ARTICLES

Disproportionation of an Element in a Zeolite. I. Crystal Structure of a Sulfur Sorption Complex of Dehydrated, Fully Cd^{2+}-Exchanged Zeolite X. Synthesis of Tetrahedral S$_4^{4+}$ and n-S$_4^{2+}$, Two New Polyatomic Cations of Sulfur

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The crystal structure of a sulfur sorption complex of fully dehydrated, fully Cd^{2+}-exchanged zeolite X, Cd$_{46}$-Si$_{100}$Al$_{92}$O$_{384}$·52S per unit cell (a = 24.925(7) Å), has been determined by single-crystal X-ray diffraction methods in the cubic space group $Fd\bar{3}$ at 21(1) °C. The crystal was prepared by ion exchange in an aqueous stream 0.05 M in Cd^{2+}, followed by dehydration at 450 °C and 2 × 10^{-6} Torr and then exposure in situ to zeolitically dry sulfur vapor. The structure was refined to the final error indices R_1 = 0.051 and R_2 = 0.043 with 362 reflections for which $I > 3\sigma(I)$. Forty-six Cd^{2+} ions are found at five crystallographic sites: 12 at site I at the centers of the hexagonal prisms (Cd−O = 2.387(8)), 8 at site I′ in the sodalite cavities near the hexagonal prisms (Cd−O = 2.325(7) Å), 7 at site II′ in the sodalite cavities (Cd−O = 2.195(8) Å), and the remaining 19 at two different site II positions, near single six-oxygen rings in the supercages, with occupancies of 7 and 12 (Cd−O = 2.155(7) and 2.251(7) Å, respectively). All fifty-two sulfur atoms disproportionated upon sorption to give sulfide anions and two new tetrasulfur cations, S$_4^{4+}$ and n-S$_4^{2+}$. Each of 12 sulfide ions coordinates to a site II Cd^{2+} ion in the supercage. S$_4^{4+}$ is tetrahedral with S−S = 2.17(2) Å, a quantum mechanical calculation gives 2.21 Å, and two of the eight sodalite cavities per unit cell are centered by one. In S$_4^{4+}$, each sulfur atom is 3.380(9) Å from three framework oxygens; with those 12 contacts, S$_4^{4+}$ is hosted and stabilized by an anionic sodalite cavity. Each supercage holds a zigzag n-S$_4^{2+}$ cluster with a torsion angle of 114(8)°. n-S$_4^{2+}$ is electron deficient, bridges covalently between two zeolite oxygens, and has a predominantly ionic interaction with a sulfide ion.

Introduction

Sulfur, like the other Group VI elements, has a high electron affinity, so it readily forms anions such as S^{2-} or S$_n^{2-}$. However, in very acidic media, the three polysulfur cations S$_n^{2+}$ (n = 4, 8, or 19) have been isolated[1-3] as stable salts of SO$_3$F$^-$, AsF$_6^-$, Sb$_2$F$_{11}^-$, and AlCl$_4^-$. In addition, the polysulfur cations S$_n^+$ (n = 5, 7, or 8) have been identified in solution as paramagnetic species by electron spin resonance (ESR).[3,4] Discussions of these polysulfur cations are available.[5-7]

Sulfur vapor contains all of the molecules S$_n$, $2 \leq n \leq 10$.[8-10] Although their structures and properties are well reviewed,[10] little is known about several of the smaller S$_n$ molecules, especially tetrasulfur S$_4$. Attempts have been made to characterize the electronic and geometrical structure of S$_4$ by experiment and theoretical calculation.[11-14] Of the eleven different isomers of S$_4$ studied[11] (branched chain (D_{3h}), cis (C_{2v}), trans (C_{2h}), puckered ring (D_{2d}), branched ring (C_s), helical (C_2), rectangular ring (D_{2h}), square ring (D_{4h}), pyramidal (C_{3v}), linear ($D_{\infty h}$), and tetrahedral (T_d)), there is no consensus about which has the lowest energy.

With their regular cavity and channel structures, zeolites offer a unique medium in which to assemble and stabilize clusters. Well-defined clusters have been found in A, X, and Y type zeolites.[15-29] By choosing different zeolites, nanoclusters with different structures and electronic properties can be built from the same sorbate. Attempts have been made to synthesize nanoclusters of semiconductors such as CdS, PbS, and PbI$_2$ inside zeolites.[30-33] Semiconductor nanoclusters demonstrate strong quantum-size effects; the band gap is a function of particle size.[34] To understand their structures and nature, X-ray diffraction, IR, XPS, optical absorption, and diffuse reflectance spectroscopy have been applied.

Fully dehydrated, fully Cd^{2+}-exchanged zeolite X (Cd$_{46}$−X) was reported in 1996.[35] Since then, the structures of the ethylene,[36] acetylene,[37] benzene,[38] and cadmium[39] sorption complexes of Cd$_{46}$−X have been reported. In the last of these, after exposure of Cd$_{46}$−X to Cd metal vapor, 18 Cd^{2+} cations per unit cell had reacted with 18 Cd^0 atoms to form 36 monatomic Cd$^+$ ions, and eight Cd^{2+} ions associated with four Cd^0 atoms to form four (Cd$_3$)$^{4+}$ clusters in four of the eight sodalite cavities per unit cell.[39]

This work was done to examine a very different sorption complex of Cd$_{46}$−X. It was thought that clusters similar to CdS

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(a semiconductor) might form. Alternatively, novel neutral clusters or rings of sulfur might be expected. The actual results were a surprise.

Experimental Section

Large single crystals of sodium zeolite X, $Na_{92}Si_{100}Al_{92}O_{384}$, were prepared in St. Petersburg, Russia.[40] One of these, a colorless octahedron with a cross-section of about 0.2 mm, was lodged in a fine Pyrex capillary for ion exchange.

Cd_{46}–X was prepared by allowing an exchange solution of $Cd(NO_3)_2$ (Aldrich, 99.999%) and $Cd(O_2CCH_3)_2$ (Aldrich, 99.99%) in the molar ratio 1:1 with a total Cd^{2+} concentration of 0.05 M to flow past the crystal at a velocity of approximately 15 mm/s at 21(1) °C for 5 days, followed by washing with distilled water at 80 °C for 1 h to wash the crystal free of occluded material. The capillary containing the crystal was attached to a vacuum system, and the crystal was fully dehydrated by increasing the temperature (ca. 25 °C/h) to 450 °C. The system was maintained at this temperature and 2×10^{-6} Torr for 48 h. After cooling to room temperature, the crystal was seen to be colorless.

Before its dehydration, the Pyrex tube extension of the crystal-containing capillary was connected via a break-off seal to a vessel containing about 0.1 g of zeolitically dry sulfur under vacuum. This sulfur had been prepared in situ by successive steps of vacuum distillation at 10^{-6} Torr for 96 h and sealed with fully dehydrated beads of zeolite 4A. After the internal seal was broken, the crystal (at the following temperatures) was exposed to sulfur vapor at 250 °C for 24 h, 330 °C for 72 h (to accelerate a possible slow process toward equilibrium), and 250 °C for 24 h. The vapor pressures of sulfur at 250 °C and 330 °C are ca. 10 and 100 Torr, respectively.[41] After the residual sulfur was condensed away from the crystal, it could be seen that the crystal was yellow.

The cubic space group $Fd\bar{3}$ was used throughout this work. This choice appeared to be appropriate, because most crystals from this synthesis batch have been refined successfully in $Fd\bar{3}$ with mean Al–O distances correctly longer than mean Si–O distances.[42] That is true for this crystal also, verifying that $Fd\bar{3}$ is correct.

The cubic unit cell constant, $a = 24.925(7)$ Å, was determined using 25 intense reflections, for which $14° < 2\theta < 22°$. Diffraction data were collected with an automated Enraf–Nonius, four-circle, computer-controlled CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation. The intensities were measured using the ω-2θ scan technique with a scan width of $(0.80 + 0.344 \tan \theta)$ in ω. The data were collected using variable scan speeds with most reflections observed at a slow scan speed, from 0.25° to 0.31° min^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3 h to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reflections in the positive octant of an F-centered unit cell, for which $2\theta < 50°$, $l > h$, and $k > h$ were recorded. Of the 1383 unique reflections examined, only the 362 reflections for which $I > 3\sigma(I)$ were used in subsequent structure determination. Calculations were performed with the structure determination program package, *MolEN*.[43]

An absorption correction was made empirically using a ψ scan.[44] This correction had little effect on the final R indices. Table 1 provides a summary of the data collection parameters.

TABLE 1: Experimental and Structure Refinement Data

chemical composition	$Cd_{46}Si_{100}Al_{92}O_{384}\cdot52S$
space group	$Fd\bar{3}$
unit cell constant at 21(1)°C, a (Å)	24.925(7)
color	yellow
ρ_{calcd} (gcm^{-3})	1.959
μ (mm^{-1})	2.12
transmission factors, min and max	0.990−0.999
diffractometer	Enraf−Nonius CAD-4
data collection temp (°C)	21(1)
radiation (Mo Kα) λ_1 (Å), λ_2 (Å)	0.70930, 0.71359
no. of reflections, n, gathered	1383
$I > 0$	766
$I > 3\sigma(I)$	362
no. of parameters, s	87
final R indices ($I > 3\sigma(I)$) R_1,[a] wR_2[b]	0.051, 0.043
($I > 0$) R_1, wR_2	0.154, 0.051
goodness-of-fit[c]	1.23

[a] $R_1 = \sum|F_o−|F_c||/\sum F_o$. [b] $wR_2 = (\sum w(F_o−|F_c|)^2/\sum wF_o^2)^{1/2}$. [c] Error in an observation of unit weight $= (\sum w(F_o−|F_c|)^2/(n\text{-}s))^{1/2}$, where n is the number of reflections and s is the number of parameters.

Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated Cd_{46}–X.[35] Isotropic refinement converged to $R_1 = 0.42$ and $wR_2 = 0.49$.

A Fourier difference electron-density function yielded three strong peaks at (0.0, 0.0, 0.0), (0.229, 0.229, 0.229), and (0.057, 0.057, 0.057), with heights of 15.1, 7.9, and 5.0 $eÅ^{-3}$, respectively. The anisotropic refinement of the framework atoms including these peaks refining isotropically as Cd^{2+} ions at Cd(1), Cd(2), and Cd(5) converged to $R_1 = 0.098$ and $wR_2 = 0.084$.

A subsequent difference Fourier synthesis revealed two more peaks at (0.289, 0.302, 0.292) and (0.205, 0.205, 0.205) with heights of 1.6 and 1.3 $eÅ^{-3}$, respectively. Inclusion of these peaks as sulfur atoms at S(2) and Cd^{2+} ions at Cd(4), respectively, lowered the error indices to $R_1 = 0.058$ and $wR_2 = 0.057$. (Cd^{2+} ions can be distinguished from S atoms by their close approaches to framework oxygens.) From the next difference Fourier synthesis, a peak of height 1.4 $eÅ^{-3}$ was found at (0.152, 0.152, 0.152), S(1), which was stable in least-squares refinement. The anisotropic refinement of all framework atoms and Cd^{2+} ions, with S(1) and S(2) refining isotropically, converged to $R_1 = 0.053$ and $wR_2 = 0.049$. An ensuing Fourier synthesis revealed four more peaks at the general positions (0.444, 0.167, 0.268), (0.403, 0.263, 0.255), (0.404, 0.351, 0.229), and (0.397, 0.391, 0.179), all with heights of ca. 0.7 $eÅ^{-3}$. Because the distances between these positions (S(3), S(4), S(5), and S(6), respectively) indicate that they are bonded together, their occupancies were refined in the ratio of 1:1:1:1.

The thermal ellipsoids of Cd(2) became elongated in subsequent refinements, indicating the presence of two nonequivalent Cd^{2+} ions at this position. It was therefore refined as Cd(2) at (0.23, 0.23, 0.23) and Cd(3) at (0.22, 0.22, 0.22). The occupancies of Cd(2) and S(2) were constrained to be equal, because they were nearly equal in refinement with an interatomic distance indicative of a CdS bond. The occupancies at all Cd and S positions were fixed at the values shown in Table 2 by the assumption of stoichiometry and the requirement of neutrality (vide infra). The final error indices with 362 reflections for which $I > 3\sigma(I)$ are $R_1 = 0.051$ and $R_2 = 0.043$. The very final refinement, the results of which are shown in Table 1, was done using the 766 reflections for which $I > 0$ to make better use of the diffraction data: $R_1 = 0.154$; $R_2 = 0.051$. This allowed the

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TABLE 2: Positional, Thermal, and Occupancy Parameters[a]

atom	wyc. pos.	site	x	y	z	$^{b}U_{11}$ or $^{d}U_{iso}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	^{c}occupancy varied	fixed
Si	96(g)		−523(1)	1237(1)	348(1)	177(16)	97(14)	119(15)	−10(17)	−20(14)	−44(18)		96
Al	96(g)		−548(1)	376(1)	1223(2)	154(17)	151(18)	132(17)	12(16)	−13(18)	3(19)		96
O(1)	96(g)		−1098(3)	15(4)	1049(3)	163(46)	373(52)	268(48)	−49(46)	20(34)	−22(47)		96
O(2)	96(g)		−15(4)	−14(4)	1461(3)	328(44)	256(42)	274(44)	27(44)	−3(45)	−8(45)		96
O(3)	96(g)		−309(3)	665(3)	616(3)	208(46)	266(48)	404(52)	62(44)	34(45)	164(42)		96
O(4)	96(g)		−661(3)	807(3)	1719(3)	412(50)	234(45)	123(42)	26(48)	57(48)	−146(38)		96
Cd(1)	16(c)	I	0	0	0	90(6)	90(6)	90(6)	−12(8)	−12(8)	−12(8)	12.3(1)	12
Cd(2)	32(e)	II	2322(1)	2322(1)	2322(1)	182(10)						12.7(1)	12
Cd(3)	32(e)	II	2213(1)	2213(1)	2213(1)	56(14)						7.3(1)	7
Cd(4)	32(e)	II′	2055(2)	2055(2)	2055(2)	141(17)						7.2(1)	7
Cd(5)	32(e)	I′	623(2)	623(2)	623(2)	492(23)	492(23)	492(23)	124(28)	124(28)	124(28)	7.9(1)	8
S(1)	32(e)	II′	1558(13)	1558(13)	1558(13)	2215(333)						7.9(6)	8
S(2)	96(g)		2840(29)	3094(31)	2338(34)	2821(249)						12.7(1)	12
S(3)	96(g)		4289(34)	1821(34)	2533(46)	1416(330)						7.6(7)	8
S(4)	96(g)		3772(47)	2661(52)	2619(54)	3321(520)						7.6(7)	8
S(5)	96(g)		4317(54)	3541(58)	2499(62)	3968(520)[e]						7.6(7)	8
S(6)	96(g)		3941(40)	3901(47)	1699(32)	1799(497)						7.6(7)	8

[a] Positional and anisotropic thermal parameters are given $\times 10^{4}$. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. [b] The anisotropic temperature factor $= \exp[(-2\pi^{2}/a^{2})(U_{11} h^{2} + U_{22} k^{2} + U_{33} l^{2} + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. [c] Occupancy factors are given as the number of atoms or ions per unit cell. [d] $B_{iso} = 8\pi^{2}U_{iso}$. [e] To achieve convergence, the shift of the isotropic thermal parameter at S(5) was constrained to be that at S(4). Otherwise, it diverged during the refinement.

TABLE 3: Selected Interatomic Distances (Å) and Angles (deg)[a]

Si−O(1)	1.629(9)	O(1)−Si−O(2)	112.7(5)
Si−O(2)	1.655(9)	O(1)−Si−O(3)	107.4(4)
Si−O(3)	1.663(9)	O(1)−Si−O(4)	110.6(4)
Si−O(4)	1.606(8)	O(2)−Si−O(3)	105.2(4)
average	**1.638**	O(2)−Si−O(4)	107.0(4)
Al−O(1)	1.696(8)	O(3)−Si−O(4)	113.9(4)
Al−O(2)	1.750(9)	O(1)−Al−O(2)	114.0(4)
Al−O(3)	1.779(9)	O(1)−Al−O(3)	105.6(4)
Al−O(4)	1.662(9)	O(1)−Al−O(4)	113.4(4)
average	**1.722**	O(2)−Al−O(3)	105.0(4)
Cd(1)−O(3)	2.387(8)	O(2)−Al−O(4)	103.5(4)
Cd(2)−O(2)	2.251(7)	O(3)−Al−O(4)	115.3(4)
Cd(3)−O(2)	2.155(7)	Si−O(1)−Al	132.2(5)
Cd(4)−O(2)	2.195(8)	Si−O(2)−Al	136.5(5)
Cd(5)−O(3)	2.325(7)	Si−O(3)−Al	125.6(5)
Cd(2)−S(2)	2.32(8)	Si−O(4)−Al	157.3(5)
S(1)−S(1)	2.17(2)	O(3)−Cd(1)−O(3)	89.1(3)/90.9(3)/180.(0)
S(1)−O(2)	3.380(9)	O(2)−Cd(2)−O(2)	111.2(3)
S(3)−S(4)	2.47(15)	O(2)−Cd(3)−O(2)	119.0(3)
S(4)−S(5)	2.60(19)	O(2)−Cd(4)−O(2)	115.6(3)
S(5)−S(6)	2.38(17)	O(3)−Cd(5)−O(3)	92.2(3)
S(3)−O(1)	2.58(8)	S(1)−S(1)−S(1)	60.0(8)
S(6)−O(1)	3.00(9)	O(2)−S(1)−O(2)	66.7(3)
S(4)−S(2)	2.73(14)	S(1)−S(1)−O(2)	116.6(4)/116.6(11)/175.89(14)
		O(2)−Cd(2)−S(2)	74(2)/111(2)/132(2)
		S(2)−S(4)−S(3)	139(6)
		S(2)−S(4)−S(5)	103(7)
		S(3)−S(4)−S(5)	116(6)
		S(4)−S(5)−S(6)	102(6)
		S(3)−S(4)−S(5)−S(6)	114(8)

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding values.

estimated standard deviations to decrease by about 24% of their former values.

Atomic scattering factors[45,46] for Si^{0}, Al^{0}, O^{-}, S^{0}, and Cd^{2+} were used. All scattering factors were modified to account for anomalous dispersion.[47] The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

Results and Discussion

Zeolite X. Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The cuboctahedron (14-hedron with 24 vertices), known as the sodalite cavity or β cage, may be viewed as the principal building block of the aluminosilicate
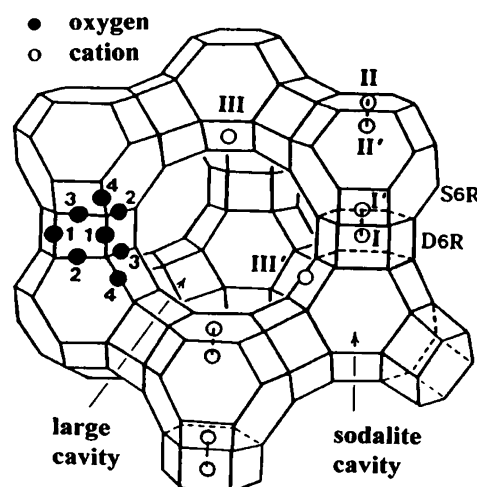

Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The numbers 1 to 4 indicate the four nonequivalent oxygen atoms. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum at about 4% of the Al positions. Extraframework cation positions are labeled with Roman numerals.

framework of the zeolite (see Figure 1). The β-cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal prisms) and, concomitantly, to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertexes of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms but are displaced from those points to give near tetrahedral angles about Si and Al. Single six-rings (S6Rs) are shared by sodalite and supercages and may be viewed as the entrances to the sodalite cavities. Each unit cell has 8 sodalite units, 8 supercages, 16 D6Rs, 16 12-rings, and 32 S6Rs.

The exchangeable cations that balance the negative charge of the aluminosilicate framework are found within the zeolite's windows and cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R, site I′ in the sodalite (β) cavity on the opposite side of either of the D6R's six-rings from site I, site II′ inside the sodalite cavity near a
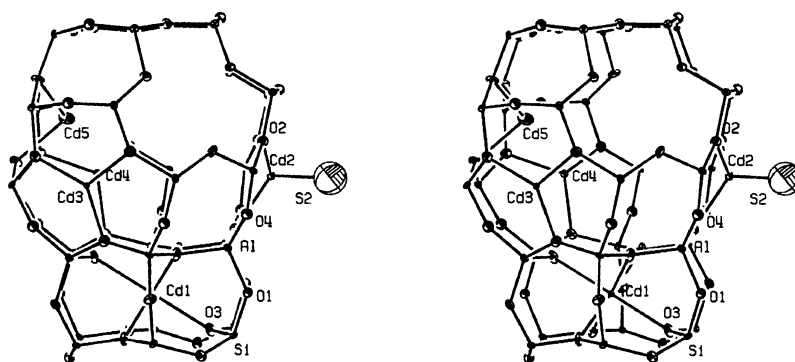
Figure 2. Stereoview of a sodalite cavity with an attached D6R in $Cd_{46}-X\cdot52S$. One Cd^{2+} ion at Cd(1) (site I), one at Cd(2) (site II), one at Cd(3) (site II), one at Cd(4) (site II′), and one at Cd(5) (site I′) are shown. Ellipsoids of 20% probability are used.

TABLE 4: Deviations (Å) of Atoms from Six-Ring Planes

position	site	displacement
	at O(3)[a]	
Cd(1)	I	1.39
Cd(5)	I′	−1.29
	at O(2)[b]	
Cd(2)	II	0.68
Cd(3)	II	0.21
Cd(4)	II′	−0.47
S(1)	II′	−2.61
S(2)		2.56

[a] The positive deviation at Cd(1) indicates that it lies within a D6R. The negative deviation at Cd(5) indicates that it is in the sodalite cavity. [b] Positive deviations indicate that the atom lies in the supercage. Negative deviations indicate that the atom is in the sodalite cavity.

S6R entrance to the supercage, site II in the supercage adjacent to a S6R, site III in the supercage opposite a sodalite four-ring (on a 2-fold axis), and site III′ on the inner surface of the supercage somewhat or substantially off that 2-fold axis.[48,49]

Cd^{2+} Ions. Forty-six Cd^{2+} ions are found at five crystallographic sites: I, two different IIs, II′, and I′ (see Table 2). In contrast, Cd^{2+} ions occupied only two sites, I (fully) and II, in fully dehydrated $Cd_{46}-X$,[35] so a substantial rearrangement of Cd^{2+} ions has occurred upon sulfur sorption. Fifteen Cd^{2+} ions per unit cell have moved into the sodalite cavities from sites I and II to I′ and II′, and those remaining at site II have become nonequivalent.

Twenty Cd^{2+} ions occupy sites I and I′. The 12 at Cd(1) occupy the octahedral site I (see Figure 2). The Cd(1)−O(3) distance, 2.387(8) Å, is just a little longer than the sum of the corresponding conventional radii,[50] 0.97 + 1.32 = 2.29 Å, indicating a reasonably good fit. The distance between the neighboring positions I and I′ is only 2.69 Å, so they cannot be occupied simultaneously because of the strong electrostatic repulsion that would result between 2+ cations. However, the simultaneous occupation of two I′ sites about a single D6R at 5.38 Å is apparently all right. Thus, $n(I) + n(I′)/2$ should be less than or equal to 16 (the number of D6Rs per unit cell), where $n(I)$ and $n(I′)$ are the numbers of cations at those sites per unit cell. Eight Cd^{2+} ions are found at site I′, Cd(5), so $n(I) + n(I′)/2 = 12 + 8/2 = 16$. Therefore, each D6R either has a Cd^{2+} ion at its center or two just outside. Each Cd(5) ion extends substantially, 1.29 Å, out of the D6R (into the sodalite unit) from its three-O(3) plane (see Figure 2 and Table 4) because of $Cd^{2+}-Cd^{2+}$ I′− I′ repulsion through the D6R.

Nineteen Cd^{2+} ions occupy the two different site II positions Cd(2) and Cd(3) in the supercage with occupancies of 12 and 7, respectively. As compared to dehydrated $Cd_{46}-X$,[35] each Cd^{2+} ion at Cd(2) has moved 0.49 Å further into the supercage

from its six-ring plane to coordinate to a sulfide ion at S(2). Correspondingly, the Cd(2)−O(2) bond has increased from 2.16-(1)[35] to 2.251(7) Å, nearly the sum of the corresponding ionic radii,[50] 2.29 Å. Correspondingly again, the O(2)−Cd(2)−O(2) bond angle has decreased from a near trigonal planar value of 119.2(5)° in empty $Cd_{46}-X$[35] to a more tetrahedral value, 111.2-(3)°. In contrast, presumably because Cd(3) is only three-coordinate, the Cd(3)−O(2) distance, 2.155(7) Å, is distictly shorter than the sum of the corresponding ionic radii,[50] 2.29 Å. These Cd(3) ions are recessed only 0.21 Å into the supercage from the plane of the three O(2) oxygens. The O(2)−Cd(3)−O(2) bond angle, 119.0(3)°, is nearly trigonal planar as in empty $Cd_{46}-X$.[35]

The remaining seven Cd^{2+} ions are at site II′, at Cd(4). Each is recessed 0.47 Å into the sodalite cavity from the S6R plane at O(2). The Cd(4)−O(2) distance, 2.195(8) Å, is again a little less than the sum of the conventional ionic radii,[50] 2.29 Å, because of three-coordination. The O(2)−Cd(4)−O(2) bond angle is 115.6(3)°.

Sulfur Ions. Sulfur ions are found at six sites: 8 at S(1) in the sodalite cavity, 12 at S(2) in the supercage, and 8 each at S(3), S(4), S(5), and S(6) in the supercage. The assignment of local structure and charge to these 52 sulfur atoms in their six fractionally filled equipoints must meet the requirement that the total charge of the sorbed sulfur species sum to zero. This is necessary because the structure shows that no oxidation nor reduction of the Cd^{2+} ions nor of the zeolite framework has occurred, nor would it have been expected.

The 12 sulfur atoms at S(2) each have only one nearest neighbor, a Cd^{2+} ion at Cd(2). From the Cd(2)−S(2) bond distance (2.32(8) Å, compare with the 2.525 Å distance in solid CdS[51]), S(2) appears to be occupied by sulfide ions. With 12 S^{2-} ions per unit cell, the remaining sulfur species must, in total, have a 24+ charge.

It is possible to place one S(1) atom in each sodalite cavity, where it could coordinate at a reasonable distance, 2.588(10) Å, to a Cd^{2+} ion at Cd(5) (at site I′). Circumstantially, the occupancies at S(1) and Cd(5) and the number of sodalite units per unit cell (all eight) support this, as does the large deviation of Cd(5) from its coordination plane (see Table 4 and compare to the deviation of Cd(2)). However, this would increase the number of sulfide ions per unit cell to 20, requiring the remaining 32 sulfur atoms to have a 40+ charge. Such cationic sulfur atoms should approach sulfur anions or oxygen anions of the zeolite framework closely, but only 24 do. An acceptable solution consistent with the long S(3)−S(4) and S(5)−S(6) bond lengths and obeying Lewis's octet rule is not possible.

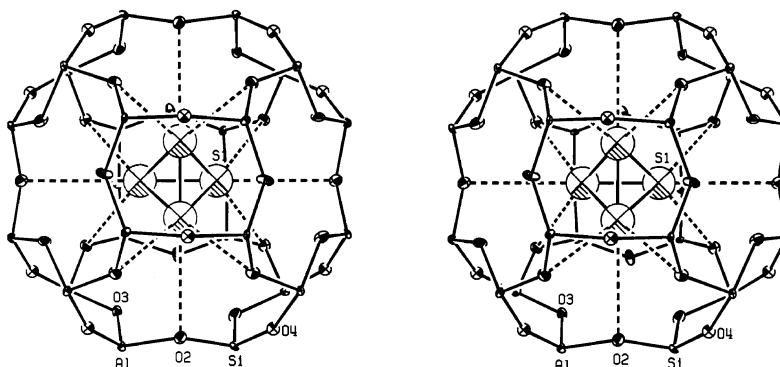The S(1)−S(1) distance in the sodalite unit, 2.17(2) Å, indicates that a bond would be present if two atoms at S(1)

Figure 3. Stereoview of a sodalite cavity with a tetrahedral sulfur cation, S_4^{4+}. Each sulfur atom is near three framework oxygens. Altogether, each S_4^{4+} cluster has 12 such S···O interactions. Ellipsoids of 20% probability are used.
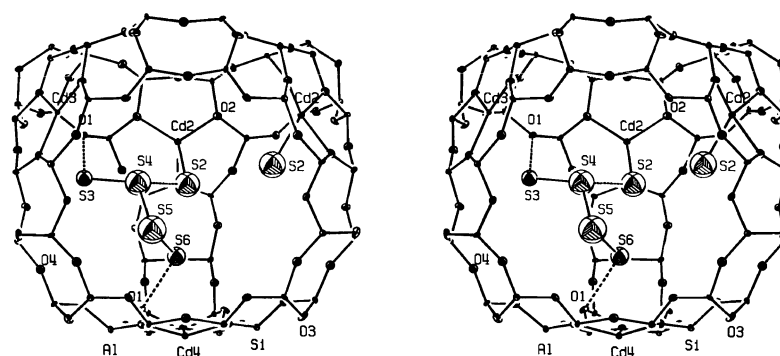

Figure 4. Stereoview of a supercage in $Cd_{46}-X\cdot52S$. Two Cd^{2+} ions at Cd(2) (site II), one at Cd(3) (site II), one at Cd(4) (site II'), two sulfurs at S(2), and one zigzag sulfur cluster, n-S_4^{2+}, are shown. Each Cd^{2+} ion at Cd(2) coordinates to three framework oxygens at O(2) and to a sulfide ion at S(2). Each terminal sulfur of each n-S_4^{2+} cluster interacts both ionically and covalently with an O(1) framework oxygen. The torsion angle of this n-S_4^{2+} cluster is $114(8)^0$. Ellipsoids of 20% probability are used.

TABLE 5: Comparison of Experimental and Calculated Bond Lengths (Å)

	exp	DFT calc[a]
P_4	2.21^b	2.216
S_4^{4+}	2.17(2)	2.206

[a] Quantum mechanical (DFT) calculations were done by Prof. John Head of the University of Hawaii using a 6-31G* basis set and a B3LYP hybrid functional. [b] The P_4 (tetrahedral) bond length was measured in the gas phase (refs 54,57,58).

were to be in the same sodalite unit. Three bonds would occur if three atoms are in the same sodalite cavity, and six bonds along the edges of a tetrahedron must be present if four atoms at S(1) occupy the same sodalite unit. The last has the lowest energy per atom (six bonds for four atoms), so possible S_2 and S_3 clusters should aggregate to form S_4. S_4 has the full symmetry of its site: atoms in S_2 and S_3 would not be expected to lie on 3-fold axes. The tetrahedral S_4 cluster seems most reasonable.

To obey G. N. Lewis's octet rule, this tetrasulfur cluster must be S_4^{4+}. Valence expansion to accept additional electrons around sulfur as in SF_6^{52-54} is not indicated because of the absence of strongly electronegative, covalently bound ligands (like F). In very good agreement with the 2.17(2) Å bond distance observed, a DFT calculation[55] (density functional theory) using a 6-31G* basis set and a B3LYP hybrid functional predicted an S–S distance of 2.206 Å for S_4^{4+} (see Table 5). Also, a frequency check verifies that this tetrahedral structure corresponds to a true minimum.[55] The S_4^{4+} cation is isoelectronic and isostructural with P_4^{54} and Si_4^{4-},[56] both of which are well-established tetrahedral species. As a check of the calculational method, 2.22 Å was calculated for the P–P bond length in P_4; the experi-

mental distance is 2.21 Å (see Table 5).[54,57,58] S_4^{4+} is stabilized by 3.380(9) Å contacts with twelve O(2) framework anions (see Figure 3). Of the eight sodalite cavities per unit cell, two are centered by a S_4^{4+} cation.

It is common for the sodalite cavities of zeolites A, X, and Y to host and stabilize cations with tetrahedral symmetry. These are often cations previously unknown to chemistry. Examples are Na_4^{3+},[20] K_4^{3+},[21] Na_5^{4+},[20,22] In_5^{7+},[23] and $Ni_4AlO_4^{3+}$.[59] Zn_7-$HAlO_4^{10+}$[60] is similarly hosted by a sodalite cavity, but it has lower symmetry. Larger cations that fill and extend out of sodalite cavities are Cs_4^{3+},[16,24,25] $Pb_7O(OH)_3^{9+}$,[61] $(Pb^{2+}, Pb^{4+})_4$-$Pb_4^{2+}O_4^{ca. 12+}$,[62,63] and the tetrahedral cation $(Cd^{2+}Zn)_8^{16+}$.[26]

Other units of zeolite structure can host cations also. The D6R often hosts monatomic cations, e.g. Cd(1) in this work (Figure 2), and the linear cation $HOPdOPdOH^{4+}$ (possibly $OPdOPdO^{4+}$) was found to fill and extend out of a D6R.[19] The tetrahedral $(Tl^+)_4Zn_{12}Tl_4$ cation[27] was found centered in a supercage. Even a 12-ring was found to host a linear Na_3^{2+} cation.[28,29]

The distances between sulfurs at S(3), S(4), S(5), and S(6) in the supercage indicate that they are bonded together (see Table 3). This zigzag n-S_4 cluster approaches three anions closely (S(3)–O(1) = 2.58(8) Å, S(6)–O(1) = 3.00(9) Å, and S(4)–S(2) = 2.73(14) Å), indicating that this cluster is also a cation. To obey Lewis's rules, with bond lengths indicating no multiple bond character (because they are quite long), it should be n-S_4^{2+}. n-S_4^{2+} is electron deficient and utilizes two electron pairs from two O(1) oxygens to complete the octet about each terminal sulfur atom to give $:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{O}}:$. The interaction between each n-S_4^{2+} cluster and a S(2) sulfide ion appears to be predominantly ionic.

This assignment of local structure and charge leads nicely to a net charge of zero for the sorbed sulfur atoms.

In the ideal zeolite composition $Cd_{48}Si_{96}Al_{96}O_{384}$, one may reasonably expect that the occupancies at Cd(3) and Cd(4) would both be increased by one Cd^{2+} ion per unit cell with no change in occupancy at the sulfur positions (see Table 2).

Ordering. The 3:1 ratio of D6Rs with a Cd^{2+} ion at site I and D6Rs with two Cd^{2+} ions at site I' (12:4 per unit cell) is indicative of long-range order with only one of the four 3-fold axes that intersect at the center of each sodalite cavity (and each supercage) surviving the sorption of sulfur. The same 3:1 ratio (6:2 per unit cell) is seen in this structure for sodalite units without S_4^{4+} cations and those with them. Such provocative ratios are often seen in the structures of complexes of zeolites A and X. Supporting this view are the 12 CdS molecules at Cd(2)−S(2).

Conclusions. Twelve sulfide ions at S(2) in the supercage each coordinate to a Cd^{2+} ion, Cd(2), at site II (Cd(2)−S(2) = 2.32(8) Å). This distance is appropriately less than that in solid CdS (2.525 Å),[51] because S(2) is one-coordinate. These Cd(2)−S(2) pairs may be viewed as individual neutral CdS molecules. Only eight of these 12 sulfide ions form a bond (mostly ionic) to a S(4) atom of an n-S_4^{2+} cation; the remaining four do not (see Figure 4). Repeated DFT calculations on the S(2) to S(6) sulfur system failed to yield a stable, neutral, largely covalent S_5 cluster.[55]

The net reaction within the zeolite upon the sorption of sulfur is

$$52\ S \rightarrow 12\ S^{2-} + 2\ S_4^{4+} + 8\ n\text{-}S_4^{2+}$$
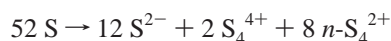
This constitutes the electronic disproportionation of an element upon sorption into a zeolite. The primary driving forces for this reaction are the need for the 3-coordinate Cd^{2+} ions to increase their coordination numbers and the strength of the resulting CdS bond. The ability of the anionic zeolite to provide a hospitable environment for the S_4^{4+} and n-S_4^{2+} cations is also important.

When a zeolite causes a sorbate to disproportionate to form cations and anions, it is behaving as a solid electrolyte.[64] The classical demonstration of this was the sorption of NO (ESR active) onto zeolite Y to give, among other products, NO^+ and NO^-.[65]

This result involving sulfur suggests that other elements may be found to disproportionate electronically upon sorption into zeolites. In particular, it suggests a new methodology for the synthesis of additional polyatomic cations of the chalcogens (S, Se, and Te). More recent results show that iodine also disproportionates fully upon sorption in Cd_{46}−X to give cations and anions. In addition, other cations, such as Ca^{2+}, may sometimes be more effective by being able to make stronger M^{2+}−anion bonds.

Summary

Two new polyatomic cations of sulfur, tetrahedral S_4^{4+} and zigzag n-S_4^{2+}, have been synthesized within the cavities of Cd_{46}−X. All of the sulfur sorbed by the zeolite has disproportionated upon sorption. Each unit cell contains two tetrahedral S_4^{4+} clusters, eight zigzag n-S_4^{2+} clusters (one per supercage), and 12 sulfide ions. Quantum mechanical calculations affirm the S_4^{4+} structure. n-S_4^{2+} is an electron-deficient cation that forms two polar-covalent bonds with zeolite framework oxygens.

Supporting Information Available: Table of calculated and observed structure factors with esds (5 pages). These F-tables are available free of charge via the Internet at http://pubs.acs.org.

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