Aryl isonitrile binding to $[Fe_4S_4]$ clusters: formation of $[Fe_4S_4]^+$ and $[\{Fe_4S_4\}_2]^{2+}$ cores

Michael Harmjanz, Wolfgang Saak,* Detlev Haase and Siegfried Pohl[†]

Fachbereich Chemie, Carl-von-Ossietzky Universität Oldenburg, Postfach 2503, D-26111 Oldenburg, Germany

Aryl isonitriles (ArNC; Ar = 2,4,6-$Me_3C_6H_2NC$ 1, 2,6-$Me_2C_6H_3NC$ 2) react with $[Fe_4S_4I_4]^{2-}$ 3 and $[Co(\eta\text{-}C_5H_5)_2]$ to afford $[Fe_4S_4I(ArNC)_9]$ 4a, b; substitution of iodide by RS^- (R = 2,4,6-$Me_3C_6H_2$) yields $[Fe_4S_4(SR)(ArNC)_9]$ 5 and reaction of $[Fe_4S_4I(2,4,6\text{-}Me_3C_6H_2NC)_9]$ 4b with $KB(4\text{-}Cl\text{-}Ph)_4$ leads to $[\{Fe_4S_4(2,4,6\text{-}Me_3C_6H_2NC)_9\}_2][B(4\text{-}ClPh)_4]_2$ 6.

Among the extended class of cuboidal Fe_4S_4 clusters, species with octahedrally coordinated iron atoms are rather uncommon. Typical examples with monodentate ligands are the well known $[Fe_4S_4(CO)_{12}]$[1] and the 2:2 site-differentiated clusters $[Fe_4S_4X_2(Bu^tNC)_6]$ (X = Cl, Br, RS).[2,3] Prior to the present work uncharged mixed-ligand clusters of the latter type with an $[Fe_4S_4]^+$ core were unknown. Even though the relevance of these clusters in biological systems is limited, especially 3:1 functionalized Fe_4S_4 clusters could serve as models for the examination of biological and non-biological catalytic processes. As demonstrated in this work these clusters also represent versatile starting materials for the formation of Fe–S clusters of higher nuclearity.

As shown elsewhere[2] alkyl isonitriles readily react with $[Fe_4S_4X_4]^{2-}$ clusters (X = Cl, Br) to yield the [2:2] site-differentiated clusters $[Fe_4S_4X_2(RNC)_6]$ containing an $[Fe_4S_4]^{2+}$ core. Aryl isonitriles (ArNC) which have slightly higher π-acceptor abilities than alkyl isonitriles[4] should stabilize lower $[Fe_4S_4]$ oxidation states. However, the complexation of Fe_4S_4 clusters by aryl isonitriles had only been realized in $[Fe_4S_4(LS_3)(ArNC)_3]^-$ (LS_3 = trithiolate ligand).[3]

When stoichiometric mixtures of the 2,6-dimethylphenylisonitrile **2** and the tetraiodo cluster anion **3** were combined in the presence of stoichiometric amounts of $[Co(\eta^5\text{-}C_5H_5)_2]$ [eqn. (1)] the novel uncharged cluster $[Fe_4S_4I(2,6\text{-}Me_2C_6H_3NC)_9]$ **4a** precipitated together with $[Co(\eta^5\text{-}C_5H_5)_2]I$ and some $N(CH_2Ph)Bu_3I$. The byproducts can easily be removed by washing the crude product with acetonitrile (yield 90%).[‡]

$$\underset{\mathbf{3}}{[Fe_4S_4I_4]^{2-}} + 9\ \underset{\mathbf{2}}{2,6\text{-}Me_2C_6H_3NC} + [Co(\eta\text{-}C_5H_5)] \rightarrow$$

$$\underset{\mathbf{4a}}{[Fe_4S_4I(2,6\text{-}Me_2C_6H_3NC)_9]} + 2\ I^- + [Co(\eta\text{-}C_5H_5)_2]I \qquad (1)$$

The formation of $[Fe_4S_4I(ArNC)_9]$ **4b** (Ar = 2,4,6-trimethylphenylisonitrile) can also be achieved as well as analogues with sterically less encumbering aryl isonitriles.

The redox behaviour of **4a** has been examined in thf by cyclic voltammetry. Chemically irreversible reduction takes place at −630 mV *vs.* SCE and a quasi-reversible oxidation wave is observed at −90 mV *vs.* SCE (i_{pa}/i_{pc} = 0.95, $E_{pa} - E_{pc}$ = 100 mV). Chemical oxidation of **4a** involving the oxidation state change $[Fe_4S_4I(ArNC)_9]^{0/+}$ was not successful. Investigation of the chemical reduction of **4a** in the presence of excess isonitrile is currently being carried out in this laboratory. This reaction should lead to $[Fe_4S_4(ArNC)_{12}]$.

Substitution reaction at the iodide site can be accomplished by addition of 1 equiv. of mesitylenethiolate to a suspension of **4a** in thf. On filtration and addition of ether $[Fe_4S_4(2,4,6\text{-}Me_3C_6H_2S)(2,6\text{-}Me_2C_6H_3NC)_9]$ **5** precipitates as red needles (yield 68%).[‡] The cyclic voltammogram of the thiolate derivative **5** in thf shows an irreversible reduction at −1040 mV, a quasi-reversible oxidation at −240 mV (i_{pa}/i_{pc} = 0.96, $E_{pa} - E_{pc}$ = 70 mV) and a quasi-reversible oxidation at 420 mV *vs.* SCE (i_{pa}/i_{pc} = 1.2, $E_{pa} - E_{pc}$ = 85 mV).

Single crystals of **5** can be obtained by addition of ether to concentrated solutions of **5** in thf. Compound **5** crystallizes as a thf solvate and its structure is shown in Fig. 1. The trigonal distortion of the $[Fe_4S_4]^+$ core originates from the different coordination environments around the iron atoms. One sulfur atom is surrounded by three octahedrally coordinated Fe^{II} and three sulfur atoms by two octahedrally Fe^{II} and one tetrahedrally coordinated Fe^{III}. The Fe–S distances form three sets, with three Fe–S bonds at the tetrahedral site Fe(1) (mean 2.247 Å), three at S(3) (mean 2.347 Å) and six at octahedrally coordinated sites Fe(2,3,4) (mean 2.379 Å). The distortion of the $[Fe_4S_4]^+$ core results in three short Fe···Fe distances (mean 3.014 Å) between the octahedrally and tetrahedrally coordinated iron sites and three long Fe···Fe distances between the octahedrally coordinated iron sites (mean 3.481 Å). The latter are comparable with those in $[Fe_4S_4(CO)_{12}]$ (mean 3.466 Å)[1] and imply no bonding interactions between those iron atoms. The iron–thiolate distance in **5** is comparable with those in $[Fe_4S_4(PhS)_2(Bu^tNC)_6]$ (mean 2.281 Å).[2]

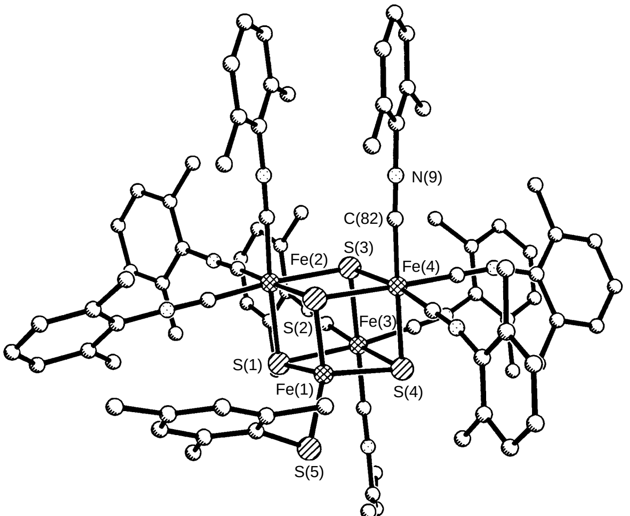

Fig. 1 Molecular structure of **5** with atom numbering scheme. Selected bond lengths (Å) and angles (°): Fe(1)–S(1) 2.253(2), Fe(1)–S(2) 2.240(2), Fe(1)–S(4) 2.248(2), Fe(1)–S(5) 2.300(2), Fe(1)···Fe(2) 2.9610(10), Fe(1)···Fe(3) 3.078(2) Fe(1)···Fe(4) 3.002(2), Fe(2)–S(1) 2.377(2), Fe(2)–S(2) 2.385(2), Fe(2)–S(3) 2.3459(15), Fe(2)···Fe(3) 3.466(2), Fe(2)···Fe(4) 3.505(2), Fe(3)- S(1) 2.387(2), Fe(3)–S(3) 2.3420(14), Fe(3)–S(4) 2.364(2), Fe(3)···Fe(4) 3.473(2), Fe(4)–S(2) 2.377(2), Fe(4)–S(3) 2.3535(15), Fe(4)–S(4) 2.383(2), Fe–C 1.835 [range 1.820(6)–1.860(6)], C(1)–S(5)–Fe(1) 103.2(2).

A condensation of the 3:1 site-differentiated cluster can easily be achieved upon reaction of $[Fe_4S_4I(2,4,6\text{-}Me_3C_6H_2NC)_9]$ **4b** with stoichiometric amounts of $KB(4\text{-}ClPh)_4$ [eqn. (2); Ar = $2,4,6\text{-}Me_3C_6H_2$].‡

$$\mathbf{2}\ \underset{\mathbf{4b}}{[Fe_4S_4I(ArNC)_9]} + 2KB(4\text{-}ClPh)_4 \rightarrow \underset{\mathbf{6}}{[\{Fe_4S_4(ArNC)_9\}_2][B(4\text{-}ClPh)_4]_2} + 2KI \qquad (2)$$

6 was characterized spectroscopically and the structure of **6** has been established by X-ray structure analysis.§ The differential pulse voltammogram of **6** shows two one-electron reduction steps at −760 and −935 mV *vs.* SCE and two one-electron oxidation steps at 200 and 460 mV *vs.* SCE, respectively.

Apart from the octahedrally ligated iron sites, the core structure of **6** is comparable with the previously synthesized neutral dicubane $[\{Fe_4S_4[P(C_6H_{11})_3]_3\}_2]$.[5] Fe–S dicubane clusters with non-phosphorus ligands are, as yet, not known. Furthermore, $[\{Fe_4S_4(2,4,6\text{-}Me_3C_6H_2NC)_9\}_2]^{2+}$ represents the first dicubane cluster including two charged $[Fe_4S_4]^+$ cores. As shown in Fig. 2 the two $[Fe_4S_4]^+$ cores are linked by two Fe–S bonds forming a central Fe_2S_2 rhombus. Compared with $[\{Fe_4S_4[P(C_6H_{11})_3]_3\}_2]$[5] the Fe···Fe distance in**6** [2.766(4) Å] within the central Fe_2S_2 unit is elongated [2.681(8) Å)] whereas the Fe–S distances are almost equal {2.285(3) Å, **6**; 2.309(7) Å, $[\{Fe_4S_4[P(C_6H_{11})_3]_3\}_2]$}. Although S(1) is additionally linked with an iron atom [Fe(1a)] of the second cuboidal fragment, the distortion of the $[Fe_4S_4]^+$ fragment from T_d symmetry mainly originates from the two structurally and electronically distinct iron sites. As a consequence the twelve Fe–S distances divide into three sets (3 + 3 + 6) and the Fe···Fe distances into two sets (3 + 3). The mean values of the Fe–S and Fe···Fe distances as well as the Fe–C distances are comparable with those in **5**.

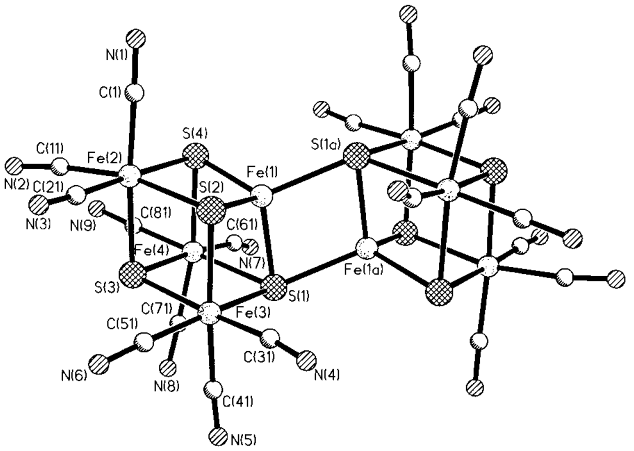

Fig. 2 Core structure of **6** with atom numbering scheme (arene moiety omitted for clarity). Selected bond lengths (Å) and angles (°): Fe(1)-S(1) 2.253(4), Fe(1)–S(2) 2.219(4), Fe(1)–S(4) 2.215(4), Fe(1)–S(1a) 2.285(3), Fe(1)–Fe(1a) 2.766(4), Fe(1)···Fe(2) 2.934(3), Fe(1)···Fe(3) 2.969(3) Fe(1)···Fe(4) 2.982(3), Fe(2)–S(2) 2.377(4), Fe(2)–S(3) 2.334(4), Fe(2)–S(4) 2.392(4), Fe(2)···Fe(3) 3.470(3), Fe(2)···Fe(4) 3.469(3), Fe(3)–S(1) 2.433(4), Fe(3)–S(2) 2.359(4), Fe(3)–S(3) 2.335(4), Fe(3)···Fe(4) 3.520(3), Fe(4)–S(1) 2.417(4), Fe(4)–S(3) 2.325(4), Fe(4)–S(4) 2.379(4), Fe–C 1.83 [range 1.78(2)–1.88(2)], S(1)–Fe(1)–S(1a) 104.91(12).

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Footnotes

† Deceased. Correspondence should be addressed to W. Saak.

‡ The used aryl isonitriles were prepared by puplished methods.[6] Cluster **3** was exclusively used as its benzyltri-*n*-butylammonium salt.[7] All reactions were carried out under a nitrogen atmosphere in dried and degassed solvents. Satisfactory elemental analyses were obtained for new compounds. **4a**: λ_{max} (thf) 327 nm. IR (KBr): 2108vs, 2058vs cm^{-1} (ν_{NC}). **4b**·Et_2O: λ_{max} (thf) 320 nm. IR (KBr): 2106vs, 2064vs cm^{-1} (ν_{NC}). **5**: λ_{max} (thf) 313 nm. IR (KBr): 2104vs, 2054vs cm^{-1} (ν_{NC}). **6**: isolated in 65% yield. λ_{max} (thf) 315 nm. IR (KBr): 2118vs, 2076vs cm^{-1} (ν_{NC}).

§ *Crystal data*: **5**·thf: $C_{94}H_{100}Fe_4N_9OS_5$, M = 1755.53, monoclinic, space group $P2_1/c$, a = 13.802(1), b = 24.633(2), c = 27.829(2) Å, β = 103.93(1)°, U = 9183.2(12) $Å^3$, T = 297(1) K, Z = 4, D_c = 1.270 g cm^{-3}, μ(Mo-Kα) = 0.783 mm^{-1}. A suitable crystal was mounted on a AED2 Siemens four-circle diffractometer. Data collection using Mo-Kα radiation (λ = 0.710 73 Å) and 2θ scans gave 12789 independent reflections (θ_{max} 23.01°), of which 9706 with $I > 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods and the solution developed using full-matrix least-squares refinement on F^2 and difference Fourier synthesis. Displacement parameters were refined for non-H atoms, H-atoms were included in fixed calculated positions.[8] At convergence, R = 0.0641, wR_2 = 0.1541, GOF = 1.182 for 885 parameters.

6·MeCN·thf: $C_{234}H_{241}B_2Cl_8Fe_8N_{19}OS_8$, M = 4343.96, triclinic, space group $P\bar{1}$, a = 19.444(8), b = 19.566(6), c = 19.752(7) Å, α = 60.66(4), β = 74.86(3), γ = 61.64(3)°, U = 5760(4) $Å^3$, T = 297(1) K , Z = 1, D_c = 1.252 g cm^{-3}, μ(Mo-Kα) = 0.709 mm^{-1}, data collection, refinement and solution as above, 10727 independent reflections (θ_{max} 20.01°), R = 0.1093, wR_2 = 0.2419, GOF = 1.195 for 1071 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/437.

References

1 L. L. Nelson, F. Y. Lo, A. D. Rae and L. F. Dahl, *J. Organomet. Chem.*, 1982, **225**, 309.

2 C. Goh, J. A. Weigel and R. H. Holm, *Inorg. Chem.*, 1994, **33**, 4861.

3 J. A. Weigel, K. K. P. Srivastava, E. P. Day, E. Münck and R. H. Holm, *J. Am. Chem. Soc.*, 1990, **112**, 8015.

4 W. S. Mialki, D. E. Wigley, T. E. Wood and R. A. Walton, *Inorg. Chem.*, 1982, **21**, 480; A. Vogler, in *Isonitrile Chemistry*, ed. I. Ugi, Academic Press, New York and London, 1971.

5 L. Cai, B. M. Segal, J. R. Long, M. J. Scott and R. H. Holm, *J. Am. Chem. Soc.*, 1995, **117** 8863; C. Goh, B. M. Segal, J. Huang, J. R. Long and R. H. Holm, *J. Am. Chem. Soc.*, 1996, **118**, 11844.

6 R. Appel, R. Kleinstück and K.-D. Ziehn, *Angew. Chem.*, 1971, **83**, 143.

7 W. Saak and S. Pohl, *Z. Naturforsch. Teil B*, 1985, **40**, 1105 and unpublished work.

8 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; SHELXTLPC and SHELXL-93, G. M. Sheldrick, University of Göttingen.

Received in Basel, Switzerland, 28th January 1997; Com. 7/00613F