# Controlling the Number of Bridging Ligands in Binuclear Iron Thiolate Complexes by Modulation of Ligand Nucleophilicities: $[Fe_2(SC_4H_9)_5]^-$, the First Complex Containing $FeS_4$ Tetrahedra Connected via Common Faces, and $[Fe_2(SC_3H_7)_6]^{2-}$, a Complex with a Bitetrahedral $M_2S_6$ Framework of Conventional Design

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Iron complexes with sterically unencumbered monofunctional thiolate ligands contain iron in a tetrahedral sulfur environment. Besides mononuclear species,[1] binuclear[2] and tetranuclear complexes[2,3] are also known. They can formally be considered as the result of condensation processes which lead to the formation of $\mu$-S thiolate bridges according to

$$n[Fe(SR)_4]^{2-} \rightleftarrows [Fe_n(\mu\text{-}SR)_{2n-2}(SR)_4]^{2-} + (2n-2)SR^- \quad (1)$$

$$n = 2, 4$$

In those instances where $n = 2$, the complexes contain two $MS_4$ tetrahedra which share a common edge,[2] whereas, in the case of $n = 4$, the $MS_4$ tetrahedra are connected via common vertices resulting in the adamantane-like cage structure.[2,3]

Recently, we were able to show that secondary thiolate ligands exhibit a rather unique coordination behavior toward divalent nickel ions.[4] The resulting complexes are cyclic tetranuclear species with square-planar metal coordination and surprisingly small Ni–S–Ni bridging angles. On the basis of these observations, we developed the idea that an electronic modulation of the thiolate-S atom might be of significant influence on the magnitude of the M–S–M angle in polynuclear complexes with $\mu$-S(*thiolate*) bridges in a more general sense. This modulation can easily be achieved by changing the number of alkyl groups attached to the $\alpha$-carbon atom. To test the hypothesis, we carried out a systematic investigation of the reaction behavior of other divalent metal ions toward 2-propanethiolate and 2-methyl-2-propanethiolate ligands. In the case of divalent cobalt, we were able to synthesize $[Co_2(SC_3H_7)_5]^-$, the first compound in which two $CoS_4$ tetrahedra share a common face.[5] In this communication, we wish to report the synthesis and structural characterization of the first homoleptic iron complex with 2-propanethiolate ligands, $[Fe_2(SC_3H_7)_6]^{2-}$ (**1**). In addition, the complex anion $[Fe_2(SC_4H_9)_5]^-$ (**2**) is described, the first binuclear iron compound with tetrahedral $MS_4$ coordination and three thiolate bridges.

The title compounds **1** and **2** were synthesized by reaction of $NaS^iC_3H_7$ with $FeCl_2{\cdot}4H_2O$ (**1**) or of $NaS^tC_4H_9$ with $FeCl_2$ (**2**) in methanolic solution.[6] Both anions were precipitated as tetramethylammonium salts, $[Me_4N]_2[Fe_2(SC_3H_7)_6]$ and $[Me_4N][Fe_2(SC_4H_9)_5]{\cdot}MeOH$, respectively, and characterized by X-ray crystallography.[7]

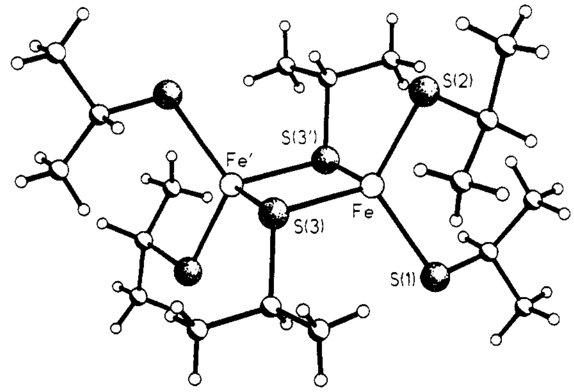

**Figure 1.** $[Fe_2(SC_3H_7)_6]^{2-}$: Molecular structure and atomic labels. Selected distances (Å) and angles (deg): Fe···Fe' = 3.091(1), Fe–S(1) = 2.332(1), Fe–S(2) = 2.329(1), Fe–S(3) = 2.388(1), Fe–S(3') = 2.382(1); S(1)–Fe–S(2) = 117.7(1), S(1)–Fe–S(3) = 111.3(1), S(1)–Fe–S(3') = 107.1(1), S(2)–Fe–S(3) = 110.3(1), S(2)–Fe–S(3') = 109.5(1), S(3)–Fe–S(3') = 99.2(1).

The structure of **1**, which has crystallographically imposed $\bar{1}$ symmetry, is shown in Figure 1. The $Fe_2S_6$ framework of the anion consists of two $FeS_4$ tetrahedra which share a common edge, the Fe···Fe and mean $Fe–S_{br}$ and $Fe–S_{term}$ distances being 3.091, 2.385, and 2.331 Å, respectively. **1** is closely related with the analogous ethanethiolate complex.[2] Obviously, the introduction of isopropyl instead of ethyl residues has no pronounced influence on the basic geometry of binuclear iron complexes.

However, the situation changes completely if we replace the isopropyl residues by *tert*-butyl groups. Though **2** has an overall composition which fits exactly into the class of complexes with the adamantane-like stereochemistry, its molecular structure does

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(1) (a) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, D. C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350–3362. (b) Millar, M.; Lee, J. F.; Koch, S. A.; Fikar, R. *Inorg. Chem.* **1982**, *21*, 4106–4108. (c) Millar, M.; Koch, S. A.; Fikar, R. *Inorg. Chim. Acta* **1984**, *88*, L15–L16.

(2) Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 418–427.

(3) Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, 3928–3936.

(4) (a) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem.* **1989**, *101*, 54–55; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 61–62. (b) Krebs, B.; Henkel, G. *Angew. Chem.* **1991**, *103*, 785–804; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769–788.

(5) Henkel, G.; Weissgräber, S. *Angew. Chem.* **1992**, *104*, 1382–1383; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1368–1369.

(6) All operations were carried out under an atmosphere of pure dinitrogen. **1**: A solution of 1.99 g of $FeCl_2{\cdot}4H_2O$ (10 mmol) in 10 mL of methanol was added dropwise to a stirred solution of 2.45 g of $NaS^iC_3H_7$ (25 mmol) in 25 mL of methanol. During this time, a dark brown color appeared. The solution was stirred for additional 25 h at room temperature and filtered. To the filtrate was added 1.10 g (10 mmol) of $Me_4NCl$ and 90 mL of ether. The mixture was cooled to –26 °C. Over a period of 4–6 days, brown crystals of $[Me_4N]_2[Fe_2(SC_4H_9)_6]$ containing the anion **1** separated from the solution. **2**: The synthetic procedure is similar to that described above. A 2.25-g amount of $NaS^tC_4H_9$ (20 mmol) in 20 mL of MeOH was used as the thiolate component. On addition of 0.63 g (5 mmol) of $FeCl_2$, the color turned to dark brown. The solution was stirred for additional 10 min and filtered to remove some black insoluble material. To the filtrate was added 0.55 g (5 mmol) of $Me_4NCl$, and the mixture was stored at –26 °C for 6 days. During that time brown crystals of $[Me_4N][Fe_2(SC_4H_9)_5]{\cdot}MeOH$ containing the anion **2** formed together with small amounts of a black crystalline product. The second phase was identified as $[Me_4N]_2[Fe_4S_4(SC_4H_9)_4]$ by X-ray crystallography.

(7) Siemens P4RA four-circle diffractometer, rotating anode generator, Mo K$\alpha$ radiation, graphite monochromator, scintillation counter, $\omega$-scan, empirical absorption corrections, $2\theta < 54°$, variable scan speed. $[Me_4N]_2[Fe_2(SC_3H_7)_6]$, monoclinic, space group $P2_1/n$, $a = 9.473(1)$ Å, $b = 14.698(2)$ Å, $c = 14.764(2)$ Å, $\beta = 107.53(1)°$, $V = 1960$ Å$^3$, $Z = 2$, $\mu(\text{Mo K}\alpha) = 1.08$ mm$^{-1}$, $D_x = 1.204$ gcm$^{-3}$, direct methods, heavy atoms anisotropic, $-CH_3$ as rigid groups, 2697 observed reflections ($I > 2\sigma(I)$), 288 variables, $R$ ($R_w$) = 0.022 (0.026). $[Me_4N][Fe_2(SC_4H_9)_5]{\cdot}MeOH$, orthorhombic, space group $Pbcn$, $a = 17.699(2)$ Å, $b = 23.021(3)$ Å, $c = 18.321(2)$ Å, $V = 7463$ Å$^3$, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.07$ mm$^{-1}$, $D_x = 1.181$ gcm$^{-3}$, direct methods, heavy atoms anisotropic, $-CH_3$ as rigid groups, 4472 observed reflections ($I > 3\sigma(I)$), 315 variables, $R$ ($R_w$) = 0.052 (0.056).

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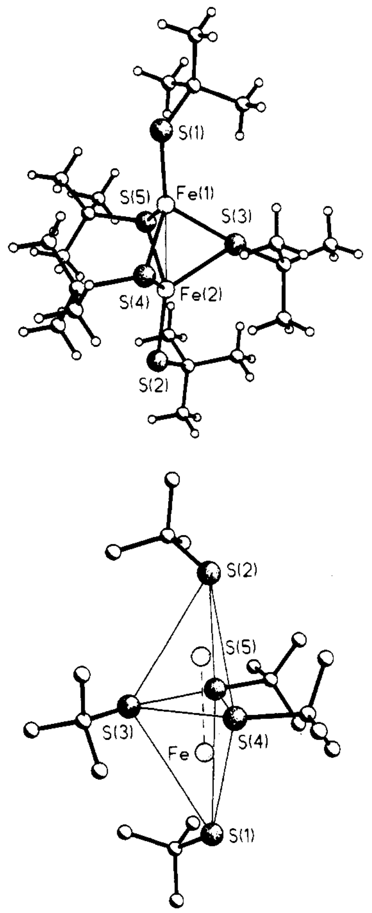

**Figure 2.** $[Fe_2(SC_4H_9)_5]^-$. Top: Molecular structure and atomic labels. Selected distances (Å) and angles (deg): Fe(1)···Fe(2) = 2.634(1), Fe(1)–S(1) = 2.269(2), Fe(1)–S(3) = 2.403(2), Fe(1)–S(4) = 2.369(2), Fe(1)–S(5) = 2.360(2); S(1)–Fe(1)–S(3) = 126.9(1), S(1)–Fe(1)–S(4) = 119.3(1), S(1)–Fe(1)–S(5) = 127.5(1), S(3)–Fe(1)–S(4) = 88.6(1), S(3)–Fe(1)–S(5) = 78.7(1), S(4)–Fe(1)–S(5) = 104.2(1), Fe(2)–S(2) = 2.252(2), Fe(2)–S(3) = 2.374(2), Fe(2)–S(4) = 2.352(2), Fe(2)–S(5) = 2.353(2), S(2)–Fe(2)–S(3) = 130.1(1), S(2)–Fe(2)–S(4) = 116.9(1), S(2)–Fe(2)–S(5) = 126.0(1), S(3)–Fe(2)–S(4) = 89.8(1), S(3)–Fe(2)–S(5) = 79.4(1), S(4)–Fe(2)–S(5) = 105.0(1). Bottom: Bitetrahedral $Fe_2S_5$ framework (without H atoms).

not (Figure 2). This unusual molecule is a binuclear complex with two iron atoms surrounded by four thiolate-S atoms each. In striking contrast to all other metal thiolates described so far, however, the two $MS_4$ tetrahedra observed here share a common face (S(3), S(4), S(5)) resulting in three thiolate bridges.

The $Fe_2S_5$ core portion of **2** therefore is a trigonal bipyramid defined by S, and the Fe atoms occupy the centers of both the upper and the lower moieties simultaneously. This bipyramid is significantly elongated due to repulsive forces between the metal atoms, which in our case approach each other up to a distance of 2.634(1) Å.[8] This value is significantly longer than that one found in $[Co_2(SC_3H_7)_5]^-$ (2.491(1) Å),[5] besides $[Ni_2(SC_6H_3(C_3H_7)_2)_5]^-$ [9] the only other example of a tetrahedral complex with three common sulfur bridges known so far.[10]

The plane of the $S_5$ bipyramid deviates from a regularly shaped triangle, the S···S distances being 3.733(1) Å (4···5), 3.335(1) Å (3···4) and 3.020(1) Å (3···5). The mean Fe–S distance in **2** is 2.350 Å for Fe(1) and 2.333 Å for Fe(2). These values are close to the upper and lower limits observed in binuclear thiolate complexes with $Fe_2S_6$ frameworks.[2,11]

The results of our investigation clearly demonstrate that the chemistry of iron with thiolate ligands is much more versatile than what had to be expected from the presently known chemical behavior. There is now substantial evidence that small, but carefully directed, electronic modulations at the ligand donor functions are capable of inducing significant structural changes within the ligand sphere of transition metal complexes.

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**Supplementary Material Available:** Complete listings of crystallographic data, atomic coordinates, bond distances and angles, and isotropic and anisotropic temperature factors (Tables S-1–S-10) (13 pages). Ordering information is given on any current masthead page.

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(8) For a detailed discussion of the degree of distortion see ref 5.

(9) After this work was finished, the structurally related nickel complex $[Ni_2(SC_6H_3(C_3H_7)_2)_5]^-$ was described: Silver, A.; Millar, M. *J. Chem. Soc., Chem. Commun.* **1992**, 948–949.

(10) Polynuclear complexes containing $MX_4$ tetrahedra which share faces are also known to exist in the system M = $Cu^+$, X = $I^-$: Hartl, H. *Angew. Chem.* **1987**, *99*, 925–927; *Angew. Chem., Int. Ed. Engl.* **1987**, *27*, 921–923 and references cited therein. However, in all these instances the copper ions do not occupy the centroids of the $I_4$ tetrahedra but reside in states with significant contributions from a trigonal coordination.

(11) Henkel, G.; Tremel, W.; Krebs, B. *Angew. Chem.* **1983**, *95*, 317–318; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 318–319; *Angew. Chem. Suppl.* **1983**, 323–346.