

A Dinuclear Iron Complex with Two Cofacial [FeS₄] Cores Linked by Covalent Ligand Periphery Clamps and Dissociable Thiolate Bridges

Dieter Sellmann,^{*,[a]} Kai P. Peters,^[a] Raquel Montón Molina,^[a] and Frank W. Heinemann^[a]

Dedicated to Professor Dr. Horst Kisch on the occasion of his 60th birthday

Keywords: Iron / S ligands / Bridging ligands / Enzyme models

As part of a long-term study of dinuclear iron complexes with sulfur-rich coordination spheres and cofacial, sterically variable binding sites for molecules relevant to nitrogenase, the complex (AsPh₄)₂ [[Fe('apS₄')]₂] (**5**) was synthesized and completely characterized ['apS₄'⁴⁻ = 1,3-bis(2,3-dimercaptobenzamido)propane(4-)]. Complex **5** contains two cofacial [Fe^{III}(S₂C₆H₄R)₂]⁻ units linked by [Fe–S–Fe] thiolate bridges and two peripheral propanediamide ligand backbones that are located on opposite sides of the molecular an-

ion and prevent the complete separation of the two [FeS₄] cores of **5** if the Fe–S–Fe bridges dissociate. No marked differences were found in the molecular parameters, spectroscopic, magnetic and electrochemical properties of the [Fe₂S₈] cores in the anion of **5** and the parent complex [[Fe(S₂C₆H₄)₂]₂]²⁻.

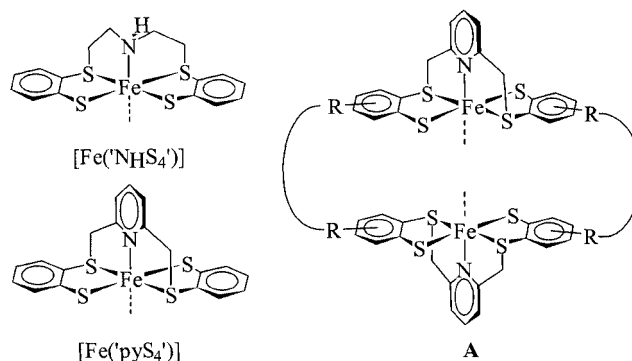
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Iron in sulfur-rich coordination spheres is the characteristic feature of the polynuclear FeMo, FeV or FeFe cofactors of nitrogenases.^[1] Interaction of N₂ with these cofactors to give metal-sulfur N₂ complexes is considered to be the primary step of N₂ fixation, and the prevalence of iron in all three types of cofactors supports current hypotheses that the resulting metal-sulfur N₂ complexes are species in which N₂ acts as a bridge between at least two [Fe(S_n)] sites held together by the other metal-sulfur bonds of the cofactor and, in addition, the surrounding enzyme protein.^[2] Low molecular weight analogues are unknown despite a prolonged search for complexes capable of modeling both structural (metal sulfur sites) and functional (binding N₂) aspects of nitrogenase cofactors.^[2]

Complex fragments such as [Fe('N_HS₄')]) and [Fe('pyS₄')]) (Scheme 1) have been shown to bind and activate or stabilize many molecules relevant to nitrogenase, such as CO, NO, N₂H₂, N₂H₄, and NH₃, though not yet N₂.^[2f,3]

To enforce the binding of N₂ to such fragments we initiated work^[4] on complexes (type A) that contain two [Fe(S_n)] sites held together by bridges (potentially modeling the en-



Scheme 1. Known complex fragments and the ultimate target molecule A

zyme protein); the [Fe('pyS₄')]) fragments favor the low-spin state of Fe^{II}, which in turn favors the binding of nitrogenase relevant molecules,^[5] and the bulky [Fe('pyS₄')]) fragments plus the spacers protect the vacant sites at the iron centers.

Such a synthetic challenge requires the complexation of iron by benzene dithiolate ligands, the formation of the [Fe('pyS₄')]) fragments, and the connection of two such fragments by bridges between benzene rings. The essential cofacial arrangement of the [Fe(S₄)] units and the regioselective formation of the py(CH₂)₂ bridge mean that all reaction steps have to be stereoselective.

To obtain cofacial dinuclear iron benzene dithiolate complexes we used our previous results on iron complexes of 2,3-dimercaptobenzoic acid,^[4] methods developed by Hahn et al. for bridging 2,3-dimercaptobenzoic acid units by α,ω-

[*] Transition Metal Complexes with Sulfur Ligands, Part 157. Part 156: D. Sellmann, D. C. F. Blum, F. W. Heinemann, J. Sutter, *Eur. J. Inorg. Chem.*, in press.

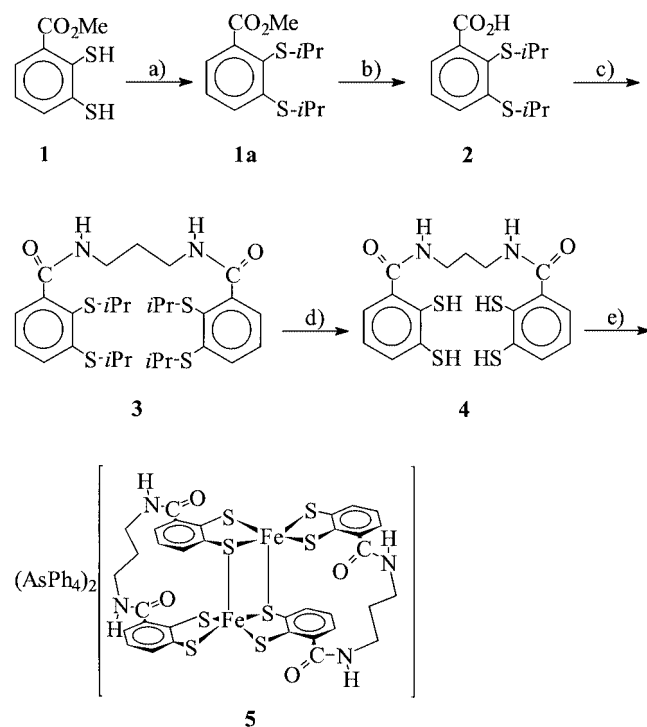
[a] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstraße 1, 91058 Erlangen, Germany
Fax: (internat.) + 49-(0)9131/852-7367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

diamines,^[6] and the fact that Fe^{III} ions and benzene dithiolate give dinuclear $[\{\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)_2\}_2]^{2-}$ anions.^[7]

Herein we report the synthesis and properties of the novel Fe^{III} complex $(\text{AsPh}_4)_2[\{\text{Fe}(\text{'apS}_4')\}_2]$ (**5**) where 'apS₄'⁴⁻ denotes a ligand in which two 1,2-benzenedithiolate units are connected by a 1,3-dicarboxamido propane bridge.

Results and Discussion

Scheme 2 summarizes the multi-step procedure leading to the target complex **5**.



Scheme 2. Synthesis of $(\text{AsPh}_4)_2[\{\text{Fe}(\text{'apS}_4')\}_2]$ (**5**) (a) + 2NaOMe, + 2*i*PrBr, MeOH, 20 h reflux; (b) (1) + NaOH_{exc.}, THF/H₂O, 44 h reflux, (2) HCl/H₂O; (c) (1) + SOCl₂_{exc.}, (2) + 0.51, 3-diaminopropane, THF; (d) (1) + 10Na, + 5C₁₀H₈, THF, (2) HCl, H₂O; (e) (1) + 4LiOMe, + FeCl₃·6H₂O, MeOH, (2) + AsPh₄Cl.

The synthesis of the tetrathiol 'apS₄'-H₄ (**4**) followed the method of Hahn et al. for related compounds.^[6] The starting material was the 2,3-dimercaptobenzoic acid methyl ester **1** ('CO₂Me-S₂'-H₂)^[4a] in which the thiol functions were protected by isopropyl groups to give **1a**. Ester hydrolysis yielded the acid **2** which was treated with SOCl₂ to give the corresponding carboxylic acid chloride. Subsequent reaction with 1,3-diaminopropane yielded the diamide **3**. Deprotection of the thioether functions with sodium naphthalenide and subsequent acidification gave the tetrathiol **4** which was isolated as a white powder in pure form.

Coordination of the tetraanion of **4** to Fe^{III} centers was achieved by deprotonating **4** with equivalent amounts of LiOMe and subsequent reaction with FeCl₃·6H₂O in boiling MeOH. A dark violet solution resulted, from which

$(\text{AsPh}_4)_2[\{\text{Fe}(\text{'apS}_4')\}_2]$ (**5**) precipitated after addition of AsPh₄Cl.

As the X-ray structure analysis of **5** showed, the tendency of the $[\text{Fe}^{\text{III}}(\text{benzenedithiolate})_2]^{1-}$ units to dimerize via [Fe–S–Fe] bridges,^[8] and the steric constraints and electronic effects resulting from the carboxamido substituents were successfully used to obtain the required diastereoisomer. MeOH was employed as solvent because its boiling point favors the formation of dinuclear instead of polynuclear (polymeric) species.

Compounds **1**, **1a**, **2**, **3**, and **4** are moderately to very soluble in organic solvents such as CH₂Cl₂, CHCl₃, THF, and DMF. Complex **5** is soluble in DMF and MeCN. All compounds were characterized by elemental analyses and spectroscopic methods.

The molecular structure of **5**·2MeOH, determined by X-ray analysis, is depicted in Figure 1, and Table 1 lists selected distances and angles.

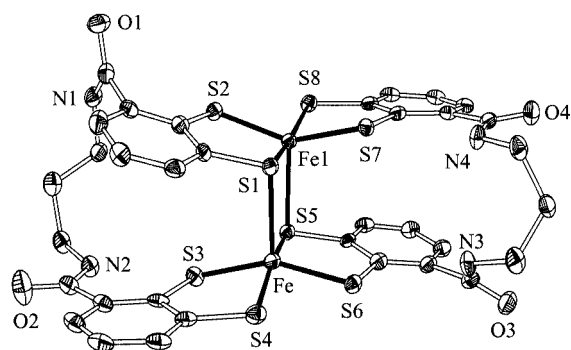


Figure 1. Molecular structure of the anion of $(\text{AsPh}_4)_2-[\{\text{Fe}(\text{'apS}_4')\}_2]\cdot 2\text{MeOH}$ (**5**·2MeOH) (50% probability ellipsoids; H atoms omitted)

Table 1. Selected distances [pm] and angles [°] of $(\text{AsPh}_4)_2-[\{\text{Fe}(\text{'apS}_4')\}_2]\cdot 2\text{MeOH}$ (**5**·2MeOH)

Distances		Angles	
Fe1–S1	222.9(2)	S8–Fe1–S1	168.55(5)
Fe1–S2	222.7(2)	S2–Fe1–S1	89.93(5)
Fe1–S7	222.4(2)	S1–Fe1–S5	95.19(5)
Fe1–S8	221.6(2)	S5–Fe2–S1	96.02(5)
Fe1–S5	248.4(2)	S4–Fe2–S5	166.21(5)
Fe2–S1	245.5(2)	S5–Fe2–S6	89.01(5)
Fe2–S3	222.9(2)		
Fe2–S4	220.8(2)		
Fe2–S5	222.8(2)		
Fe2–S6	223.1(2)		

The anion of **5**·2MeOH contains two $[\text{FeS}_4]$ units linked via two Fe–S–Fe bridges such that five-coordinate Fe centers with distorted square-pyramidal coordination result. In addition, the two $[\text{FeS}_4]$ units are connected by two peripheral propanediamide bridges between the benzene rings. These propanediamide bridges are located at opposite sides of the anion, which exhibits pseudo-*C_i* symmetry.

The bond lengths and angles within the $[\text{Fe}_2\text{S}_8]$ core are practically identical to those found in $(\text{NEt}_4)_2[\{\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)_2\}_2]$ ^[8a] (**6**) and $(\text{NBu}_4)_2[\{\text{Fe}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2\}_2]$ ^[8b] (**7**).

This indicates that the peripheral propanediamide bridges exert no steric strain on the [Fe₂S₈] core. For example, the average Fe–S distance within the [Fe(S₂C₆H₃R)₂] units amounts to 222 pm in **5** as well as in the nonbridged dinuclear species **6** and **7**. The distances between the iron centers and the (bridging) apical thiolate donors are significantly longer, by ca. 25 pm in **5**, as has also been found in **6** and **7**.

The propanediamide bridges could influence the overall structure of **5**·2MeOH in several ways. The apical thiolate donors S(1) and S(5) forming the bridges between the two iron centers occupy ring positions *meta* to the carboxamide substituents. Consequently, the carboxamide substituents could have an electron-withdrawing influence upon the thiolate donors, which is expected to be larger for the *ortho*-standing thiolate donors, disfavoring the formation of Fe–S–Fe bridges. The structure of **5**·2MeOH further shows that the carboxamide groups can adopt configurations that are in-plane with, or orthogonal to, the benzene rings. This indicates that the carboxamide substituents can rotate around the plane of the benzene ring such that, upon dissociation of the [Fe–S–Fe] bridges, the [Fe(benzenedithiolate)₂] fragments can separate to permit the insertion of small molecules between the iron centers, as in (NBu₄)₂[μ-N₂H₄{Fe(S₂C₆H₄)₂}₂].^[9] Rotation of the carboxamide substituents around the benzene rings was corroborated by the X-ray structure determination of solvent-free **5**. In this structure, all carboxamido substituents adopt a skewed conformation with regard to the benzene rings. All other distances and angles are similar to those of **5**·2MeOH. Reduction of dinuclear [{Fe^{III}(S₂C₆H₄)₂}₂]^{2–} is also known to give mononuclear [Fe^{II}(S₂C₆H₄)₂]^{2–}.^[7]

The anion of **5** and the parent [{Fe^{III}(S₂C₆H₄)₂}₂]^{2–} anion exhibit similar spectroscopic, magnetic and electrochemical properties. Both anions are paramagnetic with $\mu_{\text{eff}} = 2.4 \mu_{\text{B}}$ for **5** and $\mu_{\text{eff}} = 2.3 \mu_{\text{B}}$ for **6**,^[8c] which is indicative of two low-spin Fe^{III} centers and partial antiferromagnetic coupling through the thiolate bridges.

The ¹H NMR spectrum of **5** in [D₆]DMSO exhibits paramagnetically shifted signals between $\delta = 8$ and -45 ppm

that could not be assigned, with the exception of the AsPh₄⁺ signal at $\delta = 7.8$ ppm. In the mass spectrum, only the AsPh₄⁺ ion could be detected.

The UV/Vis spectrum of **5** shows absorptions at 314, 364, and 512 nm while that of **7** exhibits absorptions at 315, 370, and 526 nm. The cyclic voltammogram of **5** in MeCN shows five redox waves (see Figure 2). The anodic waves D and E appear to be quasi-reversible, while waves A–C are regarded as irreversible. However, the redox waves B and C resemble the quasi-reversible redox wave of **6** in DMSO at -0.99 V (vs. NHE) assigned to the redox couple [{Fe^{III}(S₂C₆H₄)₂}₂]^{2–/3–}.^[8c] Correspondingly, the waves B and C may be assigned tentatively to the redox couple [{Fe('apS₄')}]₂]^{2–/3–}.

Conclusion

In the search for dinuclear iron complexes with cofacial [FeS₄] cores as potential precursors for subsequent alkylation reactions yielding cofacial [Fe('pyS₄')]₂ fragments held together by ligand periphery clamps, (AsPh₄)₂[Fe('apS₄')]₂ (**5**) was synthesized and characterized. Structural, magnetic, spectroscopic and electrochemical properties of the anion of **5** are similar to those of the parent anion [{Fe(S₂C₆H₄)₂}₂]^{2–} (**6**). In contrast to **6** the peripheral ligand bridges of **5** prevent complete separation of the [Fe(S₂C₆H₃R)₂] entities if the [Fe–S–Fe] thiolate bridges dissociate. In addition, the structure of **5** differs from that of the dinuclear Ni complexes with similar benzenedithiolate-based tetrathiol ligands reported recently by Hahn et al.^[6d] These Ni complexes, synthesized in the search for helicates, exhibit coplanar [M(S₄)] cores arranged in a stair-like manner.

Current experiments aim to introduce, stereoselectively, α,α' -bismethylenepyridine bridges to transform **5** into the target species **A**.

Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF₂ cuvettes, solvent bands were compensated): Perkin–Elmer 16PC FTIR. NMR: JEOL-JNM-GX 270 with the protio-solvent signal used as an internal reference. Spectra were recorded at 25 °C. Mass spectra: JEOL MSTATION 700 spectrometer. Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. Magnetic susceptibility: Johnson Matthey susceptibility balance. UV/Vis: Shimadzu UV-3101 PC. Solutions were 10^{–4} M in DMF. Cyclic voltammetry was performed with a Radiometer Copenhagen IMT 102 electrochemical interface using a three-electrode cell with a glassy carbon (Radiometer Copenhagen EDI) working electrode and Pt reference and counter electrodes. Solutions were 10^{–3} M in MeCN; NBu₄[PF₆] (10^{–1} M) was used as the supporting electrolyte. Potentials were referenced to the normal hydrogen electrode (NHE) using Fc/Fc⁺ as internal standard ($E_{\text{Fc}^+/\text{Fc}}^0 = 0.4$ V vs. NHE).^[10] CO₂Me-

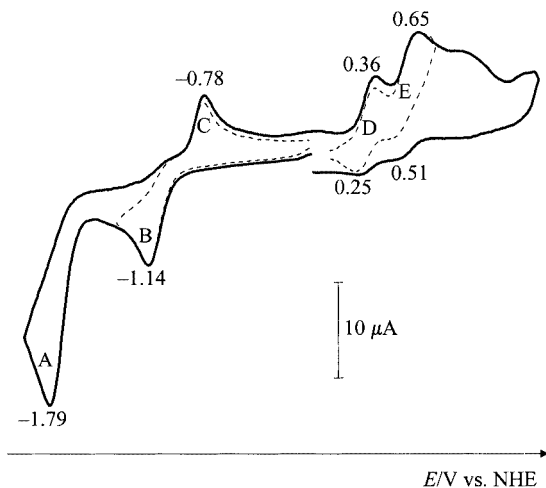


Figure 2. Cyclic voltammogram of **5** in MeCN (10^{–3} M, 10^{–1} M NBu₄PF₆, $\nu = 0.10$ V s^{–1})

$\text{S}_2\text{-H}_2$ (**1**) (2,3-dimercaptobenzoic acid methyl ester) was prepared as described in the literature.^[4a]

'CO₂Me-S₂'-iPr₂ (1a): LiOMe (50 mmol, 50 mL of a 1 M solution in MeOH) and isopropyl bromide (5.87 mL, 62.5 mmol) were added to a light yellow solution of ' $\text{CO}_2\text{Me-S}_2\text{'-H}_2$ ' (5.01 g, 25.0 mmol) in MeOH (120 mL) and the resultant lemon yellow solution heated under reflux for 20 h. After evaporation of the solvent, CH_2Cl_2 (120 mL) was added to the residue and the resulting suspension stirred for 2 h and then filtered. The filtrate was evaporated to give a brown oil that was identified by NMR spectroscopy as ' $\text{CO}_2\text{Me-S}_2\text{'-iPr}_2$ ' and was used for the synthesis of ' $\text{CO}_2\text{H-S}_2\text{'-iPr}_2$ ' (**2**) without further purification. Yield: 7 g (**1a**) (100%). ¹H NMR (CDCl_3 , 269.72 MHz): δ = 1.20 [d, $^3J_{\text{H,H}}$ = 6.7 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.37 [d, $^3J_{\text{H,H}}$ = 6.7 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 3.50 [m, 2 H, $\text{CH}(\text{CH}_3)_2$], 3.89 (s, 6 H, CO_2CH_3), 7.26 (m, 3 H, C_6H_3) ppm. MS (FD^+ , CH_2Cl_2): m/z = 284 [$\text{'CO}_2\text{Me-S}_2\text{'-iPr}_2$] $^+$.

'CO₂H-S₂'-iPr₂ (2): NaOH (0.115 mmol, 115 mL of a 1 M solution in H_2O) was added to a solution of ' $\text{CO}_2\text{Me-S}_2\text{'-iPr}_2$ ' (**1a**) (6.825 g, 0.024 mol) in THF (120 mL). The mixture was heated under reflux for 29 h, then reduced in volume to about 120 mL and heated for a further 15 h. The resulting pale pink solution was filtered. Concentrated hydrochloric acid (12 mL) was added to the filtrate and the light yellow solid that precipitated was separated, washed with water to pH = 7 and dried in vacuo. Yield: 5.66 g (**2**) (87%). ¹H NMR (CDCl_3 , 269.72 MHz): δ = 1.27 [d, $^3J_{\text{H,H}}$ = 6.6 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.38 [d, $^3J_{\text{H,H}}$ = 6.6 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 3.52 [m, 2 H, $\text{CH}(\text{CH}_3)_2$], 7.41 (m, 2 H, C_6H_3), 7.87 (vdd, 1 H, C_6H_3), 11.75 (br, 1 H, COOH) ppm. ¹³C{¹H} NMR (CDCl_3 , 67.83 MHz): δ = 22.6, 22.8 [$\text{CH}(\text{CH}_3)_2$], 36.5, 41.2 [$\text{CH}(\text{CH}_3)_2$], 127.9, 129.3, 129.8, 130.3, 136.5, 146.4 (C_6H_3), 169.1 (CO_2H) ppm. IR (KBr): $\tilde{\nu}$ = 2966 (br, O–H), 1704 cm^{-1} (s, C=O). MS (FD^+ , acetone): m/z = 270 [$\text{'CO}_2\text{H-S}_2\text{'-iPr}_2$] $^+$. $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}_2$ (270.42): calcd. C 57.74, H 6.71, S 23.72; found C 57.49, H 6.99, S 23.90.

'apS₄'-iPr₄ (3): SOCl_2 (8.5 mL) was added to solid ' $\text{CO}_2\text{H-S}_2\text{'-iPr}_2$ ' (**2**) (4.815 g, 0.018 mol) and heated to 60 °C until no further gas evolution was detected. Excess SOCl_2 was removed in vacuo; the brown oily residue obtained was dissolved in THF (30 mL) and a solution of 1,3-diaminopropane (0.745 mL, 0.009 mol) and NEt_3 (4.98 mL, 0.036 mol) in THF (20 mL) was added dropwise at 0 °C. The resulting yellow suspension was stirred at room temperature for 15 h, poured into ice water (600 mL) and stirred for a further 1 h. The mixture was extracted with Et_2O (800 mL). The Et_2O phase was dried over Na_2SO_4 , filtered and evaporated. The foam-like solid thus obtained was washed with warm pentane which was decanted. The residue was dried in vacuo yielding, again, a yellow foam-like solid material. Yield: 4.6 g (**3**) (88%). ¹H NMR (CDCl_3 , 269.72 MHz): δ = 1.19 (d, $^3J_{\text{H,H}}$ = 6.7 Hz, 12 H, CHCH_3), 1.36 [d, $^3J_{\text{H,H}}$ = 6.7 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 1.87 (m, 2 H, NCH_2CH_2), 3.46 (m, 4 H, NCH_2CH_2), 3.60 [m, 4 H, $\text{CH}(\text{CH}_3)_2$], 6.95 (br, 2 H, NH), 7.26 (m, 6 H, C_6H_3) ppm. ¹³C{¹H} NMR (CDCl_3 , 67.83 MHz): δ = 22.7, 23.2 [$\text{CH}(\text{CH}_3)_2$], 29.9 (NHCH_2CH_2), 36.0, 36.8 [$\text{CH}(\text{CH}_3)_2$], 40.5 (NCH_2CH_2), 124.6, 127.6, 128.8, 129.1, 143.8, 145.8 (C_6H_3), 169.5 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 3289 (s, N–H), 1636 (s, C=O), 1522 cm^{-1} (s, N–H). MS (FD^+ , Et_2O): m/z = 578 [$\text{'apS}_4\text{'-iPr}_4$] $^+$. $\text{C}_{29}\text{H}_{42}\text{N}_2\text{O}_2\text{S}_4$ (578.93): calcd. C 60.17, H 7.31, N 4.84, S 22.16; found C 60.27, H 7.70, N 4.58, S 21.92.

'apS₄'-H₄ (4): Small pieces of sodium (0.9 g, 39 mmol) were added to a solution of ' $\text{apS}_4\text{'-iPr}_4$ ' (**3**) (2.25 g, 3.9 mmol) and naphthalene (2.52 g, 19.5 mmol) in THF (200 mL). After stirring the resulting green suspension for 16 h at room temperature, MeOH (15 mL) was added cautiously. All solvents were evaporated and H_2O

(150 mL) was added to the yellow residue to give a yellow emulsion that was washed with Et_2O (450 mL), and the yellow aqueous phase was separated, filtered, and acidified slowly with concentrated hydrochloric acid (12 mL) at 0 °C. A white precipitate formed which after stirring at room temperature for 15 min was separated, washed with H_2O (60 mL) and dried in vacuo. Yield: 1.3 g (**4**) (81%). ¹H NMR ($[\text{D}_8]\text{THF}$, 269.72 MHz): δ = 1.87 (m, 2 H, NCH_2CH_2), 3.47 (m, 4 H, NCH_2CH_2), 7.01 (vt, 2 H, C_6H_3), 7.33 (vd, 2 H, C_6H_3), 7.40 (vd, 2 H, C_6H_3), 7.94 (br, 2 H, NH) ppm. ¹³C{¹H} NMR ($[\text{D}_8]\text{THF}$, 67.83 MHz): δ = 29.5 (NHCH_2CH_2), 36.7 (NCH_2CH_2), 124.2, 125.1, 131.3, 132.7, 133.0, 134.6 (C_6H_3), 169.2 (CONH) ppm. IR (KBr): $\tilde{\nu}$ = 3280 (m, N–H), 2526 (w, S–H), 1628 (s, C=O), 1534 cm^{-1} (s, N–H). MS (FD^+ , THF): m/z = 411 [$\text{'apS}_4\text{'-H}_4$] $^+$. $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_4$ (410.61): calcd. C 49.73, H 4.42, N 6.82, S 31.24; found C 50.32, H 4.66, N 6.85, S 30.79.

(AsPh₄)₂{Fe('apS₄')₂} (5**):** A solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (230 mg, 0.85 mmol) in MeOH (10 mL) was added to a solution of ' $\text{apS}_4\text{'-H}_4$ ' (**4**) (349 mg, 0.85 mmol) and LiOMe (3.40 mmol, 3.40 mL of a 1 M solution in MeOH) in MeOH (25 mL). The resulting purple solution was heated under reflux for 2 h. After removal of the solvent, the resultant black–violet residue was dissolved in MeOH (30 mL) to give a black violet solution that was filtered and combined with a solution of $\text{AsPh}_4\text{Cl} \cdot \text{H}_2\text{O}$ (1.23 g, 2.49 mmol) in MeOH (25 mL). Violet microcrystals precipitated and were separated, washed with MeOH (20 mL) and dried in vacuo. Yield: 395 mg (**5**) (55%). ¹H NMR ($[\text{D}_6]\text{DMSO}$, 269.72 MHz): δ = 7.8 [br, 40 H, $\text{As}(\text{C}_6\text{H}_5)_4^+$] ppm. IR (KBr): $\tilde{\nu}$ = 3273 (m, N–H), 1640 (s, C=O), 1540 cm^{-1} (s, N–H). MS (FD^+ , DMF): m/z = 383 [AsPh_4] $^+$; magnetic susceptibility: μ_{eff} = 2.4 μ_{B} . UV/Vis (DMF, 10^{-4} M): λ = 314 (22068), 364 (21139), and 512 (11464) nm ($\text{cm}^2 \text{mol}^{-1}$). $\text{C}_{82}\text{H}_{68}\text{As}_2\text{Fe}_2\text{N}_4\text{O}_4\text{S}_8$ (1691.54): calcd. C 58.22, H 4.05, N 3.31, S 15.17; found C 58.27, H 4.22, N 3.36, S 15.05.

X-ray Structure Analyses of (AsPh₄)₂{Fe('apS₄')₂}·2MeOH (5·2MeOH**) and (AsPh₄)₂{Fe('apS₄')₂} (**5**):** Single crystals were obtained by the following procedures. (AsPh₄)₂{Fe('apS₄')₂}·2MeOH (**5·2MeOH**): A solution of ' $\text{apS}_4\text{'-H}_2$ ' (44 mg, 0.11 mmol), LiOMe (0.43 mmol, 0.43 mL of a 1 M solution in MeOH) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (29 mg, 0.11 mmol) in MeOH (20 mL) was heated under reflux for 2 h. After cooling to room temperature the resulting black–violet solution was filtered and layered with a solution of AsPh_4Cl (115 mg, 0.28 mmol) in MeOH (25 mL). Black blocks of (AsPh₄)₂{Fe('apS₄')₂}·2MeOH (**5·2MeOH**) formed that were separated after one week. $\text{C}_{84}\text{H}_{76}\text{As}_2\text{Fe}_2\text{N}_4\text{O}_6\text{S}_8$ (1755.63): calcd. C 57.47, H 4.36, N 3.19, S 14.61; found C 57.87, H 4.47, N 3.29, S 14.24.

(AsPh₄)₂{Fe('apS₄')₂} (**5**): A concentrated and filtered solution of **5** in DMF was layered with the same amount of THF. Black rhombs of (AsPh₄)₂{Fe('apS₄')₂} (**5**) formed that were separated after 2 months.

Suitable single crystals were embedded in protective perfluoro polyalkyl ether oil. Intensity data were collected at 100 K on a Nonius KappaCCD diffractometer using Mo- K_α radiation (λ = 71.073 pm, graphite monochromator) (Table 2). Data were corrected for Lorentz and polarization effects and a numerical absorption correction for **5·2MeOH** and a semi-empirical absorption correction from equivalent reflections for **5** were applied. The structures were solved by direct methods, and full-matrix least-squares refinement was carried out on F^2 (SHELXTL NT 5.10).^[11] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were taken from the difference Fourier maps and refined

Table 2. Selected crystallographic data for (AsPh₄)₂[{Fe('apS₄')}]₂·2MeOH (**5**·2MeOH) and (AsPh₄)₂[{Fe('apS₄')}]₂ (**5**)^[12]

Complex	5 ·2MeOH	5
Formula	C ₈₄ H ₇₆ As ₂ Fe ₂ N ₄ O ₆ S ₈	C ₈₂ H ₆₈ As ₂ Fe ₂ N ₄ O ₄ S ₈
<i>M_r</i> [g mol ⁻¹]	1755.51	1691.42
<i>T</i> [K]	100	100
Crystal size [mm]	0.46 × 0.11 × 0.05	0.17 × 0.14 × 0.06
<i>F</i> (000)	1804	1732
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [pm]	1027.9 (1)	1188.34(5)
<i>b</i> [pm]	1634.8 (2)	1342.41(7)
<i>c</i> [pm]	2407.5 (3)	2240.5(1)
α [°]	106.126 (8)	90
β [°]	94.494 (8)	96.539(4)
γ [°]	96.871 (8)	90
<i>V</i> [nm ³]	3.8320 (8)	3.5509(3)
<i>Z</i>	2	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.521	1.582
μ [mm ⁻¹]	1.512	1.626
θ range [°]	3.52–26.37	3.43–27.50
Measured refl.	56034	32373
Unique refl.	15548	8089
<i>R</i> _{int}	0.0795	0.1296
Observed refl.	11204	4817
σ criterion	<i>F</i> _o ≥ 4.0 σ (<i>F</i>)	<i>F</i> _o ≥ 4.0 σ (<i>F</i>)
Refl. parameters	950	562
Abs. correct. <i>T</i> _{min} / <i>T</i> _{max}	0.506/0.899	0.748/0.912
<i>R</i> ₁ [<i>F</i> _o ≥ 4.0 σ (<i>F</i>)]	0.0556	0.0560
<i>wR</i> ₂ (all data)	0.1446	0.1214

with a fixed common isotropic displacement parameter. In accordance with the elemental analysis, the crystal structure of **5**·2MeOH contains two MeOH solvate molecules per unit. One MeOH molecule is disordered. The non-hydrogen atoms of the disordered solvate molecule were refined only isotropically and no hydrogen atoms were taken into account.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (SFB, 583) and the Fonds der Chemischen Industrie is gratefully acknowledged.

- [1] [1a] J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965–2982. [1b] R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013–3030. [1c] B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3012. [1d] D. C. Rees, J. B. Howard, *Curr. Opin. Chem. Biol.* **2000**, *4*, 559–566. [2] [2a] M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200*–202, 379–409. [2b] H. Deng, R. Hoffmann, *Angew. Chem.* **1993**, *105*, 1125–1128; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1062–1065. [2c] I. G. Dance, *J. Biol. Inorg. Chem.* **1996**, *1*, 581–586. [2d] K. K. Stavrev, M. C. Zerner, *Chem. Eur. J.* **1996**, *2*, 83–87. [2e] D. Sellmann, J. Sutter, *J. Biol. Inorg. Chem.* **1996**, *1*, 587–593. [2f] D. Sellmann, A. Fürsattel, J. Sutter, *Coord. Chem. Rev.* **2000**, *200*–202, 545–561. [3] [3a] D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460–469. [3b] D. Sellmann, N. Blum, F. W. Heinemann, B. A. Hess, *Chem. Eur. J.* **2001**, *7*, 1874–1880. [4] [4a] D. Sellmann, T. Becker, F. Knoch, *Chem. Ber.* **1996**, *119*, 509–519. [4b] K. P. Peters, PhD Dissertation, Universität Erlangen-Nürnberg, **2000**. [5] [5a] D. Sellmann, J. Utz, N. Blum, F. W. Heinemann, *Coord. Chem. Rev.* **1999**, *190*–192, 607–627. [5b] D. Sellmann, N.

- Blum, F. W. Heinemann, *Z. Naturforsch., B: Chem. Sci.* **2001**, *56*, 581–588. [6] [6a] F. E. Hahn, W. W. Seidel, *Angew. Chem.* **1995**, *107*, 2938–2941; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2700–2703. [6b] W. W. Seidel, F. E. Hahn, T. Lügger, *Inorg. Chem.* **1998**, *37*, 6587–6596. [6c] W. W. Seidel, F. E. Hahn, *J. Chem. Soc., Dalton Trans.* **1999**, 2237–2241. [6d] H. V. Huynh, C. Schulze-Isfort, W. W. Seidel, T. Lügger, R. Fröhlich, O. Kataeva, F. E. Hahn, *Chem. Eur. J.* **2002**, *8*, 1327–1335. [7] D. Sellmann, U. Kleine-Kleffmann, L. Zapf, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1984**, *263*, 321–331. [8] [8a] B. S. Kang, L. H. Weng, D. X. Wu, F. Wang, Z. Guo, L. R. Huang, Z. Y. Huang, H. Q. Liu, *Inorg. Chem.* **1988**, *27*, 1128–1130. [8b] D. T. Sawyer, G. S. Srivatsa, M. E. Bodini, W. P. Schaefer, R. M. Wing, *J. Am. Chem. Soc.* **1986**, *108*, 936–942. [8c] D. Sellmann, M. Geck, M. Moll, *J. Am. Chem. Soc.* **1991**, *113*, 5259–5264. [9] [9a] D. Sellmann, H. Friedrich, F. Knoch, *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 660–664. [9b] D. Sellmann, P. Kreutzer, G. Huttner, A. Frank, *Z. Naturforsch., Teil B* **1978**, *33*, 1341–1346. [10] [10a] H. M. Koepp, H. Wendt, H. Strehlow, *Z. Elektrochem.* **1960**, *64*, 483–491. [10b] G. Gritzner, J. Kuta, *Pure Appl. Chem.* **1984**, *56*, 461–466. [11] SHELXTL 5.10 Bruker AXS, Inc., Madison, WI, USA, **1998**. [12] CCDC-188177 (**5**·2MeOH) and CCDC-188178 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received July 3, 2002
[I02358]