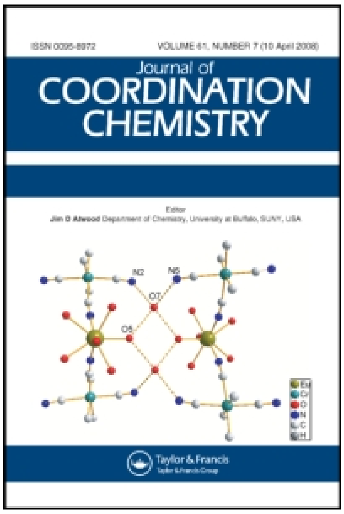

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Synthesis and crystal structure of a novel three-dimensional inorganic open-framework: $Cd_8(OH)_8(SO_4)_4$

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The title compound $Cd_8(OH)_8(SO_4)_4$ (**1**) obtained under hydrothermal conditions by reacting $Cd(OH)_2$ with 4-aminobenzenesulfonic acid in an aqueous ethanol solution was confirmed by single-crystal X-ray diffraction. Crystal data: $P2_1/c$ with $a = 6.8984(4)$, $b = 7.5640(4)$, $c = 11.3919(5)$ Å, $\beta = 119.763(2)^\circ$, $V = 516.01(5)$ Å^3, $H_8Cd_8O_{24}S_4$, $M_r = 1419.50$, $Z = 1$, $D_c = 4.568$ Mg m^{-3}, $\mu = 8.595$ mm^{-1}, $F(000) = 648$, $R = 0.023$, $wR = 0.060$ for 1208 observed reflections [$I > 2\sigma(I)$]. The crystal structure of complex **1** forms a three-dimensional (3-D) framework.

Keywords: Hydrothermal synthesis; Cadmium(II) sulfate; Crystal structure

1. Introduction

There has been growing interest in the study of open-framework architectures containing sulfate group as the building unit [1–3]. Sulfate as a tetrahedral building block may bridge sites of the coordination polymer chain to dictate the interchain geometry and even the dimensionality of the molecular structure. The possibility of obtaining an open-framework had been explored wherein the sulfate tetrahedron rather than the phosphate analogue acts as the primary building unit [4, 5]. Although a great number of cadmium coordination polymers constructed *via* fusion of octahedral–tetrahedral organic ligands have been reported [1–3], structural information on cadmium sulfates is still limited [6]. We present in this paper the synthesis and crystal structure of a novel three-dimensional open-framework: $Cd_8(OH)_8(SO_4)_4$ (**1**), which represents the first cadmium sulfate with octahedral-tetrahedral geometries and unusual coordination of sulfate.

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2. Experimental

2.1. *Materials and instrumentation*

4-Aminobenzenesulfonic acid was purchased from Acros and used without further purification. $Cd(OH)_2$ was synthesized using $Cd(NO_3)_2$ and NaOH. All solvents were of analytical grade.

IR spectra were recorded in the range 4000–500 cm^{-1} on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400/II automatic analyzer.

2.2. *Synthesis of $Cd_8(OH)_8(SO_4)_4$*

A mixture of $Cd(OH)_2$ (1 mmol), 4-aminobenzenesulfonic acid (2 mmol), H_2O (13 mL) and ethanol (5 mL) was sealed in a 25 mL Teflon-lined stainless-steel reactor and heated at 160°C for 5 days. After cooling slowly to room temperature, colorless crystals suitable for X-ray diffraction were obtained. Yield: 35%. Anal. Calcd (%) for $H_8Cd_8O_{24}S_4$: H, 0.57; S, 9.04. Found (%): H, 0.62; S, 9.13.

2.3. *X-ray crystallography*

A colorless block single crystal with dimensions of $0.40 \times 0.14 \times 0.10\,mm^3$ was selected and mounted on a glass fiber. The intensity data were collected on a Siemens SMART CCD diffractometer equipped with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 2968 reflections were collected in the range of $3.40 < \theta < 28.28°$ by using an ω-2θ scan mode, of which 1220 were unique with $R_{int} = 0.023$ and used in the succeeding structure calculations. Data intensity was corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1208 observed reflections $[I > 2\sigma(I)]$ and 91 variable parameters, and converged with weighted agreement factors. The final $R = 0.023$ and $wR = 0.060$ $(w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 1.1923P]$ where $P = (F_o^2 + 2F_c^2)/3$ with goodness-of-fit 1.338, the maximum and minimum peaks in the final difference Fourier map are 0.984 and −1.534 (close to Cd(II)) e Å^{-3}, respectively. All calculations were performed with the SHELXTL-97 package [7].

Crystallographic data for compound **1**: $H_8Cd_8O_{24}S_4$, $M_r = 1419.50$, monoclinic, $P2_1/c$, $a = 6.8984(4)$, $b = 7.5640(4)$, $c = 11.3919(5)$ Å, $\beta = 119.763(2)°$, $V = 516.01(5)$ Å^3, $Z = 1$, $D_c = 4.568\,Mg\,m^{-3}$, $\mu = 8.595\,mm^{-1}$.

3. Results and discussion

The hydrothermal reaction of $Cd(OH)_2$ with 4-aminobezenesulfonic acid in an aqueous ethanol solution unexpectedly affords $Cd_8(OH)_8(SO_4)_4$ (**1**). The occurrence of SO_4^{2-} is from decomposition of 4-aminobezenesulfonic acid under the reaction conditions.

The non-hydrogen atomic coordinates and equivalent thermal parameters are listed in table 1, and selected bond lengths and angles in tables 2 and 3, respectively. The coordination mode of sulfate and coordination environment of cadmium ions of **1** are shown in figure 1, molecular packing of the three-dimensional structure of **1** is presented in figure 2.

In $Cd_8(OH)_8(SO_4)_4$ (**1**), each oxygen atom of sulfate group participates in coordination to cadmium centers (figure 1(a)). The S atom is located at the center of

Table 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) for **1**.

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Cd(1)	6550(1)	−321(1)	1678(1)	7(1)	O(4)	8048(5)	−2991(4)	3093(3)	12(1)
Cd(2)	8278(1)	−1670(1)	5025(1)	8(1)	O(5)	8182(5)	682(4)	3764(3)	8(1)
O(1)	6572(5)	−5892(4)	3121(3)	12(1)	O(6)	4725(5)	1896(4)	235(3)	7(1)
O(2)	10395(5)	−5576(4)	3698(3)	12(1)	S(1)	8104(2)	−4896(1)	2822(1)	5(1)
O(3)	7469(5)	−5135(4)	1390(3)	13(1)					

Table 2. Selected bond lengths (Å) for **1**.

Bond	Bond length	Bond	Bond length
Cd(1)–O(1)#2	2.317(3)	Cd(2)–O(2)#7	2.444(3)
Cd(1)–O(2)#3	2.357(3)	Cd(2)–O(3)#6	2.336(3)
Cd(1)–O(4)	2.469(3)	Cd(2)–O(4)	2.349(3)
Cd(1)–O(5)	2.199(3)	Cd(2)–O(5)#4	2.254(3)
Cd(1)–O(6)	2.246(3)	Cd(2)–O(6)#5	2.224(3)
Cd(1)–O(6)#1	2.244(3)	Cd(2)#2–O(6)	2.225(3)
Cd(1)#5–O(1)	2.317(3)	Cd(2)#7–O(2)	2.444(3)
Cd(1)#8–O(2)	2.357(3)	Cd(2)#9–O(3)	2.336(3)
S(1)–O(1)	1.469(3)	S(1)–O(3)	1.475(3)
S(1)–O(2)	1.481(3)	S(1)–O(4)	1.478(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$; #2 $-x+1, y+1/2, -z+1/2$; #3 $-x+2, y+1/2, -z+1/2$; #4 $-x+2, -y, -z+1$; #5 $-x+1, y-1/2, -z+1/2$; #6 $x, -y-1/2, z+1/2$; #7 $-x+2, -y-1, -z+1$; #8 $-x+2, y-1/2, -z+1/2$; #9 $x, -y-1/2, z-1/2$.

Table 3. Selected bond angles (°) for **1**.

Bond angle	(°)	Bond angle	(°)
O(1)#2–Cd(1)–O(4)	83.7(5)	O(6)#5–Cd(2)–O(4)	92.4(5)
O(2)#3–Cd(1)–O(4)	85.9(7)	O(2)#7–Cd(2)–O(5)	158.5(7)
O(5)–Cd(1)–O(6)#1	167.4(3)	O(2)#3–Cd(1)–O(6)	98.9(3)
O(5)–Cd(1)–O(6)	109.4(8)	O(5)–Cd(2)–O(6)#5	124.4(9)
O(6)#1–Cd(1)–O(6)	83.0(5)	O(5)–Cd(2)–O(5)#4	79.0(4)
O(1)#2–Cd(1)–O(5)	87.6(8)	O(3)#6–Cd(2)–O(5)	91.2(4)
O(1)#2–Cd(1)–O(6)	90.0(3)	O(4)–Cd(2)–O(5)	76.9(1)
O(2)#3–Cd(1)–O(5)	101.5(5)	O(1)–S(1)–O(3)	109.9(2)
O(4)–Cd(1)–O(5)	75.6(7)	O(1)–S(1)–O(2)	108.4(2)
O(4)–Cd(1)–O(6)#1	92.0(1)	O(1)–S(1)–O(4)	110.7(4)
O(4)–Cd(1)–O(6)	171.8(1)	O(2)–S(1)–O(3)	109.5(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$; #2 $x+1, y+1/2, -z+1/2$; #3 $-x+2, y+1/2, -z+1/2$; #4 $-x+2, -y, -z+1$; #5 $-x+1, y-1/2, -z+1/2$; #6 $x, y-1/2, +1/2$; #7 $-x+2, -y-1, -z+1$.

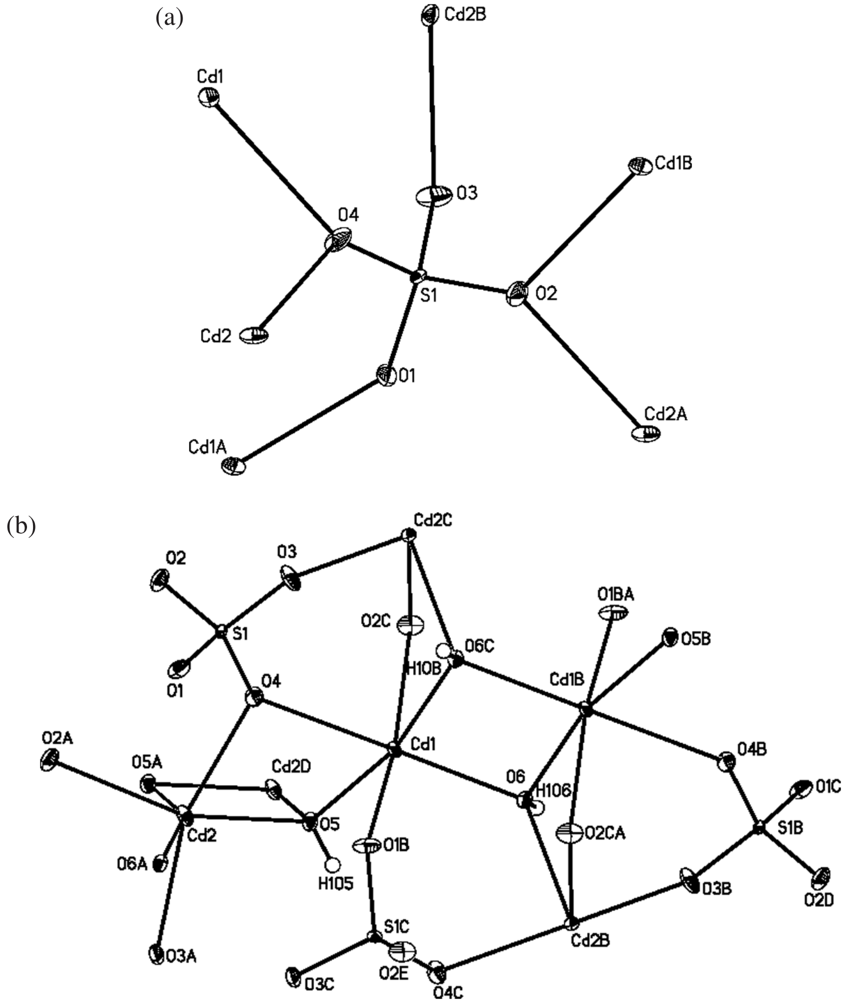

Figure 1. Perspective views of **1**: (a) the coordination mode of sulfate group; (b) the coordination environment of cadmium ions.

a slightly distorted $\{SO_4\}$ tetrahedron with S–O distances from 1.469 to 1.481 Å and bond angles from 108.42(18) to 110.74(18)°. The S atom makes six S-O-Cd linkages through two [S-O-Cd] and two 3-coordinated oxygen atoms [S-μ_3-O-Cd_2]; the coordination modes and bond distances of sulfate resemble those of $La(OH)SO_4$ [8].

There exist two μ_3-OH groups in the structure of **1**. The calculation of bond valence sums [9] indicated that the O5, O6 atoms are ascribed to OH groups (corresponding Σs value is 1.17) [8]. Thus, the linkages of two adjacent cadmium ions are different, one is via Cd-μ_3-OH-Cd, while the other via Cd-μ_3-O-Cd (O coordinated to two Cd and one S atoms) bonds. As shown in figure 1(b), there are two unique Cd(II) ions in an asymmetric unit of $Cd_8(OH)_8(SO_4)_4$. Each cadmium possesses a similar distorted octahedral geometry, being surrounded by six oxygen atoms, of which three oxygen atoms are from three μ_3-OH groups [HO-μ_3-Cd_3 bridge] with Cd-O distances from 2.199(3) to 2.267(3) Å, two oxygen atoms from two different μ_3-O of sulfate

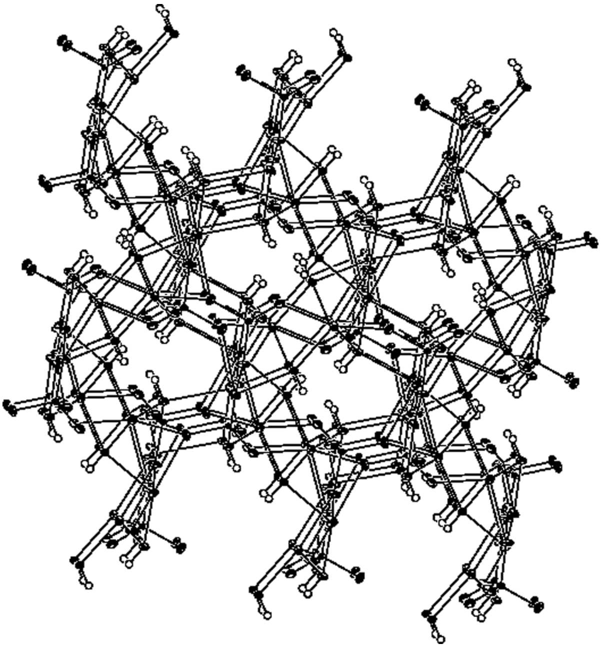

Figure 2. The packing array of three-dimensional structure of **1** viewed along the *c*-axis.

groups [S-μ_3-O-Cd$_2$ bridge] with Cd-O distances from 2.349(3) to 2.469(3) Å, and one oxygen atom is from two-coordinate oxygen atoms of SO_4^{2-} [S-O-Cd bridge] with Cd-O distances ranging from 2.317(3) to 2.336(3) Å. The Cd-O$_{sulfate}$ distances are all longer than those of [Cd(μ_4-SO$_4$)(bpy)]$_n$ (bpy = 4,4′-bipyridine, Cd-O 2.279(8)–2.285(8) Å) [6]. In **1**, the Cd $\cdots$ Cd separations are from 3.362(1) to 3.518(1) Å, and the Cd-O-Cd bond angles are in the range of 94.2(1)–127.5(1)°. Furthermore, each cadmium ion and three adjacent cadmium ions form an infinite three-dimensional framework, constructed through linking octahedral cadmium ions with tetrahedral SO_4^{2-} building units and μ_3-OH groups (figure 2).

The IR spectrum of **1** shows a strong absorption centered at 3492 cm^{-1}, corresponding to the stretching vibration of the hydroxyl group ν(O–H). A strong broad absorption at 1150 cm^{-1} and two moderate absorptions at 610 cm^{-1} are due to the characteristic vibrations for SO$_4$ group [6, 8].

In summary, a three-dimensional structure of cadmium compounds $Cd_8(OH)_8(SO_4)_4$ was hydrothermally synthesized and structurally characterized. Compound **1** is a novel hydroxide cadmium sulfate complex.

Supplementary material

Crystallographic details of the complex were deposited at the Kristallstruktur Data Center as No. CSD-415601. Copies of the data can be obtained free of charge on Web site: http://icsd.fiz-karlsruhe.de. E-mail: crysdata@fiz-karlsruhe.de.

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