One-dimensional Hydrogen-bonded Chloride-Hydrate Assembly $\{[(H_2O)_4Cl_2]^{2-}\}_\infty$

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A hydrogen-bonded chloride-hydrate assembly $\{[(H_2O)_4Cl_2]^{2-}\}_\infty$ has been ion-countered by the complex cations $[Fe([9]aneS_3)_2]^{2+}$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane). In $\{[(H_2O)_4Cl_2]^{2-}\}_\infty$, four water molecules and two chloride ions are self-assembled to form a one-dimensional supramolecular array of O–H···O and O–H···Cl hydrogen bonding, which consists of fused four- and six-membered rings. The discrete cation $[Fe([9]aneS_3)_2]^{2+}$ has a nearly regular octahedral FeS_6 core with an average Fe–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-countered 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 $\{[(H_2O)_4Cl_2]^{2-}\}_\infty$ countered by complex cations $[Fe([9]aneS_3)_2]^{2+}$. The synthesis and structure of the product are presented in this paper.

Experimental Section

1,4,7-Trithiacyclononane and $FeCl_2 \cdot 4H_2O$ 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 ^{1}H 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 ([9]aneS$_3$) (360 mg, 0.20 mmol) in methanol (20 mL) was added with stirring a solution of $FeCl_2 \cdot 4H_2O$ (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}): ν_{O-H} = 3363 (br), ν_{C-S} = 932 (s), 916 (s), 907 (m). – Magnetic moment: μ_{eff} = 0.55 μ_B at 298 K. – MS (FAB): *m/z* = 416 $[Fe([9]aneS_3)_2 - 1]^+$, 237 $[Fe([9]aneS_3)]^+$. – ^{1}H NMR ([D$_6$]Me$_2$SO): δ = 2.98 (s, C*H*$_2$). – $C_{12}H_{24}Cl_2S_6Fe \cdot 4H_2O$ (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	$C_{12}H_{32}O_4Cl_2S_6Fe$
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	MoK_α (λ = 0.71073 Å)
Reflections collected	5149
Independence reflections	2716 (R_{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

* $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$; GoF = $[\Sigma w(|F_o| - F_c|)^2/(N_{obs} - N_{param})]^{1/2}$; 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 $[Fe([9]aneS_3)_2]Cl_2 \cdot 4H_2O$ ($0.35 \times 0.32 \times 0.26$ mm^3) was mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 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 (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 $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{max}$ = 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 $FeCl_2 \cdot 4H_2O$ and [9]aneS$_3$ in methanol at reflux and subsequent cooling of the resulting purple solution yielded purple single crystals of $[Fe([9]aneS_3)_2]Cl_2 \cdot 4H_2O$ (**1**). The elemental analysis and infrared and mass spectroscopic data support this formulation. The $[Fe([9]aneS_3)_2]^{2+}$ species was found to be diamagnetic since only a singlet peak at δ = 2.98 due to the methylene protons was observed in the ^{1}H NMR spectrum. However, magnetic susceptibility measurements of solid samples at r. t. indicated an effective magnetic moment μ_{eff} = 0.55 μ_B. This value was dependent on the preparation of the solid sample and may be indicative

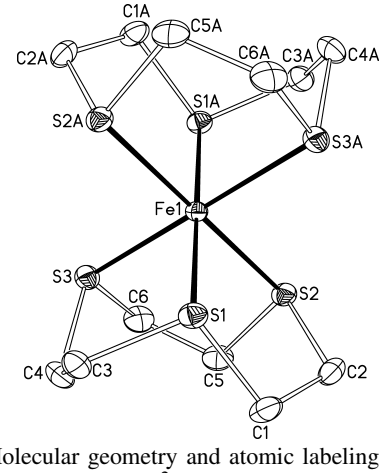

Fig. 1. Molecular geometry and atomic labeling scheme of the cation $[Fe([9]aneS_3)_2]^{2+}$ in **1**.

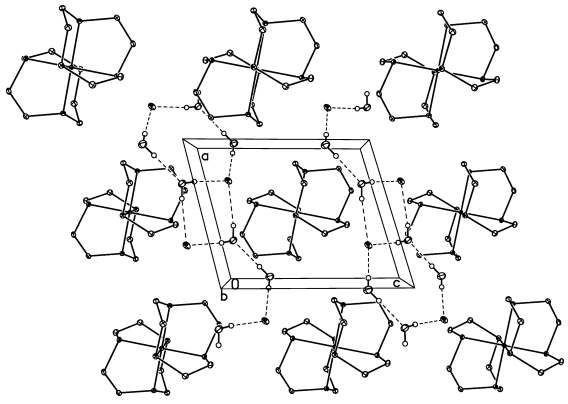

Fig. 2. Packing view of $[Fe([9]aneS_3)_2]Cl_2 \cdot 4H_2O$ (**1**) along the crystallographic *b* axis of the crystal, showing $[Fe([9]aneS_3)_2]^{2+}$ cations and $[(H_2O)_4Cl_2]^{2-}$ anions.

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 ν_{C-S} absorptions in the range 900–940 cm^{-1} expected for the [9]aneS$_3$ 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 $[Fe([9]aneS_3)_2]$ and $[Fe([9]aneS_3)]$ with the characteristic isotopic distribution patterns. Several similar complexes, $[Fe([9]aneS_3)_2][ClO_4]_2$, and $[Fe([9]aneS_3)_2][PF_6]_2$ were isolated from a similar reaction by using other iron(II) salts [13].

Crystals of **1** consist of discrete, well separated $[Fe([9]aneS_3)_2]^{2+}$ cations and two chloride anions associated with four water molecules. The ORTEP drawing of the complex $[Fe([9]aneS_3)_2]^{2+}$ 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]aneS$_3$ 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 $[Fe([9]aneS_3)_2][PF_6]_2$ [13] and $[Fe([9]aneS_3)_2][FeCl_4]$ [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] 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 $\{[(H_2O)_4Cl_2]^{2-}\}_\infty$ is ion-countered by the complex cations $[Fe([9]aneS_3)_2]^{2+}$, 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.

Table 3. Hydrogen bonding parameters (Å, deg) in the $[(H_2O)_4Cl_2]^{2-}$ 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)

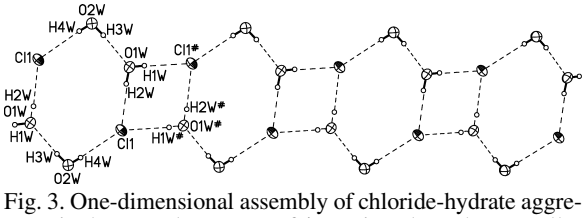

Fig. 3. One-dimensional assembly of chloride-hydrate aggregates in the crystal structure of **1** running along the crystallographic *a* axis.

Acknowledgements

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