

One-dimensional Hydrogen-bonded Chloride-Hydrate Assembly $\{[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}\}_\infty$

Ji-Xiang Dai, Fang-Hui Wu, Wen-Rui Yao, and Qian-Feng Zhang

Department of Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, China

Reprint requests to Dr. Qian-Feng Zhang. Fax.: 86-555-2311552. E-mail: zhangqf@ahut.edu.cn

Z. Naturforsch. **2007**, 62b, 491–494; received November 26, 2006

A hydrogen-bonded chloride-hydrate assembly $\{[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}\}_\infty$ has been ion-counteracted by the complex cations $[\text{Fe}(\text{[9]aneS}_3)_2]^{2+}$ ($[\text{9]aneS}_3$ = 1,4,7-trithiacyclononane). In $\{[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}\}_\infty$, four water molecules and two chloride ions are self-assembled to form a one-dimensional supramolecular array of $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonding, which consists of fused four- and six-membered rings. The discrete cation $[\text{Fe}(\text{[9]aneS}_3)_2]^{2+}$ has a nearly regular octahedral FeS_6 core with an average $\text{Fe}-\text{S}$ bond length of 2.2586(5) Å.

Key words: Supramolecular Chemistry, Hydrogen Bond, Chloride-Hydrate, Self-Assembly, Iron(II) Complex

Introduction

The functional self-assembly of molecular frameworks has attracted intense interest due to the intricate structural topologies in *Nature* [1]. The foundation of the programmed self-assembly is built upon a detailed understanding of the way in which weak interactions participate in a reversible and self-correcting cooperative process that can respond to changes in environmental conditions including solvent, pH, temperature, concentration *etc.* [2, 3]. Self-assembly can often lead to host complexes that are very efficient for uptake and release of guests under controlled conditions [2, 4]. In recent years, molecular complexes have been found to serve as effective building blocks for the construction of various supramolecular arrays for the stabilization of discrete water morphologies [5]. One-dimensional chains and tapes of water clusters are notably stabilized in the templates of metal-organic supramolecular channels [6]. Therein the chloride-hydrate chains are ion-counteracted by the cationic metal-organic host [7]. During our research in self-assembly processes we have isolated a one-dimensional hydrogen-bonded chloride-hydrate assembly $\{[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}\}_\infty$ counteracted by complex cations $[\text{Fe}(\text{[9]aneS}_3)_2]^{2+}$. The synthesis and structure of the product are presented in this paper.

Experimental Section

1,4,7-Trithiacyclononane and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased and used without further purification. Synthetic procedures were carried out in air. The infrared spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and the mass spectrum was measured on a Finnigan TSQ 7000 spectrometer. The ^1H NMR spectrum was recorded on a Bruker ALX 300 spectrometer operating at 300 MHz with chemical shifts (δ , ppm) given with reference to SiMe_4 . The magnetic moment for the solid sample was measured by a Sherwood magnetic susceptibility balance at room temperature.

Synthesis

To a solution of 1,4,7-trithiacyclononane ($[\text{9]aneS}_3$) (360 mg, 0.20 mmol) in methanol (20 mL) was added with stirring a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (200 mg, 0.10 mmol) in methanol (10 mL) at r. t. The solution was refluxed for 2 h, during which time the color changed to purple. The purple solution was cooled down to 0 °C, and purple crystals were harvested in a yield of 64 % (362 mg). – IR (KBr disc, cm^{-1}): $\nu_{\text{O}-\text{H}}$ = 3363 (br), $\nu_{\text{C}-\text{S}}$ = 932 (s), 916 (s), 907 (m). – Magnetic moment: μ_{eff} = 0.55 μ_{B} at 298 K. – MS (FAB): m/z = 416 $[\text{Fe}(\text{[9]aneS}_3)_2 - 1]^+$, 237 $[\text{Fe}(\text{[9]aneS}_3)]^+$. – ^1H NMR ($[\text{D}_6]\text{Me}_2\text{SO}$): δ = 2.98 (s, CH_2). – $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{S}_6\text{Fe} \cdot 4\text{H}_2\text{O}$ (559.49): calcd. C 25.74, H 5.72; found C 25.68, H 5.71.

Table 1. Crystal data, data collection parameters and details of the structure refinement of **1**.

Empirical formula	$\text{C}_{12}\text{H}_{32}\text{O}_4\text{Cl}_2\text{S}_6\text{Fe}$
Formula weight	559.49
Color, habit	purple, block
Crystal size [mm^3]	$0.35 \times 0.32 \times 0.28$
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	7.6772(9)
b [Å]	8.9347(11)
c [Å]	9.0049(11)
α [deg]	94.428(2)
β [deg]	103.446(2)
γ [deg]	108.233(2)
Volume [Å ³]	563.02(12)
Z	1
Calc. density [g cm^{-3}]	1.65
Absorption coefficient [mm^{-1}]	1.48
Temperature [K]	293(2)
$F(000)$ [e]	292
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$ Å)
Reflections collected	5149
Independence reflections	2716 ($R_{\text{int}} = 0.022$)
Reflections with $I \geq 2\sigma(I)$	2483
Parameters refined	131
Final R indices (all data)*	$R1 = 0.032$, $wR2 = 0.072$
Goodness of fit (GoF)*	1.068
Final difference peaks [e Å^{-3}]	+0.46, −0.26

* $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$; $\text{GoF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$; weighting scheme $w = [\sigma^2(F_o^2) + 0.0281P^2 + 0.1836P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (deg) in **1** with estimated standard deviations in units of the last significant figure in parentheses.

Fe(1)–S(1)	2.2607(5)	Fe(1)–S(2)	2.2513(5)
Fe(1)–S(3)	2.2639(5)	S(1)–C(1)	1.8405(18)
S(2)–C(2)	1.8261(18)	S(1)–C(3)	1.8178(19)
S(3)–C(4)	1.8330(19)	S(2)–C(5)	1.8303(19)
S(3)–C(6)	1.8157(19)		
S(2)–Fe(1)–S(1)	89.938(16)	S(2)–Fe(1)–S(1) ^{#1}	90.063(16)
S(1)–Fe(1)–S(1) ^{#1}	180.0	S(2)–Fe(1)–S(3) ^{#1}	90.044(16)
S(1)–Fe(1)–S(3) ^{#1}	90.299(17)	S(2)–Fe(1)–S(3)	89.956(16)
S(1)–Fe(1)–S(3)	89.701(17)	S(3) ^{#1} –Fe(1)–S(3)	180.0

Symmetry code: ^{#1} $-x + 1, -y, -z + 1$.

Crystal structure determination

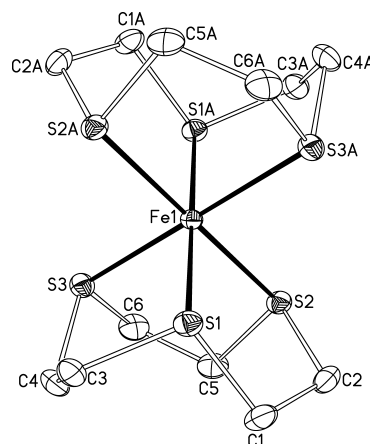
A purple single crystal of $[\text{Fe}(\text{[9]aneS}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ($0.35 \times 0.32 \times 0.26 \text{ mm}^3$) was mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K using an ω scan mode. The collected frames were processed with the software SAINT [8]. The data was corrected for absorption using the program SADABS [9]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [10]. All non-hydrogen atoms were refined anisotropically. The positions of the

hydrogen atoms on their respective parent carbon atoms were generated geometrically ($\text{C–H} = 0.95$ Å) and assigned isotropic displacement parameters before the final cycle of least-squares refinement. The water molecules were also refined anisotropically and the corresponding oxygen atoms were treated with hydrogen atoms found from subsequent difference Fourier electronic density maps. The final $R = 0.0287$, $wR = 0.0702$ ($w = [\sigma^2(F_o^2) + 0.0281P^2 + 0.1836P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}} = 0.000$ and $S = 1.067$ were obtained for 2715 observed reflections with $I \geq 2\sigma(I)$ and 131 variables. The crystallographic and structure refinement data are given in Table 1, selected bond lengths and angles are listed in Table 2.

Crystal data (excluding structure factors) have been deposited with The Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC 628299. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data.request/cif.

Results and Discussion

Reaction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{9]aneS}_3$ in methanol at reflux and subsequent cooling of the resulting purple solution yielded purple single crystals of $[\text{Fe}(\text{[9]aneS}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (**1**). The elemental analysis and infrared and mass spectroscopic data support this formulation. The $[\text{Fe}(\text{[9]aneS}_3)_2]^{2+}$ species was found to be diamagnetic since only a singlet peak at $\delta = 2.98$ due to the methylene protons was observed in the ^1H NMR spectrum. However, magnetic susceptibility measurements of solid samples at r.t. indicated an effective magnetic moment $\mu_{\text{eff}} = 0.55 \mu_{\text{B}}$. This value was dependent on the preparation of the solid sample and may be indicative

Fig. 1. Molecular geometry and atomic labeling scheme of the cation $[\text{Fe}(\text{[9]aneS}_3)_2]^{2+}$ in **1**.

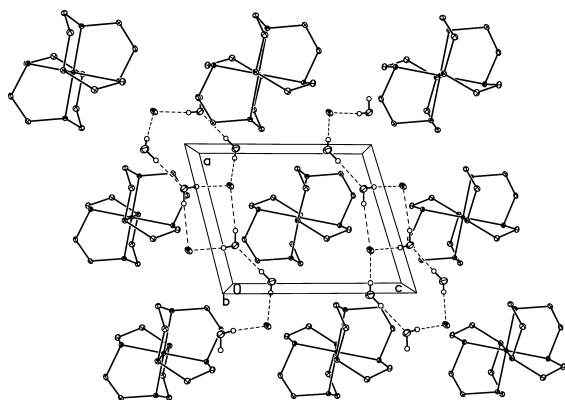


Fig. 2. Packing view of $[\text{Fe}([9]\text{aneS}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (**1**) along the crystallographic *b* axis of the crystal, showing $[\text{Fe}([9]\text{aneS}_3)_2]^{2+}$ cations and $[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}$ anions.

of impurities of Fe(III) in solid **1**. Nevertheless, the present complex still is typical of low-spin iron(II) in an octahedral ligand field [11]. The IR spectrum of **1** reveals $\nu_{\text{C-S}}$ absorptions in the range 900–940 cm^{-1} expected for the [9]aneS₃ ligands [12]. A weak broad absorption at 3363 cm^{-1} attributed to water molecules can also be observed. The positive ion FAB mass spectrum of the complex shows the two ions $[\text{Fe}([9]\text{aneS}_3)_2]$ and $[\text{Fe}([9]\text{aneS}_3)]$ with the characteristic isotopic distribution patterns. Several similar complexes, $[\text{Fe}([9]\text{aneS}_3)_2][\text{ClO}_4]_2$, and $[\text{Fe}([9]\text{aneS}_3)_2][\text{PF}_6]_2$ were isolated from a similar reaction by using other iron(II) salts [13].

Crystals of **1** consist of discrete, well separated $[\text{Fe}([9]\text{aneS}_3)_2]^{2+}$ cations and two chloride anions associated with four water molecules. The ORTEP drawing of the complex $[\text{Fe}([9]\text{aneS}_3)_2]^{2+}$ cation is shown in Fig. 1. The metal atom occupies a crystallographic inversion center, and has a nearly regular octahedral environment of six sulfur atoms from two [9]aneS₃ ligands. The average S–Fe–S angle of near 90° and the average Fe–S distance of 2.2586(5) Å agree well with data of the previously reported structures of $[\text{Fe}([9]\text{aneS}_3)_2][\text{PF}_6]_2$ [13] and $[\text{Fe}([9]\text{aneS}_3)_2][\text{FeCl}_4]$ [14].

In the crystal structure of **1**, two crystallographically independent water molecules (O1W and O2W) and one chloride ion (Cl1) are observed. Owing to crystal symmetry, four water molecules and two chloride ions have self-assembled to give a one-dimensional supramolecular array (see Fig. 2) of O–H···O and O–H···Cl hydrogen bonding in fused four- and six-membered rings running along the [100]

Table 3. Hydrogen bonding parameters (Å, deg) in the $[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}$ anions in **1** as shown in Fig. 3. (Symmetry code: #1 $-x+1, -y, -z+1$).

O–H···A	O–H	O···A	H···A	O–H···A
O2W–H3W···O1W	0.80(3)	2.05(3)	2.845(3)	174.1(2)
O1W–H1W···Cl1	0.77(3)	2.42(3)	3.180(2)	171.9(2)
O2W–H4W···Cl1 ^{#1}	0.74(3)	2.61(3)	3.337(2)	170.6(2)

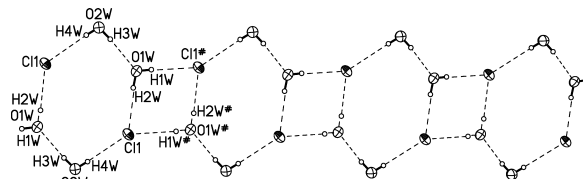


Fig. 3. One-dimensional assembly of chloride-hydrate aggregates in the crystal structure of **1** running along the crystallographic *a* axis.

direction (see Fig. 3 and Table 3). The O–H···O and O–H···Cl angles are 174.1(2) and 172.1(2)°, respectively. In the six-membered ring, the O···Cl···O angle is 128.8(2)°, while the O···O···Cl angles are 100.7(2) and 125.1(2)°. The average O···O distance of 2.845 Å in **1** is close to the corresponding O···O distance in ice at –10 °C [15]. The average O···Cl distance of 3.188 Å falls in the range for hydrogen-bonds between water and chloride anions [7]. The mean deviation of the six-membered ring from the least-squares plane is only 0.172 Å, and the dihedral angle between six- and four-membered rings is 11.9°. The four-membered ring comprises two water molecules and two chloride anions generating a cyclic motif R_2^2 (8) in the Etter's graph notation [16]. This one-dimensional hydrogen-bonded chloride-hydrate assembly $\{[(\text{H}_2\text{O})_4\text{Cl}_2]^{2-}\}_\infty$ is ion-counteracted by the complex cations $[\text{Fe}([9]\text{aneS}_3)_2]^{2+}$, as shown in Fig. 2. The structure of the chloride-hydrate chain formed here is comparable to the structure of a self-assembled chain of water. It is interesting to note that a chloride-hydrate self-assembly is stabilized by the metal-organic complex host as a template generated by non-covalent interactions.

Acknowledgements

This work was supported by the Natural Science Foundation of Education Bureau of Anhui Province (grant no. 2006kj035a). Q.-F. Z. thanks the Science and Technological Fund of Anhui Province for Outstanding Youth (06046100) and the Research Fund for the Returned Overseas Talents of Anhui Province (2006Z041).

- [1] M. W. Hosseini, *Acc. Chem. Res.* **2005**, 38, 313–323, and references therein.
- [2] M. Fujita, *Molecular Self-Assembly. Organic versus Inorganic Approaches; Structure and Bonding*, Vol. 96, Springer-Verlag, Berlin, **2000**.
- [3] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.
- [4] J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, **1995**.
- [5] J. P. Zhang, Y. Y. Lin, X. C. Huang, X. M. Chen, *Inorg. Chem.* **2005**, 44, 3146–3150.
- [6] F. Li, T. H. Li, W. Su, S. Y. Gao, R. Cao, *Eur. J. Inorg. Chem.* **2006**, 1582–1587.
- [7] A. K. Ghosh, D. Ghoshal, J. Ribas, G. Mostafa, N. R. Chaudhuri, *Cryst. Growth Des.* **2006**, 6, 36–39.
- [8] SMART, SAINT+ for Windows NT (version 6.02a), Bruker AXS Inc., Madison, Wisconsin (USA) **1998**.
- [9] G. M. Sheldrick, SADABS, University of Göttingen, Göttingen (Germany) **1996**.
- [10] G. M. Sheldrick, SHELXTL (version 5.1), Bruker AXS Inc., Madison, Wisconsin (USA) **1997**.
- [11] K. Wiegardt, W. Schmidt, W. Herrmann, H.-J. Küppers, *Inorg. Chem.* **1983**, 22, 2953–2956.
- [12] D. Sellmann, L. Zapf, *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 807–808.
- [13] K. Wiegardt, H.-J. Küppers, J. Weiss, *Inorg. Chem.* **1985**, 24, 3067–3071.
- [14] V. A. Grillo, L. R. Gahan, G. R. Hanson, T. W. Hambly, *Polyhedron* **1996**, 15, 559–563.
- [15] A. H. Narten, W. E. Thiessen, L. Blum, *Science* **1982**, 217, 1033–1034.
- [16] M. C. Etter, J. C. MacDonald, J. Bernstein, *Acta Crystallogr.* **1990**, B46, 256–262.