

# Formation of an Iron(III) Oxo Cubane Core $\text{Fe}_4(\mu^4\text{-O})_4$ from $\text{FeCl}_3$ and the Unsymmetrical Tripodal Ligand $\text{N}[(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})]$

F. Ekkehardt Hahn, Christoph Jocher, and Thomas Lügger

Institut für Anorganische und Analytische Chemie and NRW Graduate School of Chemistry, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm Straße 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. F. E. Hahn. E-mail: fehahn@uni-muenster.de

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The coordination chemistry of the unsymmetric, aliphatic, tetradentate tripodal ligand  $\text{N}[(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})]$  **H<sub>4</sub>-1** with iron chlorides was investigated. The disodium salt of the deprotonated ligand  $\text{Na}_2(\text{H}_2\text{-1})$  reacts with  $\text{FeCl}_3$  to yield a yellow precipitate which upon recrystallization from DMSO/ $\text{CH}_2\text{Cl}_2$  gives red crystals of the octanuclear iron(III) complex  $[\{\text{Fe}^{\text{III}}\text{Cl}(\text{H}_2\text{-1})\}_4\text{Fe}^{\text{III}}_4(\mu^4\text{-O})_4\text{Cl}_4] \cdot 2 \cdot 4\text{CH}_2\text{Cl}_2$  containing a central  $\text{Fe}_4(\mu^4\text{-O})_4$  cubane core. Crystals of  $2 \cdot 4\text{DMF}$  were obtained by slow oxidation of the green iron(II) complex obtained from ferrous chloride and  $\text{Na}_2(\text{H}_2\text{-1})$  after recrystallization from DMF. The structure determination of  $2 \cdot 4\text{CH}_2\text{Cl}_2$  also revealed the presence of the iron(III) oxo cubane core. The core is surrounded by four iron atoms each coordinated by  $\eta^4\text{-(H}_2\text{-1)}^{2-}$  and  $\text{Cl}^-$  ligands.

**Key words:** Tripodal Ligand, Iron(III), Oxo Cubane, Crystal Structure

## Introduction

Beginning with the first syntheses of triethanolamine (tea) [1] in 1861 and tris(2-aminoethyl)amine (tren) in 1926 [2] a large number of metal complexes of these simple symmetrically substituted tripods have been investigated [3]. Some years ago we initiated a program to synthesize unsymmetrically functionalized aliphatic tripodal ligands and to study their coordination chemistry. Initially, tren-like tetraamines with different ligand-arm lengths were investigated [4]. Later, ligands with an unsymmetrical topology and different donor groups ( $\text{NH}_2$ , OH, SH) were studied [5]. Up to now only few complexes with unsymmetrical aliphatic tripodal ligands with  $\text{NNO}_2$  [5a, 6] or  $\text{NN}_2\text{O}$  [5a, 7] donor sets have been synthesized. Polynuclear iron complexes with the symmetrical ligands tea and tren are known. They exhibit interesting structural features like a hexanuclear ferric wheel [8] or an oxygen

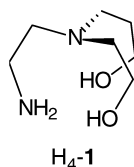
atom coordinated in a square-planar fashion by four iron centers [9]. We report here on the coordination chemistry of the unsymmetrical  $\text{NNO}_2$  tripod **H<sub>4</sub>-1** (Scheme 1) [10] with  $\text{Fe}^{\text{III}}$ , or with  $\text{Fe}^{\text{II}}$  followed by aerial oxidation, to give an octanuclear  $\text{Fe}^{\text{III}}$  complex containing a central  $\text{Fe}_4(\mu^4\text{-O})_4$  cubane core.

## Experimental Section

Ligand **H<sub>4</sub>-1** was prepared according to a published procedure [10].

$[\{\text{Fe}^{\text{III}}\text{Cl}(\text{H}_2\text{-1})\}_4\text{Fe}^{\text{III}}_4(\mu^4\text{-O})_4\text{Cl}_4] \cdot 2$  from  $\text{FeCl}_2$  (route A): A suspension of anhydrous ferrous chloride (126 mg, 1.0 mmol) in THF (60 ml) was reacted with a solution of  $\text{Na}_2(\text{H}_2\text{-1})$  obtained from 162 mg (1 mmol) of **H<sub>4</sub>-1** and 48 mg (2 mmol) of NaH in THF (10 ml). The reaction mixture was stirred for 24 h and then filtered. The residue was washed with THF (10 ml) and extracted with DMF (30 ml). The dark green DMF extract was cooled to  $-30^\circ\text{C}$ . A dark green precipitate was obtained after 24 h. The precipitate was isolated by filtration and dried under vacuum. Yield: 30 mg. – Elemental analysis for  $[(\text{H}_2\text{-1})\text{Fe}\cdot\text{FeCl}_2\cdot\text{DMF}]$ ,  $\text{C}_{10}\text{H}_{23}\text{N}_3\text{O}_3\text{Fe}_2\text{Cl}_2$  (415.91): calcd. C 28.88, H 5.57, N 10.10; found C 29.30, H 5.24, N 9.75.

Air was allowed to diffuse slowly into a sample of 10 mg (24  $\mu\text{mol}$ ) of the green powder obtained in the previous reac-



Scheme 1. Ligand **H<sub>4</sub>-1**.

tion in DMF (1 ml). The color of the solution changed from green to red over a period of 4 weeks and dark red crystals of **2**·2DMF formed.

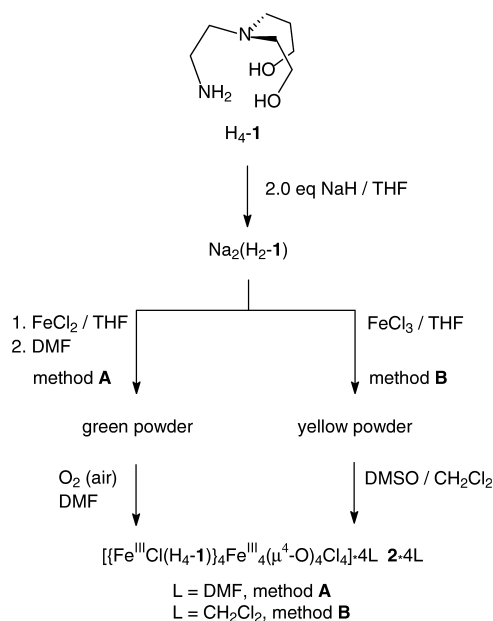
Yield: 8 mg (18  $\mu$ mol, 75%). – MALDI-TOF MS (337.0 nm, 3 ns):  $m/z$  (%) = 1397 (25) [**2** - Cl]<sup>+</sup>, 1361 (62) [**2** - 2 Cl]<sup>+</sup>, 1324 (51) [**2** - 3 Cl]<sup>+</sup>.

[{Fe<sup>III</sup>Cl(H<sub>2</sub>-**1**)}<sub>4</sub>Fe<sup>III</sup><sub>4</sub>( $\mu^4$ -O)<sub>4</sub>Cl<sub>4</sub>] **2** from FeCl<sub>3</sub> (route **B**): Sodium hydride (48 mg, 2.0 mmol) was added to a solution of the ligand H<sub>4</sub>-**1** (162 mg, 1.0 mmol) in THF (20 ml). The resulting suspension was added to a solution of ferric chloride (163 mg, 1.0 mmol) in THF (100 ml). The reaction mixture was stirred for 48 h. A yellow residue was isolated by filtration, washed with THF (20 ml) and dried under vacuum. The yellow powder obtained was dissolved in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (1:1). Diffusion of pentane into this red solution produced dark red crystals of **2**·4CH<sub>2</sub>Cl<sub>2</sub>. Yield: 30 mg ( $\mu$ mol, 14%). UV/vis (DMF, 298 K):  $\lambda_{\text{max}}$  (relative intensity) = 305 nm (1), 490 nm (0.05). – <sup>57</sup>Fe Mößbauer Spectroscopy (20 K): IS (QS) = 0.24 (1.24), 0.25 (0.59) mm s<sup>-1</sup>.

**X-ray structure determination:** Red crystals of **2**·4CH<sub>2</sub>Cl<sub>2</sub> were obtained by recrystallization of **2** obtained from FeCl<sub>3</sub> and Na<sub>2</sub>(H<sub>2</sub>-**1**) from DMSO/CH<sub>2</sub>Cl<sub>2</sub>. Formula C<sub>32</sub>H<sub>72</sub>N<sub>8</sub>Cl<sub>16</sub>Fe<sub>8</sub>O<sub>12</sub>,  $M = 1774.98$ , red crystal 0.56 × 0.47 × 0.30 mm<sup>3</sup>,  $a = 13.0141(5)$ ,  $b = 13.0897(6)$ ,  $c = 19.8395(8)$  Å,  $\alpha = 96.7300(10)$ ,  $\beta = 108.6380(10)$ ,  $\gamma = 91.8810(10)^\circ$ ,  $V = 3171.5(2)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.859$  g cm<sup>-3</sup>,  $\mu = 2.505$  mm<sup>-1</sup>, empirical absorption correction (0.3344 ≤  $T$  ≤ 0.5203),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 123(2)$  K,  $\omega$  and  $\phi$  scans, 24275 reflections collected ( $\pm h, \pm k, \pm l$ ) in the range  $3.1 \leq 2\theta \leq 50.0^\circ$ , 11171 independent ( $R_{\text{int}} = 0.0205$ ) and 9952 observed reflections [ $I \geq 2\sigma(I)$ ], 694 refined parameters,  $R = 0.0383$ ,  $wR2 = 0.1019$ , max. residual electron density 1.401 (−1.087) e Å<sup>-3</sup>, anisotropic displacement parameters for all non-hydrogen atoms, hydrogen atoms on calculated positions and refined as riding atoms. X-ray intensities were measured using a Bruker AXS Apex diffractometer equipped with a rotating anode. Structure solution with SHELXS-97 [11] by heavy atom methods and refined with SHELXL-97 [12]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 239771. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

## Results and Discussion

The salt Na<sub>2</sub>(H<sub>2</sub>-**1**) of the deprotonated ligand H<sub>4</sub>-**1** reacts with FeCl<sub>3</sub>, or with FeCl<sub>2</sub> followed by aerial oxidation, to give the octanuclear complex [{Fe<sup>III</sup>Cl-



Scheme 2. Preparation of the oxo cubane [{Fe<sup>III</sup>Cl(H<sub>2</sub>-**1**)}<sub>4</sub>-Fe<sup>III</sup><sub>4</sub>( $\mu^4$ -O)<sub>4</sub>Cl<sub>4</sub>] **2** from FeCl<sub>2</sub> (method A) and from FeCl<sub>3</sub> (method B).

(H<sub>2</sub>-**1**)}<sub>4</sub>Fe<sup>III</sup><sub>4</sub>( $\mu^4$ -O)<sub>4</sub>Cl<sub>4</sub>] **2** (Scheme 2), which crystallized depending on the solvent as **2**·4CH<sub>2</sub>Cl<sub>2</sub> (method A) or **2**·4DMF (method B). Crystals of **2**·4CH<sub>2</sub>Cl<sub>2</sub> were investigated by X-ray structure analysis (Fig. 1). The X-ray diffraction analysis of **2**·4DMF showed the same complex **2**, but it suffered from a disorder of the DMF molecules and is therefore not described any further.

The core of complex **2** resembles the cube geometry found in the ubiquitous Fe<sub>4</sub>S<sub>4</sub> ferredoxins [13]. Four corners of the cube are bridged by  $\mu^4$ -oxygen atoms. Each of these coordinates to three iron atoms of the core and one outer iron atom. Each iron atom of the core unit is coordinated by three core oxygen atoms, two bridging oxygen atoms of the ligand (H<sub>2</sub>-**1**)<sup>2-</sup> and one terminal chlorine atom (Scheme 3). The outer iron atoms are coordinated by one tetradentate ligand (H<sub>2</sub>-**1**)<sup>2-</sup> one chlorine atom and one oxygen atom of the Fe<sub>4</sub>O<sub>4</sub> core (Scheme 3). Both types of iron atoms are thus coordinated in an octahedral fashion by an O<sub>5</sub>Cl (core iron atoms) or an N<sub>2</sub>O<sub>3</sub>Cl (outer iron atoms) donor set. This difference in coordination environment leads to two resonances in the <sup>57</sup>Fe Mößbauer spectrum.

Complex **2** shows no crystallographically imposed symmetry. However, the environment for the four

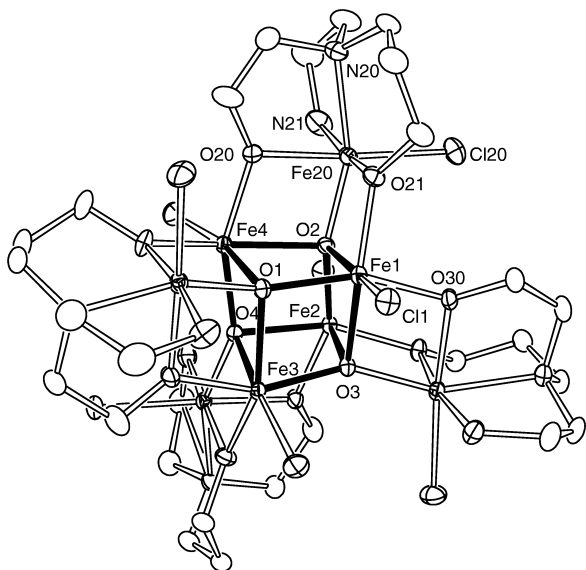
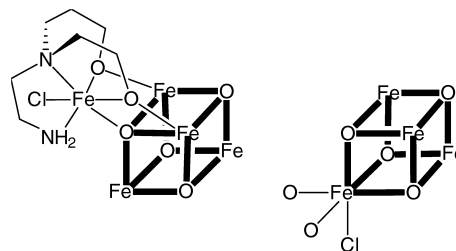


Fig. 1. Molecular structure of complex  $[\{\text{Fe}^{\text{III}}\text{Cl}(\text{H}_2\text{-1})\}_4\text{-Fe}^{\text{III}}(\mu^4\text{-O})_4\text{Cl}_4]$  **2**. Hydrogen atoms have been omitted. Although the complex shows no crystallographic symmetry, the four core iron atoms as well as the four outer iron atoms show a very similar coordination environment. Therefore selected bond lengths [Å] and angles [°] for 1/4 of the complex are listed: Fe1-Cl1 2.3438(9), Fe1-O1 1.935(2), Fe1-O2 2.166(2), Fe1-O3 2.128(2), Fe1-O21 1.976(2), Fe1-O30 1.962(2), Fe20-Cl20 2.3322(9), Fe20-O2 1.899(2), Fe20-O20 2.019(2), Fe20-O21 1.978(2), Fe20-N20 2.203(3), Fe20-N21 2.135(3), O2-Fe2 1.942(2), O2-Fe4 2.130(2); Cl1-Fe1-O1 94.01(7), Cl1-Fe1-O2 173.30(6), Cl1-Fe1-O3 107.69(6), Cl1-Fe1-O21 97.77(7), Cl1-Fe1-O30 90.85(7), O1-Fe1-O2 81.58(8), O1-Fe1-O3 80.72(8), O1-Fe1-O21 106.03(9), O1-Fe1-O30 155.89(9), O2-Fe1-O3 76.69(8), O2-Fe1-O21 78.75(8), O2-Fe1-O30 95.22(9), O3-Fe1-O21 153.24(9), O3-Fe1-O30 75.31(8), O21-Fe1-O30 96.65(9), Cl20-Fe20-O2 104.73(7), Cl20-Fe20-O20 175.06(7), Cl20-Fe20-O21 93.92(7), Cl20-Fe20-N20 97.60(8), Cl20-Fe20-N21 88.66(9), O2-Fe20-O20 79.20(9), O2-Fe20-O21 85.47(9), O2-Fe20-N20 157.50(10), O2-Fe20-N21 101.71(11), O20-Fe20-O21 89.35(10), O20-Fe20-N20 78.65(10), O20-Fe20-N21 87.58(11), O21-Fe20-N20 90.41(10), O21-Fe20-N21 171.50(11), N20-Fe20-N21 81.22(12), Fe1-O2-Fe2 103.03(9), Fe1-O2-Fe4 96.93(8), Fe1-O2-Fe20 95.82(9), Fe2-O2-Fe4 98.45(9), Fe2-O2-Fe20 150.31(12), Fe4-O2-Fe20 101.84(9).



Scheme 3. Coordination environment of the iron atoms forming the  $\text{Fe}_4(\mu\text{-O})_4$  core (left) and of the outer iron atoms (right).

core iron atoms as well as of the four outer iron atoms is very similar. Therefore bond parameters for only one core and one outer iron atom are discussed. Each core iron atom maintains two long Fe-O bonds (Fe1-O2 2.166(2), Fe1-O3 2.128(2) Å) and one which is shorter (Fe1-O1 1.935(2) Å), all three being edges of the core. The Fe-O bonds of the core iron atoms to the bridging oxygen atoms of the ligand  $(\text{H}_2\text{-1})^{2-}$  (Fe1-O21 1.976(2), Fe1-O30 1.962(2) Å) are in the range of the short Fe-O distances within the  $\text{Fe}_4\text{O}_4$  core. The Fe-Cl distances to core and outer iron atoms fall in a small range around 2.32 Å.

We assume that the oxo cubane constitutes a thermodynamic sink under the reaction conditions employed. However, it was surprising that the oxo cubane formed regardless of the oxidation state of the iron starting material. Besides  $[\text{Fe}_8(\mu^4\text{-O})_4(\mu\text{-pz})_{12}\text{Cl}_4]$  [14] complex **2** is only the second example of a complex containing an  $\text{Fe}^{\text{III}}_4\text{O}_4$  cubane core.

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