

# Crystal Structure of a Hydrogen Sulfide Sorption Complex of Dehydrated Partially Cobalt(II)-Exchanged Zeolite A

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The crystal structure of a hydrogen sulfide sorption complex of partially Co(II)-exchanged zeolite A,  $\text{Co}_4\text{Na}_4\text{-A}\cdot 11\text{H}_2\text{S}$  ( $a = 12.149(2)$  Å) has been determined by single-crystal X-ray diffraction techniques in the cubic space group  $Pm\bar{3}m$  at 21(1) °C. The crystal of  $\text{Co}_4\text{Na}_4\text{-A}$  (initially light pink) was dehydrated at 380 °C and  $2 \times 10^{-6}$  Torr for 2 days (deep blue), followed by exposure to ca. 700 Torr of hydrogen sulfide gas at room temperature (black). The structure was refined to the final error indices  $R_1 = 0.055$  and  $R_w = 0.051$  with 171 reflections for which  $I > 3\sigma(I)$ . Four Co(II) ions are found at 6-oxygen ring sites where each coordinates to three framework oxygens at 2.24(1) Å. Each Co(II) ion is recessed 0.65 Å into the large cavity from the (111) plane of the nearest framework oxygens and coordinates at 2.60(2) Å to one  $\text{H}_2\text{S}$  sulfur in the large cavity. Each of four  $\text{Na}^+$  ions lies between a 4-ring and an 8-ring in the large cavity, where it coordinates to a framework oxygen at 2.75 Å and to an  $\text{H}_2\text{S}$  sulfur in the large cavity at 2.87 Å. Each of three additional  $\text{H}_2\text{S}$  molecules is near the center of an 8-oxygen ring, where it coordinates to one or two  $\text{Na}^+$  ions and “hydrogen bonds” with 8-ring oxygens.

## Introduction

The Co(II) ions in dehydrated partially Co(II)-exchanged zeolite A,  $\text{Co}_4\text{Na}_4\text{-A}$ ,<sup>1</sup> are coordinatively unsaturated, three-coordinate planar. Consequently, an unusual chemistry takes place within the voids of the zeolitic framework. The small molecules  $\text{CO}$ ,<sup>1</sup> cyclopropane,<sup>2</sup>  $\text{C}_2\text{H}_4$ ,<sup>3</sup>  $\text{C}_2\text{H}_2$ ,<sup>4</sup>  $\text{NO}_2$ ,<sup>5</sup>  $\text{Cl}_2$ ,<sup>6</sup>  $\text{Br}_2$ ,<sup>7</sup> and  $\text{CS}_2$ <sup>8</sup> have been found to complex to these Co(II) ions in the zeolite, and an oxidative addition reaction takes place when  $\text{NO}^5$  reacts with dry  $\text{Co}_4\text{Na}_4\text{-A}$ .

The catalytic properties of transition-metal ion exchanged zeolites are well-known. In such zeolites, it is observed that a sorbate can greatly affect the coordination geometry of a transition-metal ion. Using the partially Co(II)- and the partially Ni(II)-exchanged forms of zeolite 4A, Klier observed the formation of three-, four-, and six-coordinate Ni(II) and Co(II) complexes by reflectance spectroscopy.<sup>9,10</sup> X-ray diffraction studies have confirmed the existence of three-coordinate Co(II)<sup>1</sup> and Mn(II)<sup>11</sup> species and have demonstrated the presence of five-coordinate Mn(II) in a partial hydrate.<sup>11</sup> Intrazeolitic transition-metal complexes were also characterized spectroscopically: Klier and Ralek<sup>9</sup> studied complexes of Co(II) and Ni(II) with  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and cyclopropane in zeolite A.

Other structures involving either Co(II) or sulfur or both have been determined in zeolite A. In the crystal structure of a dimethyl disulfide sorption complex of dehydrated partially Co(II)-exchanged zeolite A ( $\text{Co}_4\text{Na}_4\text{-A}$ ), homolytic cleavage of the S–S bond in dimethyl disulfide by cobalt(II) ions occurred: each  $\text{CH}_3\text{S}$  group complexes to a cobalt ion in a bent manner.<sup>12</sup> In the sulfur sorption complex of  $\text{Na}_{12}\text{-A}$ ,<sup>13</sup> two equivalent  $\text{S}_8$  rings in the crown configuration lie parallel to each other in the large cavity of the zeolite. Alternating sulfur atoms in each ring coordinate to  $\text{Na}^+$  ions; the remaining sulfurs interact more weakly with framework oxygens. In the structure

of a chlorine sorption complex of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ , each of four  $\text{Cl}_2$  molecules bridges between a Co(II) ion on a threefold axis and an 8-ring  $\text{Na}^+$  ion.<sup>6</sup> In the structure of a carbon disulfide complex of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ , each of four  $\text{CS}_2$  molecules bridges between a Co(II) ion and three 8-ring framework oxygens, and two of these  $\text{CS}_2$  molecules each associates further with an 8-ring  $\text{Na}^+$  ion.<sup>8</sup> The crystal structure of a bromine sorption complex of dehydrated partially  $\text{Co}_4\text{Na}_4\text{-A}$  has been determined.<sup>7</sup> In that structure, 3.5 tribromide ions are found per unit cell, indicating that Co(II) had been oxidized.

This work was undertaken to investigate the shifts in cation and framework positions upon the sorption of hydrogen sulfide, and to observe the cation–sorbate interactions in the complex.

## Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method.<sup>14</sup> Ion exchange with an aqueous solution of 0.1 M  $\text{Co}(\text{NO}_3)_2$  was done by the static (batch) method.<sup>1</sup> This yielded a material whose approximate stoichiometry was  $\text{Co}_4\text{Na}_4\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot x\text{H}_2\text{O}$  per unit cell, subsequently to be referred to as  $\text{Co}_4\text{Na}_4\text{-A}$ , exclusive of water molecules. One of the largest single crystals from this experiment, a light pink cube about 0.08 mm along on edge, was selected for X-ray diffraction study. It was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by gradually increasing its temperature (ca. 25 °C/h to 380 °C) at a constant pressure of  $2 \times 10^{-6}$  Torr. Finally the system was maintained at this state for 48 h. After the crystal, now deep blue, was cooled to room temperature, it was treated with ca. 700 Torr of  $\text{H}_2\text{S}$  gas at room temperature. After 80 min, the crystal, still in its  $\text{H}_2\text{S}$  atmosphere, was sealed in its capillary from the vacuum line by torch. Microscopic examination showed that it had become black.

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**TABLE 1: Positional, Thermal, and Occupancy Parameters<sup>a</sup>**

atom	Wyc. pos.	x	y	z	$\beta_{11}^b$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	occupancy <sup>c</sup>	
											varied	fixed
(Si,Al)	24(k)	0	1824(3)	3671(3)	27(2)	19(2)	14(2)	0	0	10(5)	24.0 <sup>d</sup>	
O(1)	12(h)	0	2080(10)	5000	140(20)	100(20)	50(10)	0	0	0	12.0	
O(2)	12(i)	0	2978(6)	2978(6)	60(10)	24(6)	24(6)	0	0	10(20)	12.0	
O(3)	24(m)	1134(5)	1134(5)	3305(7)	61(4)	61(4)	91(9)	100(10)	-60(10)	-60(10)	24.0	
Co	8(g)	2165(3)	2165(3)	2165(3)	38(2)	38(2)	38(2)	32(6)	32(6)	32(6)	3.8(1)	4.0
Na	24(l)	1680(30)	3600(40)	5000	120(40)	280(6)	30(20)	170(80)	0	0	4.1(3)	4.0
S(1)	24(m)	3220(10)	3220(10)	3700(20)	250(20)	250(20)	960(80)	-190(50)	-320(40)	-320(40)	7.5(2)	8.0
S(2)	6(f)	690(30)	5000	5000	360(60)	70(10)	70(10)	0	0	0	3.1(1)	3.0

<sup>a</sup> 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. <sup>b</sup> The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>c</sup> Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup> Occupancy for (Si) = 12; occupancy for (Al) = 12.

### X-ray Data Collection

The cubic space group  $Pm\bar{3}m$  (no systematic absences) was used throughout this work for reasons discussed previously.<sup>15,16</sup> Briefly, data are not available to allow a full and reliable refinement of a structure of this complexity in the less approximate space group  $Fm\bar{3}c$ . Preliminary crystallographic experiments and subsequent data collection were performed with an automated four-circle Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator. Mo K $\alpha$  radiation was used for all experiments (K $\alpha_1$ ,  $\lambda = 0.70930$  Å; K $\alpha_2$ ,  $\lambda = 0.71359$  Å). The cubic unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which  $19^\circ < 2\theta < 24^\circ$ , is 12.149(2) Å. The  $\omega$ - $2\theta$  scan technique was used. The data were collected at variable scan speeds. Most reflections were observed at slow speeds from 0.23 and to 0.32 deg/min in  $\omega$ . 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 for which  $2\theta \leq 70^\circ$  were examined by counter methods.

The raw data were corrected for Lorentz and polarization effects including beam monochromatization, and the resultant estimated standard deviations were assigned to each reflection by the computer programs BEGIN and GENESIS.<sup>17</sup> An absorption correction ( $\mu R = 0.056$ ) was judged to be negligible and was not applied.<sup>18</sup> Of the 870 pairs of reflections examined, the 171 reflections for which the net count exceeded 3 times its standard deviation were used in subsequent structure determination.

### Structure Determination

Least-squares refinement was initiated by using the Co(II) cation coordinates and framework positions ((Si,Al), O(1), O(2), and O(3)) of Co<sub>4</sub>Na<sub>4</sub>A.<sup>1</sup> Anisotropic refinement quickly converged to  $R_1 = (\sum |F_o - |F_c||) / \sum F_o = 0.17$  and  $R_w = [\sum w(F_o - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.23$ . The subsequent difference Fourier function revealed one large peak at (0.062, 0.5, 0.5) with height 4.8(1) e Å<sup>-3</sup>. Least-squares refinement including this peak as sulfur atoms converged to  $R_1 = 0.15$  and  $R_w = 0.21$ . This peak, at S(2), was very stable in least-squares refinement. If it is attributed to Na<sup>+</sup>, the occupancy number exceeds 3, which is not possible at this position; impossibly short (1.68 Å) Na<sup>+</sup>-Na<sup>+</sup> interactions would exist. Also the distance between this peak and the nearest framework oxygen, 3.6(1) Å, is too long for a Na<sup>+</sup> to framework-oxygen approach. Accordingly, this peak cannot be a Na<sup>+</sup> ion. The small thermal parameter of the sulfur atoms at S(2) suggest that these atoms might all be equivalent. Full-matrix least-squares refinement converged to the occupancies of Co = 3.78(5) and S(2) = 3.05(9).

**TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup>**

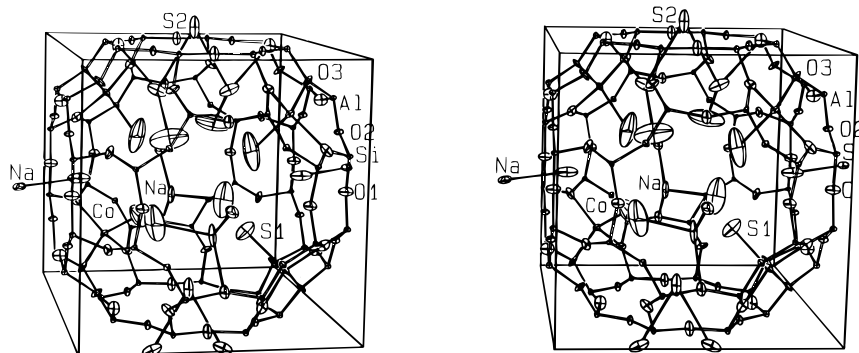
(Si,Al)-O(1)	1.64(1)	O(1)-(Si,Al)-O(2)	110.1(6)
(Si,Al)-O(2)	1.64(1)	O(1)-(Si,Al)-O(3)	110.9(4)
(Si,Al)-O(3)	1.67(1)	O(2)-(Si,Al)-O(3)	107.0(2)
Co-O(3)	2.24(1)	O(3)-(Si,Al)-O(3)	110.9(3)
Co-S(1)	2.60(2)	(Si,Al)-O(1)-(Si,Al)	158(1)
Na-O(1)	2.75(5)	(Si,Al)-O(2)-(Si,Al)	152.0(4)
Na-O(2)	3.28(3)	(Si,Al)-O(3)-(Si,Al)	139.0(5)
Na-S(1)	2.87(3)	O(3)-Co-O(3)	112.1(2)
Na-S(2)	3.31(4)	Na-S(2)-Na	61(1)
Na-Na	3.40(7)	S(1)-Na-S(2)	123(1)
S(1)-O(3)	3.61(1)		
S(2)-O(1)	3.64(2)		
S(2)-O(2)	3.57(1)		
S(1)-S(1)	3.79(4)/4.41(2)		
S(1)-S(2)	4.08(3)/4.77(4)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value. Small but systematic errors are present in these values because the space group used is only approximate.

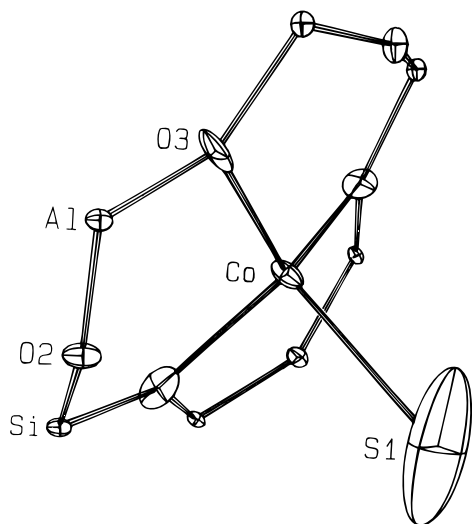
A subsequent difference Fourier synthesis revealed two peaks at (0.300, 0.300, 0.397) and (0.166, 0.352, 0.5), with peak heights 1.8(1) and 1.5(1) e Å<sup>-3</sup>, respectively; these were stable in least-squares refinement. The latter peak was especially stable and refined to a small thermal parameter by least-squares. Also the distance of this peak from the nearest framework oxygen, O(1), was 2.75(5) Å, too short for this peak to be sulfur, so it must represent Na<sup>+</sup> ions. Anisotropic refinement including these atoms as S(1) and Na, respectively, rapidly converged to  $R_1 = 0.057$  and  $R_w = 0.056$  (see Table 1).

The occupancy numbers at S(1) and Na refined to ca. 7.5(2) and 4.1(3), respectively. The occupancy at S(1) was fixed at 8.0, its maximum value; otherwise impossibly short (0.82 Å) S-S interactions would exist. Four of these eight H<sub>2</sub>S molecules would coordinate to Co(II) ions and the remaining four would be associated with framework oxygens and Na<sup>+</sup> ions. Hydrogen atoms were not found. The final difference Fourier function was featureless. Finally, least-squares refinement with the occupancies fixed at the values shown in Table 1 converged to  $R_1 = 0.060$  and  $R_w = 0.054$ .

All crystallographic calculations were done using MolEN<sup>17</sup> supplied by Enraf-Nonius. The full-matrix least-squares program used minimized  $\sum w(F_o - |F_c|)^2$ ; the weight of an observation was the reciprocal square of  $\sigma(F)$ , its standard deviation. Atomic scattering factors<sup>19,20</sup> for S<sup>0</sup> (valence), O<sup>-</sup>, Co<sup>2+</sup>, Na<sup>+</sup>, and (Si,Al)<sup>1.75+</sup> were used. The function describing (Si,Al)<sup>1.75+</sup> is the mean of the Si<sup>0</sup>, Si<sup>4+</sup>, Al<sup>0</sup>, and Al<sup>3+</sup> functions. All scattering factors were modified to account for anomalous dispersion.<sup>21,22</sup> The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.



**Figure 1.** One unit cell of the hydrogen sulfide complex of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$  is shown in stereoview. Four  $\text{Co}^{2+}$  ions at Co and four  $\text{Na}^+$  ions at Na can be seen. Eight hydrogen sulfide molecules at S(1) and three hydrogen sulfide molecules at S(2) are shown. The Si and Al atoms are labeled to indicate that they alternate, although only their average position was determined. Ellipsoids of 20% probability are used.



**Figure 2.** Coordination environment of the  $\text{Co}^{2+}$  ion. Each of the four  $\text{Co}^{2+}$  ions per unit cell coordinates to three framework oxygens and to one  $\text{H}_2\text{S}$  sulfur in the large cavity. The top left rear 6-ring in Figure 1 is shown. Ellipsoids of 20% probability are used.

**TABLE 3: Deviations of Atoms ( $\text{\AA}$ ) from the (111) Plane at O(3)<sup>a</sup>**

O(2)	0.26(1)
Co	0.65(1)
S(1)	3.20(2)

<sup>a</sup> A positive deviation indicates that the atom extends into the large cavity.

## Discussion

In the hydrogen sulfide complex of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ , four  $\text{Co}(\text{II})$  ions at Co lie near 6-ring centers on threefold axes of the unit cell (see Figures 1 and 2). Each is recessed 0.65(1)  $\text{\AA}$  into the large cavity from the (111) plane at O(3) (see Table 3). Compared to dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ ,<sup>10</sup> each of these  $\text{Co}(\text{II})$  ions lies 0.31  $\text{\AA}$  deeper into the large cavity to coordinate more tetrahedrally to a  $\text{H}_2\text{S}$  molecule (see Table 4). As a consequence of the movement of the  $\text{Co}(\text{II})$  ion into the large cavity upon complexation, the  $\text{Co}(\text{II})\text{-O}(3)$  bonds lengthen somewhat from 2.08(2)  $\text{\AA}$  in the dehydrated structure to 2.24(1)  $\text{\AA}$  (see Table 4). These bonds similarly lengthened, to 2.204(9) and 2.249(5)  $\text{\AA}$ , respectively, in previous studies of  $\text{Co}_4\text{Na}_4\text{-A}$  treated with  $\text{CS}_2$ <sup>8</sup> and  $(\text{CH}_3)_2\text{S}_2$ <sup>12</sup> (dimethyl disulfide). (Although the effect is clear, these bond distances should not be taken literally because only some sort of average O(3) position has been determined: only half of the O(3) oxygens bind to  $\text{Co}^{2+}$  ions.)

The four  $\text{Na}^+$  ions per unit cell are found at unusual sites in the large cavity, each between a 4-ring and an 8-ring where

each coordinates to one O(1) (see Figure 1). In order to accommodate the molecules of  $\text{H}_2\text{S}$  at S(1) and S(2) more favorably, each  $\text{Na}^+$  ion has relocated from a more conventional 6-ring site in dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$  to a large-cavity position (see Figures 3 and 4). Each  $\text{Na}^+$  ion is 2.75(5)  $\text{\AA}$  from O(1) and 3.28(3)  $\text{\AA}$  from two O(2)'s (see interatomic distances in Table 2). These distances are substantially longer than the sum of the ionic radii of  $\text{Na}^+$  and  $\text{O}^{2-}$ ,  $0.97 + 1.32 = 2.29 \text{\AA}$ ,<sup>23</sup> suggesting that this bonding is relatively weak. Similarly long distances, 2.57  $\text{\AA}$  to O(1) and 2.96  $\text{\AA}$  to two O(2)'s, were seen before in  $\text{Co}_4\text{Na}_4\text{-A}\cdot 4\text{Cl}_2$ .<sup>6</sup>

In dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ ,<sup>10</sup> four  $\text{Co}(\text{II})$  ions and four  $\text{Na}^+$  ions are located on threefold axes close to 6-ring planes. However, in the structure of the  $\text{CS}_2$  sorption complex of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ ,<sup>8</sup> one  $\text{Na}^+$  ion relocated to an 8-ring plane. In the dimethyl disulfide sorption complex of  $\text{Co}_4\text{Na}_4\text{-A}$ ,<sup>12</sup> two  $\text{Na}^+$  ions are in the planes of 8-rings. In each of these structures,  $\text{Na}^+$  ions have relocated from 6-ring sites to accommodate guest molecules. For similar reasons, all four  $\text{Na}^+$  ions in this structure relocated from 6-rings upon  $\text{H}_2\text{S}$  sorption, each to make two favorable approaches to  $\text{H}_2\text{S}$  molecules, to one at S(1) and to another at S(2) (see Table 2 and Figure 3). In most complexes of  $\text{Co}_4\text{Na}_4\text{-A}$ , no  $\text{Na}^+$  ions at all relocate to new sites. The relocation of all four had not been seen before.

Eleven  $\text{H}_2\text{S}$  molecules are sorbed per unit cell. They are all in the large cavity (see Figure 1); the sodalite cavity is empty of both molecules and ions. Eight molecules of  $\text{H}_2\text{S}$  are found near threefold axes of the unit cell and are recessed 3.20(2)  $\text{\AA}$  into the large cavity from the (111) planes at O(3) (see Table 3). The remaining three  $\text{H}_2\text{S}$  molecules lie on fourfold axes, at 8-ring sites, 0.83  $\text{\AA}$  from 8-ring planes. Four of the eight  $\text{H}_2\text{S}$  molecules near threefold axes coordinate to  $\text{Co}(\text{II})$  ions (see Figure 2), and the remaining four interact with  $\text{Na}^+$  (see Figures 3 and 4). The atomic coordinates of the first four  $\text{H}_2\text{S}$  molecules must therefore be somewhat different from those of the second four; unfortunately they could not be resolved crystallographically.

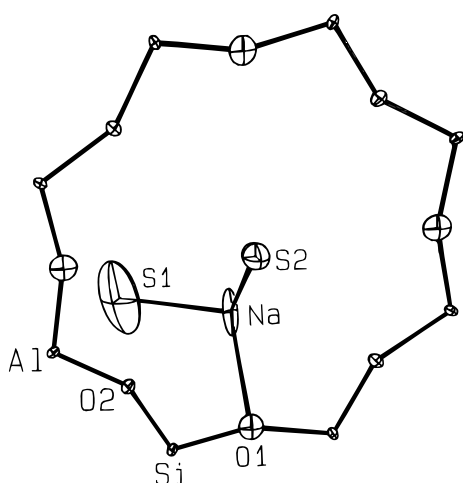
The  $\text{Co}(\text{II})\text{-S}$  bond lengths, 2.60(2)  $\text{\AA}$ , are approximately equal to the sum of the ionic radius of  $\text{Co}^{2+}$  and the van der Waals radius of sulfur,  $0.74 + 1.85 = 2.59 \text{\AA}$ .<sup>23</sup> For comparison, the  $\text{Co}(\text{II})\text{-S}$  distance in the structure of the dimethyl disulfide sorption complex is 2.52(2)  $\text{\AA}$ . Also, the interatomic distance between  $\text{Na}^+$  and the  $\text{H}_2\text{S}$  molecules at S(1), 2.87(3)  $\text{\AA}$ , is approximately equal to the sum of the van der Waals radius of sulfur and the ionic radius of  $\text{Na}^+$ ,  $1.85 + 0.97 = 2.82 \text{\AA}$ .<sup>23</sup>  $\text{Na}^+$  to S(2) is somewhat longer (see Table 2).

The four  $\text{Co}(\text{II})$  ions per unit cell cannot be tetrahedrally arranged about the large cavity, nor, therefore, can the  $\text{Na}^+$  ions. If this arrangement is tried, it is found that two of four  $\text{H}_2\text{S}$

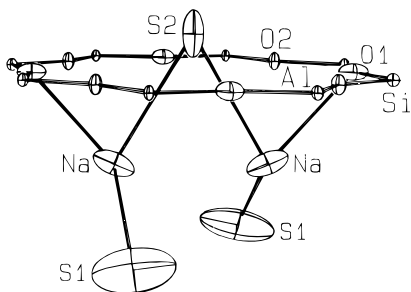
**TABLE 4: Fractional Coordinate of Cobalt(II), Deviations of Ions from 6-Ring Planes, and Co(II)–O(3) Distances, in Co<sub>4</sub>Na<sub>4</sub>-A and Its Sorption Complexes**

zeolite <sup>a</sup>	fractional coord of cobalt <sup>b</sup>	deviations <sup>c</sup> from the (111) plane at O(3), Å		Co(II)–O(3), Å <sup>b</sup>	ref
		Co(II)	Na <sup>+</sup>		
Co <sub>4</sub> Na <sub>4</sub> -A, dehydrated	0.200(2)	0.34	–0.56	2.077(18)	1
Co <sub>4</sub> Na <sub>4</sub> -A·4CS <sub>2</sub>	0.2070(4)	0.48	–0.61	2.204(7)	8
Co <sub>4</sub> Na <sub>4</sub> -A·4CO	0.208(1)	0.53	–0.58	2.113(15)	1
Co <sub>4</sub> Na <sub>4</sub> -A·4NO <sub>2</sub>	0.208(2)	0.50	–0.15	2.132(6)	5
Co <sub>4</sub> Na <sub>4</sub> -A·16Br	0.2088(3)	0.53	–0.31	2.155(7)	7
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>2</sub> H <sub>4</sub>	0.2106(2)	0.58	–0.55	2.148(7)	3
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>2</sub> H <sub>2</sub>	0.2111(3)	0.58	–0.13	2.193(7)	4
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>3</sub> H <sub>6</sub>	0.2124(3)	0.61	–0.09	2.174(7)	2
Co <sub>4</sub> Na <sub>4</sub> -A·11H <sub>2</sub> S	0.2165(3)	0.65	d	2.24(1)	this work
Co <sub>4</sub> Na <sub>4</sub> -A·4Cl <sub>2</sub>	0.2189(3)	0.73	d	2.244(6)	6

<sup>a</sup> All of these materials are deep blue in color, with the exception of the NO<sub>2</sub> and H<sub>2</sub>S complexes which are brown-black and black, respectively. The blue color has been attributed to the near tetrahedral nature of cobalt(II) in these complexes, whether the sorbed molecules are held by a  $\sigma$  or  $\pi$  interaction. <sup>b</sup> Numbers in parentheses are the esd's in the units of least significant digit given for the corresponding value. <sup>c</sup> A negative deviation indicates that the ion lies on the same side of the plane as the origin, that is, inside the sodalite unit. <sup>d</sup> These ions are located at qualitatively different sites within the zeolite lattice.



**Figure 3.** Front 8-ring of Figure 1, showing a Na<sup>+</sup> ion coordinated to two H<sub>2</sub>S molecules at S1 and S2. Ellipsoids of 20% probability are used.



**Figure 4.** Top 8-ring of Figure 1 showing that one H<sub>2</sub>S molecule at S2 bridges two Na<sup>+</sup> ions, each of which bonds to one H<sub>2</sub>S molecule at S(1). Ellipsoids of 20% probability are used.

molecules at S(1) which coordinate to Co must also coordinate to Na. Also, two of the Na<sup>+</sup> ions cannot interact with the sulfur atoms at S(1); each Na<sup>+</sup> should, to justify its relocation to a new site. Finally, two of the Na<sup>+</sup> ions must each be 2.10(5) Å from an S(2) sulfur, which is far less than the sum of the corresponding radii. The most suitable arrangement of Co<sup>2+</sup> ions, one which requires that some Co<sup>2+</sup> ions occupy adjacent 6-rings, but which keeps these contacts to a minimum, is shown in Figure 1: two Co<sup>2+</sup> ions occupy adjacent 6-rings and the remaining two occupy adjacent 6-rings on the opposite side of the large cavity.

Each Na<sup>+</sup> ion, in addition to its interaction with the zeolite framework (*vide supra*), coordinates to both S(1) and S(2). Two

of these four Na<sup>+</sup> ions share one of the H<sub>2</sub>S molecules at S(2), which therefore bridges between them (see Figure 4).

The three sulfur atoms at S(2) associate with 8-ring oxygens and Na<sup>+</sup> ions (see Figures 3 and 4). It appears that the H<sub>2</sub>S molecules at S(2) make weak hydrogen bonds with these oxygens: each S(2) atom is 3.57(1) Å from four O(2) oxygens and 3.64(2) Å from four O(1)'s (see interatomic distances in Table 2). An S–H...O distance is not readily available from the literature for comparison. However, the S–H...S “hydrogen bonding” distance is 3.94 Å<sup>24</sup> and the S–H...O distance would be expected to be substantially shorter. (The S–H bond length in the H<sub>2</sub>S molecule is 1.33 Å and the H–S–H bond angle is 92.2°.<sup>25</sup>)

The H<sub>2</sub>S sulfurs at S(2) are displaced by a small distance, 0.83 Å, from the 8-ring center in a direction normal to the 8-ring plane. This is consistent with the presence of a repulsive interaction between the sulfur atoms and those of the 8-ring oxygens to which the H<sub>2</sub>S molecules do not “hydrogen bond”. The asymmetry of the bonding of these H<sub>2</sub>S molecules argues that their sulfurs are only approximately on fourfold axes.

The shortest of the S (of H<sub>2</sub>S) to O (framework) distances in this structure is 3.57(1) Å for S(2) to O(2). This distance is somewhat greater than the sum of the van der Waals radii<sup>23</sup> of sulfur and oxygen, 1.40 + 1.85 = 3.25 Å. (It should be the average of a “hydrogen bonding” distance to two O(2)'s and a S–O repulsive distance, as has just been discussed, to two others.) Also the Na–S(2) distance, 3.31(4) Å, is substantially longer than the sum of the ionic radius of Na<sup>+</sup> and the van der Waals radius of sulfur, 0.97 + 1.85 = 2.82 Å. In this structure, an interaction distance of *ca.* 3.79(4) Å is possible between H<sub>2</sub>S molecules; this is almost the same as the sum of the van der Waals radii of two sulfur atoms, 1.85 + 1.85 = 3.70 Å.<sup>23</sup> The thermal parameter at S(2), because it is quite small, shows that the sulfur atoms at S(2) are reasonably well held in place by some or all of these interactions (see Figures 3 and 4).

Because H<sub>2</sub>S and sodium zeolite A are colorless, the color in Co<sub>4</sub>Na<sub>4</sub>-A and its complexes must involve the cobalt ions. The complexed Co(II) ions in the CO, cyclopropane, C<sub>2</sub>H<sub>4</sub>, Cl<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> sorption complexes of Co<sub>4</sub>Na<sub>4</sub>-A are all blue. The black color of Co<sub>4</sub>Na<sub>4</sub>-A·11H<sub>2</sub>S indicates that the electronic structure of the cobalt ion must be substantially modified by coordination to H<sub>2</sub>S. This is consistent with the unusually large deviation of Co from the 6-ring plane (see Table 4), which indicates a strong Co–SH<sub>2</sub> interaction.

Fellmuth et al.<sup>26</sup> confirmed that dissociative H<sub>2</sub>S sorption occurred on Na-A and Na-X. However this was not seen on

highly Ca<sup>2+</sup>-exchanged zeolites A and X.<sup>27</sup> They also observed that dissociative sorption on M<sub>2</sub>Na-A (M = divalent cation) decreases considerably as the divalent-cation exchange percentage increases to approximately 50%.

Karge and Rasco<sup>28</sup> used infrared spectroscopy to investigate H<sub>2</sub>S chemisorption on faujasite-type zeolites. They found that on alumina-rich faujasites (type X) heterolytic dissociative chemisorption occurs (H<sub>2</sub>S → HS<sup>-</sup> + H<sup>+</sup>), and that the H<sup>+</sup> ions formed surface hydroxyls with the lattice oxygens.

The interatomic distance, 2.87(3) Å, between Na<sup>+</sup> and S indicates that this sulfur is of an H<sub>2</sub>S molecule and not an SH<sup>-</sup> anion. This distance is almost the same as the sum of the van der Waals radius of sulfur and the ionic radius of Na<sup>+</sup> ion, 1.84 + 0.97 = 2.81 Å. For comparison, the Na<sup>+</sup>-SH<sup>-</sup> bond distance is approximately 2.37 Å, which is estimated by Schofield *et al.*<sup>29</sup> as follows:

$$r_e(\text{Na}-\text{OH}_2) - r_e(\text{Na}-\text{OH}) = r_e(\text{Na}-\text{SH}_2) - r_e(\text{Na}-\text{SH})$$

where  $r_e(\text{Na}-\text{OH}_2) = 2.05$  Å,  $r_e(\text{Na}-\text{OH}) = 1.93$  Å, and  $r_e(\text{Na}-\text{SH}_2) = 2.49$  Å. Therefore, it is clear that H<sub>2</sub>S molecules coordinate to Na<sup>+</sup> without dissociation (SH<sub>2</sub> → H<sup>+</sup> + SH<sup>-</sup>).

If H<sub>2</sub>S were to coordinate dissociatively to Co(II), the Co-SH bond distance should be about 1.43 + 0.74 = 2.17 Å. This distance is estimated as follows: the Ni(II)-SH<sup>30</sup> distance is 2.14 Å, Fe(II)-SH<sup>31</sup> is 2.24 Å, and Na-SH<sup>29</sup> is 2.37 Å. From these bond distances, we can estimate that the average bond radius of SH<sup>-</sup> (2.14 - 0.72 = 1.42 Å, 2.24 - 0.76 = 1.48 Å, and 2.37 - 0.97 = 1.40 Å, respectively) is about 1.43 Å. Additionally, the Co(II)-SCH<sub>3</sub><sup>31</sup> bond distance is 2.18 Å. The interatomic distance between Co(II) and sulfur at S(1) is 2.60(2) Å, which is almost the same as the sum of the van der Waals radius of sulfur and the ionic radius of Co<sup>2+</sup>, 1.85 + 0.74 = 2.59 Å. It is clear, then, that this sulfur is of an H<sub>2</sub>S molecule and not an SH<sup>-</sup> anion and that H<sub>2</sub>S coordinates without dissociation to Co(II) in this structure.

Sugioka *et al.*<sup>32</sup> investigated the effect of sulfiding with hydrogen sulfide on the catalytic activity and selectivity of M<sub>2</sub>Na-A (M = Ag, Cd, Zn, Co, Ni) in the isomerization of 1-butene and in the dehydration of 1-butanol. They found that M<sub>2</sub>Na-A showed no catalytic activity for the isomerization before absorbing hydrogen sulfide. The reaction and catalytic activities of these M<sub>2</sub>Na-A zeolites were remarkably enhanced by absorbing hydrogen sulfide at 300 °C, indicating that hydrogen sulfide sorbed into M<sub>2</sub>Na-A dissociates to form acidic hydroxyl groups. Their proposed mechanisms for the isomerization of 1-butene (to form 2-butene) and for the dehydration of 1-butanol (to form 1-butene, which is easily isomerized into 2-butene) involve the Brønsted acid sites formed by treatment with hydrogen sulfide. They assume that the M<sup>2+</sup> ions in M<sub>2</sub>Na-A zeolites are incorporated into metal sulfide particles after sulfiding at 300 °C and that the metal sulfide particles thus formed are located inside the large cavities of the zeolites with high dispersion. From this experimental result, we can conclude that dissociative H<sub>2</sub>S chemisorption on M<sub>2</sub>Na-A zeolites occurs only at temperatures substantially higher than that used in this work.

The distance between the Na<sup>+</sup> ions which are bridged by H<sub>2</sub>S at S(2) (see Figure 4) is 3.4 Å. This intercationic distance seems short, but it is far longer than the sum, 1.94 Å, of their ionic radii.<sup>23</sup>

Exchanging divalent cations into a zeolite generally increases its effective pore opening by diminishing the cation population. In zeolite A, ion exchange with a divalent cation such as Co(II) opens the apparent window size to its maximum. Because the 8-ring channels of Co<sub>4</sub>Na<sub>4</sub>-A are not blocked by cations, the polar H<sub>2</sub>S molecules may enter freely to interact with cations and framework oxygens in zeolite A.

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**Supporting Information 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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