr)_2(H_2O)_2]_3(CF_3SO_3)_6$ was easily prepared from aqueous solutions of the salt and the ligand.[8,9] Infrared spectra show the presence of uncoordinated triflate ions, and coordinated 4-ethyltriazole and water. The ligand-field spectrum recorded[10] at room temperature shows a broad band at 11 300 cm^{-1}, in agreement with high-spin Fe(II). Upon cooling to liquid-nitrogen temperature, the compound changes from white to purple and an additional band at 18000 cm^{-1} is observed in the diffuse reflectance spectrum. The presence of this additional band suggests low-spin Fe(II).[11] The magnetic susceptibility of the compound as a function of temperature[12] is depicted in Figure

---

(1) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 82–195.

(2) König, E. *Coord. Chem. Rev.* **1968**, *3*, 471–495.

(3) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293–325.

(4) Abbreviations used: HS = high spin; LS = low spin; tr = 1,2,4-triazole; Et = ethyl.

(5) Driessen, W. L.; Van der Voort, P. H. *Inorg. Chim. Acta* **1977**, *21*, 217–222.

(6) Franke, P. L.; Haasnoot, J. G.; Zuur, A. P. *Inorg. Chim. Acta* **1982**, *59*, 5–9.

(7) Vos, G. Ph.D. Thesis, State University Leiden, in preparation.

(8) In a typical preparation 0.01 mol of $Fe(H_2O)_6(CF_3SO_3)_2$ in 10 mL of H_2O containing a trace of HO_3SCF_3 was added to 0.03 mol of 4-ethyltriazole in 10 mL of water. Almost white crystals appear upon standing.[9]

(9) The compound correctly analyzes as $Fe(C_{10}H_{18}F_6O_8S_2N_6)$ (C,H,N,S,F). The compound is named as bis[triaquatris(4-ethyltriazole-N^1)-iron(II)-N^2,$N^{2'}$,$N^{2''}$]iron(II) hexakis(trifluoromethylsulfonate).

(10) Obtained as the solid-state diffuse reflectance spectrum on a Beckman DK-2A with MgO as a reference.

(11) Low-spin Fe(II) species with a FeN_6 chromophore have bands at about 17000–19000 cm^{-1} in most cases.[1-3]

0002-7863/83/1505-1682$01.50/0 © 1983 American Chemical Society

Table I. Relevant Distances (Å) and Angles (deg) in $[Fe_3(4\text{-Ettr})_6(H_2O)_6](CF_3SO_3)_6$

	temp, K	
	300	105
Fe1···Fe2	3.840 (1)	3.795 (2)
Fe1-N1	2.174 (4)	2.031 (6)
Fe2-N2	2.157 (4)	2.176 (6)
Fe2-Ow	2.156 (4)	2.166 (6)
N1-Fe1-N1'	90.6 (2)	92.4 (2)
N1-Fe1-N1"	88.5 (3)	87.7 (4)
N1-Fe1-N1'"	178.7 (3)	179.8 (4)
N1'-Fe1-N1'"	90.4 (3)	87.5 (4)
N2-Fe2-Ow	89.3 (2)	89.7 (2)
N2-Fe2-Ow'	92.9 (2)	95.2 (3)
Ow-Fe2-Ow'	86.5 (2)	86.6 (2)

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

1. The change in the susceptibility near 203 K corresponds with a change to the low-spin state for one-third of the iron ions. Mössbauer spectra[13] show a similar phase transition. At 300 K two quadrupole doublets are observed in the ratio 1:2, corresponding to high-spin Fe(II) (isomers shifts 1.41 and 1.35 mm/s respectively; quadrupole splittings 1.73 and 2.68 mm/s, respectively). At 150 K the low-intensity doublet has changed into a singlet (isomer shift 0.78 m/s) corresponding to low-spin iron(II). Two spectra are shown in Figure 2. The transition to the low-spin state is found at 203 ± 3 K.

To study the details of this very unusual phase transition and the connected HS-LS change, we decided to determine the crystal structure at both 300 and 105 K.[14-16] An illustration of the cation geometry (at 300 K only) is shown in Figure 3, together with some information about the numbering. The low-temperature structure is essentially the same, except for a significant shortening of the band involving the central iron ion. Some relevant structural parameters are compared in Table I. The observed decrease in the Fe-N bond length for the central iron ion clearly reflects 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.[1,3] The structure type described in this paper is interesting from several points of view. In the first place the different chemical environments of the outer two metal ions, compared with the central one, opens the route to mixed-metal species, which allows for the detailed study of the magnetic exchange through the triazole ligand. Secondly, by choosing a diamagnetic central metal ion (e.g., low-spin iron or cadmium), the study of the weak exchange between the two outside metal ions becomes possible. This will permit the study of the often disputed J_{13} exchange in linear trinuclear compounds.[18] Studies of these types are ongoing in our laboratories.

Acknowledgment. The investigations were supported in part by the Netherlands Organization for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Supplementary Material Available: Listing of the atomic coordinates and thermal parameters (6 pages). Ordering information is given on any current masthead page.

---

(12) Magnetic susceptibilities were obtained in the 80-300 K region by using a Faraday balance (data obtained by B. van der Griendt). $Hg[Co(NCS)_4]$ was used as a calibrant.

(13) Mössbauer spectra were obtained in the temperature region 2-300 K (data obtained by A. M. van der Kraan and P. C. M. Gubbens, IRI, Delft). Disodium pentacyanonitrosyliron was used as a calibrant.

(14) Crystal data at 300 K: trigonal; $a = 14.488$ (5) Å, $c = 19.858$ (5) Å; $\gamma = 120°$; $Z = 2$; space group $P\bar{3}1c$; Mo $K\alpha$ radiation; 992 independent nonzero $[I < 2\,\sigma(I)]$ reflections with 2θ between 4 and 46°; $R = 0.0462$; $R_w = 0.0413$. Iron atoms positions were located by a Patterson map; other atoms came from Fourier maps. Hydrogens were placed at calculated positions; non-hydrogen atoms were refined anisotropically.

(15) Crystal data at 105 K: $a = 14.265$ (7) Å, $c = 19.632$ (2) Å; 1112 independent nonzero reflections with 2θ between 4 and 44°; $R = 0.0638$; $R_w = 0.0753$; other data are the same as at 300 K. Refinements started with the atomic positions of the 300 K structure.

(16) Atomic coordinates and thermal parameters are available as supplementary material. Full details of both crystal structures will be reported in a later paper,[17] together with a detailed analysis of the Mössbauer spectra.

(17) Vos, G.; De Graaff, R. A. G.; Haasnoot, J. G.; Van der Kraan, A. M.; De Vaal, P.; Reedijk, J. *Inorg. Chem.*, manuscript in preparation.

(18) Mackey, D. J.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 702-704.

2,2-Dimethylpropanethial: A Long-Lived Aliphatic Thioaldehyde

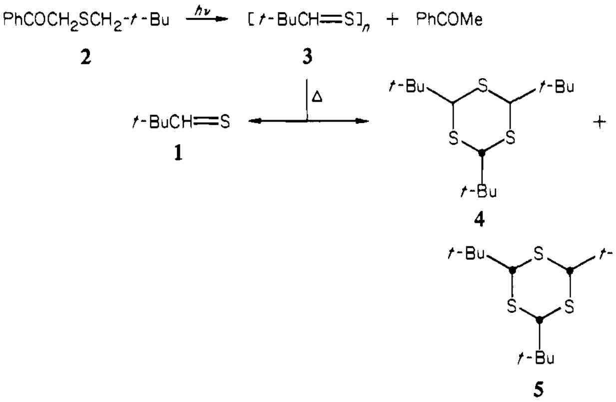
E. Vedejs* and D. A. Perry

S. M. McElvain Laboratory of Organic Chemistry
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

Received November 29, 1982

Simple aliphatic thioaldehydes RCH=S have not previously been isolated or observed on the laboratory time scale due to rapid formation of trimers or polymers.[1] Experience gained in synthetic projects caused us to suspect that these decomposition pathways may require catalysis and that intrinsic thioaldehyde lifetimes might be greater than has been supposed. Experiments described below support this hypothesis. The surprisingly stable title compound **1** is the first aliphatic thioaldehyde known to survive in solution.

Photolysis[1e] of phenacyl neopentyl sulfide **2** affords an insoluble white polymer **3** together with complex minor products, but little if any thioaldehyde trimer.[2] Heating **3** in a simple vacuum distillation apparatus (approximately ≥250 °C) results in 2,2-dimethylpropanethial (**1**, >50% yield distilled)[3] together with



---

(1) Reviews: (a) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1. (b) Wagner, A., "Methoden der Organishen Chemie"; Muller, E., Ed; Houben-Weyl: Berlin, 1955; Vol. IX, 699. (c) Duus, F. "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, **1978**, Vol. 3, 373. (d) See also "Organic Compounds of Sulphur, Selenium, and Tellurium"; The Chemical Society: London; Vols. 1 to current. (e) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.

(2) Neopentylmagnesium chloride in ether was treated with 1 equiv of sulfur to give 40% 2,2-dimethylpropanethiol after acid workup. Reaction with phenacyl chloride + Et_3N (THF) gave **2**, 97%. Photolysis in benzene + 5% 2,3-dimethylbutadiene gave 60% polymer **3**. Photolysis gave only 30% polymer in benzene alone and approximately 5% in THF.

(3) A simple cold trap at -196 °C was connected via a two-way vacuum stopcock to a container of $CHCl_3$ or $CDCl_3$ and a second container of polymer **3** under a plug of glass wool. Enough $CHCl_3$ was transferred under vacuum to coat the cold trap with a film of frozen $CHCl_3$. The polymer was then heated with a small Bunsen flame until pink distillate appeared in the cold trap (approximately 1-2 min). Warming the distillate to 20 °C gave a characteristic pink solution of **1**. To define the temperature for appearance of **1**, **3** was stirred with diphenyl ether and heated. A pink color appeared at approximately 250 °C. Alternatively, a solution containing **1** (together with ethanol and some $(CH_3)_3CH(SH)OC_2H_5$) codistilled with xylene from TsOH catalyzed decomposition of $(CH_3)_3CH(SH)OC_2H_5$ in xylene at approximately 140 °C. The starting material was made from *t*-BuLi + $S{=}CHOC_2H_5$ and purified by bulb-to-bulb vacuum distillation at room temperature. This solution gives 30-40% of trapping products such as **7** or **9**.