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The Crystal Structure of a Sulfur Sorption Complex of the Dehydrated Partially Co²⁺-Exchanged Zeolite A

Young Hoon Yeom, Seong Hwan Song[†], and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea
[†]Department of Chemical Engineering, Dongseo University, Pusan 616-010, Korea
Received May 24, 1995

The crystal structure of a sulfur sorption complex of the dehydrated partially Co²⁺ exchanged zeolite A ($a = 12.058(2)$ Å) has been determined by single-crystal X-ray techniques. The crystal structure was solved and refined in cubic space group $Pm3m$ at 21(1) °C. Ion Exchange with aqueous 0.05 M Co(NO₃)₂ was done by the static method. The crystal of Na₄Co₄-A was dehydrated at 380 °C and 2×10^{-6} Torr for 2 days, followed by exposure to about 100 Torr of sulfur at 330 °C for 72 h. Full matrix least-squares refinement converged to $R_1 = 0.084$ and $R_w = 0.074$ with 102 reflections for which $I > 3\sigma(I)$. Crystallographic analysis shows that 2.8 Co²⁺ ions and 4 Na⁺ ions per unit cell occupy 6-ring sites on the threefold axes. 1.2 Co²⁺ ions occupy the 8-ring sites on fourfold axes. 2.8 Co²⁺ ions at Co(1) are recessed 0.66 Å into the large cavity and 4 Na⁺ ion at Na(1) are recessed 0.77 Å into the sodalite cavity from the (111) plane of O(3)'s. Approximately 16 sulfur atoms were sorbed per unit cell. Two S₈ rings, each in a butterfly form, are found in the large cavity. The bond length between S and its adjacent S is 2.27(3) Å. The distance between 6-ring Co²⁺ ion and its adjacent sulfur is 2.53 (2) Å and that between 8-ring Co²⁺ ions and its adjacent sulfur is 2.72(9) Å. The angles of S-S'-S and S'-S-S' in octasulfur rings are 119.0(2)° and 113.0(2)°, respectively.

Introduction

The crystal structure of a sulfur sorption complex of Na₁₂-A[1] has been reported. Reversible isotherms for sulfur sorption onto Ca²⁺-exchanged zeolite A and the sodium form of zeolite X have been determined previously.[2] About 16 sulfur atoms per unit cell were sorbed in the crystal of dehydrated Na₁₂-A. The heats of sorption (−25 and −31 Kcal /mol, respectively)[2] also indicate that these complexes are relatively stable. Such systems afford an unique opportunity for investigating the configurations of physical sorption complexes crystallographically.

Many different forms of sulfur allotropes occur in the solid, liquid, and gas phase such as S_n ($1 < n < 12$, $n = 18$, 20 and ∞).[3] During last 30 years about 24 allotropes containing cyclic S₈ have been described.[3] The S₈ is the most stable configuration at STP. The stability is probably due to cross-ring resonance.[4] The other properties of S₈ are well reviewed.[5] Furthermore, Spitzer,[6] Ward,[7] Ozin,[8] Anderson,[9] and Gautier[10] have studied S₈ in solution and in single crystals.

Zeolites provide an attractive host for the encapsulation of semiconductor, organic and inorganic complexes. The present work was initiated to investigate what kind of sulfur allotropes can be formed inside the limited dimensions of zeolite cavities. If a cyclic S₈ is formed, it will be interesting to study the locations and the bonding characteristics of the sorbed S₈ molecules and the interaction between sulfur and cations in the zeolite cavities.

Experimental Section

Crystals of zeolite A were prepared by a modification of Charnell's method,[11] including a second crystallization using seed crystals from the first synthesis. Ion exchange with aqueous solution of 0.1 M Co(NO₃)₂ was done by the static method.[12] This yielded material whose approximate stoichiometry was Na₄Co₄Al₁₂Si₁₂O₄₈·xH₂O per unit cell, subsequently to be referred to as Na₄Co₄-A, exclusive of water molecules.[13] One of the largest single crystals from this experiment, about 0.08 mm along an edge, was selected for X-ray diffraction study. The crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by gradual increasing its temperature (*ca.* 25 °C/h to 360 °C at the constant pressure of 2×10^{-6} Torr). Finally, the system was maintained at this state for 48 h. The crystal became deep blue after dehydration. Similarly, about 2 g of finely divided and sublimed sulfur powder was dehydrated at 100 °C and 10^{-6} Torr for 96 h. The crystal was contacted

Table 1. [a]Positional, Thermal, and Occupancy Parameters of the Sulfur Sorption Complex of Na_4Co_4-A

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[c]
(Si, Al)	24(k)	0	1836(8)	3658(6)	32(5)	23(5)	32(5)	0	0	10(10)	24.0[d]
O(1)	12(h)	0	1980(30)	5000	80(30)	170(40)	−10(20)	0	0	0	12.0
O(2)	12(i)	0	2970(10)	2970(10)	60(20)	20(10)	20(10)	0	0	30(40)	12.0
O(3)	24(m)	1130(10)	1130(10)	3290(10)	100(10)	100(10)	70(20)	140(40)	−10(40)	−10(40)	24.0
Co(1)	8(g)	2170(10)	2170(10)	2170(10)	39(70)	39(70)	39(70)	−10(20)	−10(20)	−10(20)	2.8
Na(1)	8(g)	1470(20)	1470(20)	1470(20)	90(20)	90(20)	90(20)	150(50)	150(50)	150(50)	4.0
Co(2)	24(m)	470(80)	4600(50)	4600(50)	9(5)[e]						1.2
S(1)	8(g)	3380(20)	3380(20)	3380(20)	34(3)						8.0
S(2)	24(l)	2450(30)	3570(40)	5000	17(2)						8.0

[a]Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b]The anisotropic temperature factor=exp$[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell. [d]Occupancy for (Si)=12; occupancy for (Al)=12. [e]Isotropic thermal parameter in units of $Å^2$.

with sulfur under vacuum and maintained at 250 ℃ for 24 h, then at 330 ℃ for 72 h, and finally at 250 ℃ for 24 h. After the crystal was treated with sulfur, its color became deep-black.

Preliminary crystallographic experiment and subsequent data collection were performed with an automated four-circle Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and a Micro-Vax3100 computer. Molybdenum radiation was used for all experiments ($K_{\alpha 1}$, $\lambda=0.70930$ Å; $K_{\alpha 2}$, $\lambda=0.71359$ Å). The unit cell constant determined by least-squares refinement of 25 intense reflections for which $19° \leq 2\theta \leq 24°$ is 12.058(2) Å. The space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.[14,15] Reflections from two intensity-equivalent regions of reciprocal space (hkl, $0 \leq h \leq k \leq l$ and lhk, $0 \leq l \leq h \leq k$) were examined. The intensities were measured using ω-2θ scan technique over a scan width of (0.08+ 0.344 tanθ) in ω. Most reflections were observed at slow scan speeds, ranging between 0.249 and 0.305 in ω min^{-1}. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor the stability of crystal and X-ray source. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each regions of reciprocal space, the intensities of all lattice points for which $2\theta \leq 70°$ were recorded. The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the computer program, PAINT and WEIGHT.[16] An adsorption correction ($\mu R=0.08$) was judged to be negligible and was not applied.[17] The 102 reflections for which the net count exceeded three times its standard deviation were used in subsequent structure determinations.

Structure Determination

Full-matrix least-squares refinement was initiated using framework atoms [(Si, Al), O(1), O(2), and O(3)], Co^{2+} and Na^+ found for the Na_4Co_4-A treated with Br_2[13] (see Table 1). Anisotropic refinement of the framework atoms and isotropic refinement of cations converged to an $R_1=[\Sigma|F_o-|F_c||]/\Sigma|F_o|)=0.286$ and $R_w=[\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2]^{1/2}=0.409$. The Co^{2+} ions at Co(1) and Na$^+$ ions at Na(1) are associated with 6-rings and lie on two nonequivalent 3-fold axes. The occupancy numbers of Co^{2+} ions and Na$^+$ ions on the threefold axes were refined to Co=2.76(8) and Na=4.43(25), respectively (see Table 1). From a difference Fourier synthesis, sulfur positions, S(1) and S(2), were located. Similarly to sulfur sorption complex of Na_{12}-A, isotropic thermal parameters of S(1) and S(2) were fixed both at 25, and the occupancy numbers of S(1) and S(2) were refined to 7.4(3) and 8.3(4), respectively. These numbers were fixed both at 8.0, the maximum occupancy number of S(1), because the distance between S(1) and S(2) indicated that they were bonded to each other. The full-matrix least-squares refinement converged to $R_1=0.129$ and $R_w=0.132$.

A subsequent Fourier function revealed a peak at (0.046, 0.45, 0.45) with a height of 2.30(26) eÅ^{-3}. This peak was assigned to Co^{2+} ion for the following reasons: (1) when this peak was assigned to Na$^+$ ion, the thermal parameter of this peak was nonpositive definite and its occupancy number was 4.2(3). Accordingly the sum of the total cation charge per unit cell became *ca.* 15.0, which is greater than +12, the cationic charge of zeolite A; (2) when this peak was assigned to Co^{2+} ion, the thermal parameter of this peak was chemically reasonable and its occupancy number was 1.41 (12). Therefore the sum of the total cationic charge per unit cell was about +12.

The principal cations, Co^{2+}(1) and Na$^+$(1), were allowed to refine anisotropically (see Table 2). The final refinement, including these positions converged to $R_1=0.084$ and $R_w=0.074$.

The largest peak on the final difference Fourier functions was featureless except an insignificant one at the origin with a height 1.92(36) eÅ^{-3}.

In order to increase the size of the data set, 127 and 171 reflections for which $I>2\sigma(I)$ and $I>\sigma(I)$, respectively, were used in the least-squares refinement. Least-squares refinements converged to $R_1=0.097$ and $R_w=0.074$ for which for

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

(Si,Al)-O(1)	1.62(1)	O(2)-(Si,Al)-O(3)	108.8(9)
(Si,Al)-O(2)	1.60(2)	O(3)-(Si,Al)-O(3)	109.1(7)
(Si,Al)-O(3)	1.67(1)	(Si,Al)-O(1)-(Si,Al)	168.(2)
Co(1)-O(3)	2.23(1)	(Si,Al)-O(2)-(Si,Al)	152.1(9)
Co(2)-O(2)	2.83(6)	(Si,Al)-O(3)-(Si,Al)	140.(1)
Na(1)-O(3)	2.36(3)	S(2)-S(1)-Co(1)	100.(1)
Co(1)-S(1)	2.53(2)	S(1)-Co(1)-O(3)	107.4(4)
Co(2)-S(2)	2.72(9)	S(1)-S(2)-S(1)	119.(2)
S(1)-S(2)	2.27(3)	S(2)-S(1)-S(2)	113.(2)
O(1)-(Si,Al)-O(2)	115.(2)	O(3)-Co(1)-O(3)	111.4(4)
O(1)-(Si,Al)-O(3)	108.8(9)	O(3)-Na(1)-O(3)	108.9(9)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.
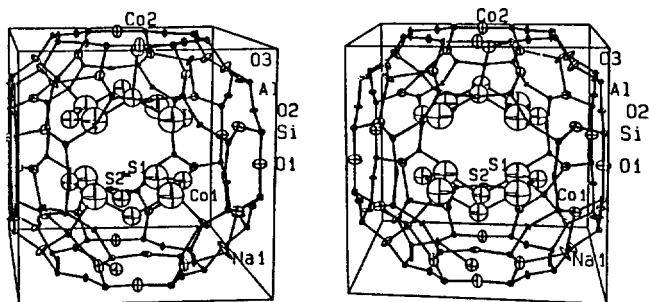
Figure 1. The unit cell of the sulfur sorption complex of the dehydrated Na₄₀Co₄₀-A is shown in stereoview. Three Co²⁺ ions at Co(1), one Co²⁺ ion at Co(2), four Na⁺ ions at Na(1), and two S₈ clusters, each in butterfly form, are found in large cavity. About 80% of the unit cells may have this arrangement. The remaining 20% of unit cells may have two Co²⁺ ions at Co(1), two Co²⁺ ions at Co(2), four Na⁺ ions at Na(1), and two S₈ clusters. Ellipsoids of 20% probability are used.

$I>2\sigma(I)$ and $R_1=0.142$ and $R_w=0.080$ for which $I>\sigma(I)$, respectively. No new features appeared on Fourier function, and no significant structural changes were observed upon least-squares refinement.

Atomic scattering factors for (Si, Al)$^{1.75+}$, Na⁺, O⁻, and S⁰ were used.[18] In the last cycle of least-squares refinement, all shifts were less than 2% of their corresponding esd's. The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2. A stereoview of the structure is shown in Figure 1.

Discussion

It has been reported that sulfur has a tendency to form S₈ rings not only in the element, but also in compounds.[5] Approximately 16 sulfur atoms are sorbed per unit cell of Na₄Co₄-A. These sulfur atoms form two equivalent S₈ rings in the butterfly configuration which lie parallel to each other in the large cavity of the zeolite A. The crystal structure of Na₁₂-A·2S₈ was solved and discussed by Seff.[1] In this structure, two equivalent S₈ rings in the crown configuration lie parallel to each other in the large cavity of the zeolite A.

Table 3. Deviations of Atoms (Å) from (111) Plane at O(3)

O(2)	0.28(1)	Na(1)	−0.77(2)
Co(1)	0.66(1)	S(1)	3.19(1)

A negative deviation indicates that the atom lies on the same side of the plane as the origin.

Cyclo-S₈ crystallizes mainly in orthorhombic sulfur (α-S₈) and two monoclinic forms (β-S₈ and γ-S₈).[5,19] The orthorhombic sulfur (α-S₈) is stable up to 96 ℃; liquid sulfur above this temperature is usually cooled to monoclinic β sulfur (β-S₈). Orthorhombic sulfur (α-S₈) is thermodynamically the most stable form and occurs in large yellow crystals. Orthorhombic sulfur (α-S₈) is "crankshaft" form (S-S bond lengths ≅2.05 Å, S-S-S bond angles=107.3-109.0° and S-S-S-S torsion angles ≅98.5°).[19] The first monoclinic sulfur (β-S₈) has the following configuration: S-S bond lengths=2.05-2.06 Å, S-S-S bond angles=105.8-108.3° and S-S-S-S torsion angles=96.4-101.3°. The second monoclinic form, Muthman's γ-S₈, consists of crown shaped S₈ molecule (S-S bond lengths=2.02-2.06 Å, S-S-S bond angles=106.8-108.5° and S-S-S-S torsion angles=97.9°-100.1°). There are also another forms of the S₈ allotropes such as regular puckered form, tub, chair, cradle, and butterfly forms.[20]

In the structure of Na₄Co₄-A·2S₈, two nonequivalent atoms, S(1) and S(2), alternate to form two S₈ rings (see Figure 1). Four sulfur atoms at S(1) in single S₈ ring occupy 4 identical sites of the 6-oxygen rings on threefold axes. These sulfur atoms lie relatively far inside the large cavity, 3.19(1) Å from the (111) plane at O(3)'s and interact with the cations of Co²⁺ ions at the Co(1) that are coordinated to 6-ring oxygens on three-fold axes of zeolite A structure (see Table 1 and Figure 1). On the other hand, the sites of four sulfur atoms at S(2) in single S₈ ring are located on 24(l) positions. Two sulfur atoms at S(2) are located at the beneath of the plane of four sulfur atoms at S(1) and the remaining two sulfur atoms at S(2) are located at the part on the plane of the four sulfur atoms at S(1) (see Figure 1).

The molecular symmetry of the octasulfur ring in Na₄Co₄-A·S₈ is $mm2$ (C_{2v}), substantially more symmetrical than $2(C_2)$ as is found[21,22] in orthorhombic sulfur, but less symmetric than the ideal symmetry found[23] in the vapor phase, $\bar{8}2m$ (D_{4d}). The closest approach distance between the two S₈ rings is 3.45 Å, slightly shorter than the sum (3.70 Å) of the van der Waals radii for sulfur.

Each sulfur atom in the sulfur rings makes two important approaches to a nonsulfur atom (see Figure 1 and Table 2). The S(1)-Co(1) distance, 2.53(2) Å, is about same as the sum of the corresponding van der Waals radius of sulfur atom and ionic radius of Co²⁺ ion, 1.85+0.74=2.59 Å,[24] and the S(2)-Co(2) distance, 2.72(9) Å, is slightly longer than the sum of the corresponding van der Waals radius and ionic radius.

Four Na⁺ ions at Na(1) lie relatively far inside the sodalite cavity, 0.77(2) Å from the (111) plane at O(3)'s (see Table 3). These Na⁺ ions are trigonally coordinated to their respective sets of three O(3) framework oxygens at 2.36(3) Å. For comparison, the sum of the conventional ionic radii of Na⁺ ion (0.97 Å) and O²⁻ (1.32 Å) is 2.29 Å.[25] About 2.8 Co²⁺ ions at Co(1) lie on the threefold axes of 6-oxygen rings

of the unit cell. Each Co^{2+} ion at Co(1) is bound to the 3 equivalent O(3) framework oxygens of its 6-ring at a distance of 2.23(1) Å. Each Co^{2+} ion at Co(1) recessed about 0.66 Å into large cavity from the plane of the three O(3) atoms (see Table 3). This indicates that Co^{2+} ions move toward tetrahedral coordination (S(1)-Co(1)-O(3)=107.4(4)°).

About 1.2 Co^{2+} ions at Co(2) are associated with 8-ring oxygens (see Figure 1). The crystal structure of iodine sorption complex of partially cobalt(II)-exchanged zeolite A has been determined.[23] In this structure, all of the Co^{2+} ions lie at the 6-ring sites on 3-fold axes. It is unusual that bivalent and relatively small cations occupy the 8-ring sites in zeolite A structure. Comparing with the structure of dehydrated Na_4Co_4-A, about 1.2 Co^{2+} ions at Co(1) have moved into 8-ring sites from 6-oxygen ring sites on three fold-axes in zeolite A upon the sorption of sulfur. The distance between Co^{2+} ion at Co(2) and sulfur atoms at S(2) in S_8-ring is 2.72(9) Å. It is slightly longer than the sum of ionic radius of Co^{2+} and van der Waals radius of sulfur, 0.74+1.85 =2.59 Å. These Co^{2+} ions at Co(2) are weakly bound to two framework oxygens: Co(2)-O(1)=2.83(6) Å.

The large thermal motions of the octasulfur ring obscure the observations of significant structure differences between these results and the previous findings. The S(1)-S(2) bond length, 2.27(3) Å, is little longer than that found in monoclinic sulfur, 2.06 Å.[19] The S-S bond[26] distances differ upon substances and their bonds are flexible; the lengths vary from 1.8 to 3.0 Å and the torsion angles vary 0° to 180°.[27] In the crystal structure of Na_{12}-A·2S$_8$, the S(1)-S(2) bond length is 1.94(8) Å.[1] It is shorter than that found in ideal octasulfur ring. In this structure, the interatomic bond angles of S(1)-S(2)-S(1) and S(2)-S(1)-S(2) are 119.(2) and 113.(2)°, respectively. In the crystal structure of Na_{12}-A·2S$_8$, the interatomic bond angles of S(1)-S(2)-S(1) and S(2)-S(1)-S(2) are 128.(9)° and 119(8)°, respectively.[1] The S-S-S angles in Co_4 Na_4-A·16S, averaging 116°, are insignificantly greater than that found in monoclinic sulfur, 108.5.[19]

Acknowledgment. This work was supported by the Korean Science and Engineering Foundation (Grant No. 951-0303-013-2).

Supplementary Material Available. Tables of observed and calculated structure factors with esd's (2 pages). Ordering information is given on any current masthead page.

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