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# Iodine Sorption Complexes of Partially Cobalt(II) Exchanged Zeolite A. Two Crystal Structures of $Co_{3.5}Na_5Si_{12}Al_{12}O_{48} \cdot 2.5I_2$ and $Co_{3.5}Na_5Si_{12}Al_{12}O_{48} \cdot 5.0I_2$

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Two crystal structures of iodine sorption complexes of dehydrated partially Co(II)-exchanged zeolite A, $Co_{3.5}Na_5$-A·$xI_2$, $x = 2.5$ and 5.0, have been determined by single crystal X-ray diffraction techniques. Both structures were solved and refined in cubic space group, $Pm3m$ at 21(1)°C. The structures of $Co_{3.5}Na_5$-A·$2.5I_2$ ($a = 12.173(1)$ Å) and $Co_{3.5}Na_5$-A·$5.0I_2$ ($a = 12.130(1)$ Å) were refined to the final error indices, $R_1 = 0.081$ and $R_2 = 0.077$ with 261 reflections and $R_1 = 0.103$ and $R_2 = 0.112$ with 225 reflections, respectively, for which $I > 3\sigma(I)$. In both structures, 3.5 $Co^{2+}$ ions and 4.5 $Na^+$ ions per unit cell lie at two crystallographically different 6-ring positions. 0.5 $Na^+$ ion lines in an 8-oxygen ring plance. Dehydrated $Co_{3.5}Na_5$-A sorbs 2.5 iodine molecules per unit cell at 70°C (vapor pressure of $I_2$ is *ca.* 8.3 torr) within 30 minutes and 5 iodine molecules per unit cell at 80°C (vapor pressure of $I_2$ is *ca.* 14.3 torr) within 24 hours. Each iodine molecule makes a close approach, along its axis to framework oxygen atom with I-I-O = 175°.

## Introduction

The crystal structures of a bromine complex in synthetic zeolite 4A[1] and a similar iodine complex in zeolite 5A[2] have been reported. In each of these sorption complexes, it was found that approximately six dihalogen molecules were sorbed per unit cell; 6 bromine molecules in $Na_{12}$-A[1] and 5.65 iodine molecules in $Ca_4Na_4$-A[2]. The bromine molecules did not interact with the anionic framework or with the $Na^+$ ions[1]. $I_2$ molecules, however, were involved in charge-transfer complexes with the framework 8-ring oxygens[2]. No iodine-$Ca^{2+}$ or iodine-$Na^+$ interaction was observed[1,2].

Several structures of $Cl_2$ and $Br_2$ sorption complexes of $Ag^+$, Eu(II), and Co(II)-exchanged zeolite A have been determined[3-5]. In the structure of a chlorine sorption complex of vacuum-dehydrated Eu(II)-exchanged zeolite A, chlorine gas is reported to have oxidized Eu(II) to Ei(IV)[4]. Chlorine gas has also oxidized hexasilver to AgCl as observed in the structure of a chlorine sorption complex of dehydrated, fully $Ag^+$-exchanged zeolite $A^3$. Additional six molecules per unit

cell are sorbed, which form charge transfer complexes with frame work oxygens (O-Cl-Cl = 166(2)°). 6 bromine molecules are sorbed in the dehydrated $Ag_{12}$-A; 3.6 $B_2$ molecules interact to draw with 3.6 of the 8.0 6-ring $Ag^+$ ions into largecavity and 2.4 $Br_2$ molecules form charge transfer complexes with framework oxide ions (O-Br-Br = 174(4)°).[6] When $Cl_2$ gas was sorbed onto a single-crystal of vacuum-dehydrated $Co_4Na_4$-A, the chlorine molecules were coordinated to the Co(II) ion in a bent manner. The chlorine molecule is equatorially basic with respect to the hard acid Co(II) and the dichlorine bond is lengthened by a large amount, approximately 0.5 Å, upon complexation[5].

This work was undertaken to further investigate the sorption properties of zeolite A and to determine the positions of the sorbed iodine molecules.

## Experimental Section

Single crystals of the synthetic molecular sieve sodium zeolite 4A, $Na_{12}Si_{12}Al_{12}O_{48} \cdot 27H_2O$, were prepared by a modi-

**Table 1.** [a]Positional, Thermal and Occupancy Parameters for the Iodine Sorption Complex of Dehydrated Co₃.₅Na₅-A

Crystal 1. Dehydrated Co₃.₅Na₅-A·2.5I₂

| Atom | Wyc. pos. | $x$ | $y$ | $z$ | $\beta_{11}^b$ or $B_{iso}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Occupancy factor |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (Si,Al) | 24(k) | 0 | 1823(3) | 3687(2) | 37(2) | 27(2) | 22(2) | 0 | 0 | 6(4) | 1[c] |
| O(1) | 12(h) | 0 | 2070(10) | 5000 | 120(10) | 70(10) | 30(10) | 0 | 0 | 0 | 1 |
| O(2) | 12(i) | 0 | 2940(7) | 2940(7) | 120(10) | 40(5) | 40(5) | 0 | 0 | 50(10) | 1 |
| O(3) | 24(m) | 1139(5) | 1139(5) | 3318(6) | 56(4) | 56(4) | 79(8) | 40(10) | -10(10) | -10(10) | 1 |
| Co(1) | 8(g) | 2085(4) | 2085(4) | 2085(4) | 67(3) | 67(3) | 67(3) | 48(6) | 48(6) | 48(6) | 7/16 |
| Na(1) | 8(g) | 1650(20) | 1650(20) | 1650(20) | 240(20) | 240(20) | 240(20) | 110(4) | 110(4) | 110(4) | 9/16 |
| Na(2) | 12(i) | 0 | 4500(80) | 4500(80) | 4(4) | | | | | | 1/24 |
| I(1) | 24(l) | 1500(20) | 4260(20) | 5000 | 510(40) | 350(40) | 290(30) | -130(60) | 0 | 0 | 5/48 |
| I(2) | 24(l) | 2580(30) | 3750(30) | 5000 | 540(50) | 610(60) | 720(70) | 610(80) | 0 | 0 | 5/48 |

Crystal 2. Dehydrated Co₃.₅Na₅-A·5.0I₂

| Atom | Wyc. pos. | $x$ | $y$ | $z$ | $\beta_{11}^b$ or $B_{iso}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Occupancy factor |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (Si,Al) | 24(k) | 0 | 1801(5) | 3677(4) | 24(3) | 26(3) | 20(3) | 0 | 0 | -5(7) | 1[c] |
| O(1) | 12(h) | 0 | 2050(20) | 5000 | 80(20) | 90(20) | 10(10) | 0 | 0 | 0 | 1 |
| O(2) | 12(i) | 0 | 3000(10) | 3000(10) | 90(20) | 26(8) | 26(8) | 0 | 0 | 80(20) | 1 |
| O(3) | 24(m) | 1110(8) | 1110(8) | 3210(10) | 57(7) | 57(7) | 50(10) | 60(20) | -70(10) | -70(10) | 1 |
| Co(1) | 8(g) | 2155(7) | 2155(7) | 2155(7) | 46(4) | 46(4) | 46(4) | 59(9) | 59(9) | 59(9) | 7/16 |
| Na(1) | 8(g) | 1670(20) | 1670(20) | 1670(20) | 80(10) | 80(10) | 80(10) | 80(30) | 80(30) | 80(30) | 9/16 |
| Na(2) | 12(i) | 0 | 4400(100) | 4400(100) | 1(3) | | | | | | 1/24 |
| I(1) | 24(l) | 1490(7) | 4502(9) | 5000 | 100(9) | 240(20) | 240(20) | -150(20) | 0 | 0 | 5/24 |
| I(2) | 24(l) | 2790(10) | 3670(20) | 5000 | 210(20) | 330(30) | 920(60) | -20(50) | 0 | 0 | 5/24 |

[a]Positional and anisotropic thermal parameters are given × 10⁴. 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[−($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$)]. Rms displacements can be calculated from $\beta_{ij}$ values by using the formula $\mu_i = 0.225$ a $(\beta_{ij})^{1/2}$, where $a = 12.173(1)$ Å for Co₃.₅Na₅-A·2.5I₂ and $a = 12.130(1)$ Å for Co₃.₅Na₅-A·5.0I₂. [c]Occupancy for (Si) = 0.5; occupancy for (Al) = 0.5.

fied Charnell procedure[7]. The ion exchange of crystals of zeolite 4A with 0.1 M Co(NO₃)₂ solution was conducted by the static method[8]. These exchanges yielded materials whose approximate stoichiometries were Co₃.₅Na₅Si₁₂Al₁₂O₄₈ ·x H₂O per unit cell, subsequently to be referred to as Co₃.₅Na₅-A[9], exclusive of water molecules. Two of the largest single crystals from this experiment which are about 0.08 mm long in an edge were selected for X-ray diffraction study. Each crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated by gradually incrementing its temperature (ca. 25°/hr) to 360 °C at a constant pressure of 2 × 10⁻⁶ torr. Finally, the system was maintained at this state for 48 hrs. To prepare the iodine complexes, one dehydrated Co₃.₅Na₅-A crystal was treated with zeolitically dried I₂ vapor (vapor pressure of I₂ was 8.3 torr) at 70 °C for 30 minutes and the other crystal at 80 °C (vapor pressure of I₂ was 14.3 torr) for 24 hours[10]. Each crystal, which was initially deep-blue in color, became almost lack after exposure to iodine vapor. Each crystal in its iodine atmosphere was sealed in its capillary by torch.

The cubic space group Pm3m (no systematic absences) was used instead of Fm3c for reason described previously[11,12]. Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and a PDP micro 11/73 computer. Mo Kα radiation was used for all experi-

ments (K_α1, λ = 0.70930 Å; K_α2, λ = 0.71359 Å). The unit cell constants determined by a least-squares refinement of 25 intense reflections for which 19°<2θ<24° are 12.173(1) Å for Co₃.₅Na₅-A· 2.5I₂ and 12.130(1) Å for Co₃.₅Na₅-A·5.0I₂, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space ($h$ $k$ $l$, $h \le k \le l$ and $l$ $k$ $h$, $l \le k \le h$) were examined using ω−2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at the slow scan speed, ranging between 0.119° and 0.384° in ω/min. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each region of reciprocal space, the intensities of all lattice points for which 2θ < 70° were recorded.

The raw data from each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection by the computer programs, PAINT and WEIGHT[13]. An absorption correction ($\mu = 3.40$ mm⁻¹ and $\mu R = 0.19$ for Co₃.₅Na₅-A·2.5I₂, and $\mu = 5.68$ mm⁻¹ and $\mu R = 0.32$ for Co₃.₅Na₅-A·5.0I₂) was judged to be unnecessary and was not applied.[6] Of the 852 pairs of reflections for the crystal of Co₃.₅Na₅-A·2.5I₂ and 849

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

| | Co₃.₅Na₅–A·2.5I₂ | Co₃.₅Na₅–A·5.0I₂ |
|---|---|---|
| (Si,Al)–O(1) | 1.626(4) | 1.632(6) |
| (Si,Al)–O(2) | 1.626(4) | 1.671(8) |
| (Si,Al)–O(3) | 1.679(5) | 1.684(9) |
| Na(1)–O(3) | 2.214(9) | 2.110(10) |
| Na(2)–O(1) | 3.02(2) | 2.95(4) |
| Na(2)–O(2) | 2.68(7) | 2.50(10) |
| Co(1)–O(3) | 2.22(1) | 2.20(2) |
| I(1)–O(1) | 3.23(3) | 3.48(2) |
| I(1)–I(2) | 2.76(4) | 2.72(3) |
| O(1)–(Si,Al)–O(2) | 113.1(5) | 108.9(8) |
| O(1)–(Si,Al)–O(3) | 110.8(3) | 114.9(6) |
| O(2)–(Si,Al)–O(3) | 105.3(2) | 105.6(3) |
| O(3)–(Si,Al)–O(3) | 111.4(3) | 103.5(4) |
| (Si,Al)–O(1)–(Si,Al) | 158.6(8) | 159.0(10) |
| (Si,Al)–O(2)–(Si,Al) | 157.6(4) | 148.8(7) |
| (Si,Al)–O(3)–(Si,Al) | 138.4(4) | 133.1(7) |
| O(3)–Na(1)–O(3) | 115.8(7) | 118.2(6) |
| O(3)–Co(1)–O(3) | 115.7(2) | 109.7(3) |
| O(1)–Na(2)–O(2) | 56.4(1) | 59.2(4) |
| O(1)–I(1)–I(2) | 174.0(10) | 175.7(5) |

Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

pairs for the crystal of Co₃.₅Na₅–A·5.0I₂, only 261 and 225 pairs, for which $I < 3\sigma(I)$, respectively, were used in subsequent structure determinations.

The initial structural parameters used in least-squares refinement were those previously found for Co²⁺, (Si, Al), O(1), O(1), O(2) and O(3) positions in the structure of Co₄Na₄–A treated with Cl₂ gas[5]. From the initial difference Fourier map, I(1) and I(2) were readily located and refined (see Tables 1 and 2). In the zeolite A structure 12, monopositive cations (or 6 dipositive catons) per unit cell should be found. Therefore, from a subsequent difference Fourier map, Na(1) and Na(2) are located.

The ions at Co(1) and Na(1) are associated with 6–rings and lie on threefold axes[14] (see Table 1). The number of ions per unit cell at these position cannot sum to more than 8, otherwise unacceptable close interionic distances would occur. With the constraint that the sum of the occupancies at Co(1) and Na(1) be 8 per unit cell, full–matrix least-squares refinement converged to Co(1) = 3.5 and Na(1) = 4.5 (see Table 1). Alternative assignment of chemical identities showed *ca.* Na⁺ ions and 2.5 Co²⁺ ions which are on the threefold axes of unit cell. This is not acceptable in zeolite A structure. Furthermore similar positions of Co(1) and Na(1) were found in the previous structure.[8] Successive least-squares refinements indicated that the atoms at I(1) and I(2) are diiodine molecules (I(1)–I(2) = *ca.* 2.74 Å). Accordingly, the occupancy at I(1) was constrained to equal that at I(2). The occupancy of I(1)–I(2) was refined to be 2.5 for the first crystal and 5.0 for the second crystal, respectively (see Tables 1 and 2).

The structure of Co₃.₅Na₅–A·2.5I₂ and that of Co₃.₅Na₅–A·5.0I₂ were refined to give the final error indices $R_1 = 0.081$ and $R_2 = 0.077$, and $R_1 = 0.103$ and $R_2 = 0.112$, respectively. The final difference Fourier map was featureless except one

**Table 3.** Deviation of Atom (Å) from the (111) Plane at O(3)

| Atom | Co₃.₅Na₅–A·2.5I₂ | Co₃.₅Na₅–A·5.0I₂ |
|---|---|---|
| O(2) | –0.200(5) | –0.400(8) |
| Co(1) | –0.458(13) | –0.725(11) |
| Na(1) | 0.464(3) | 0.287(5) |

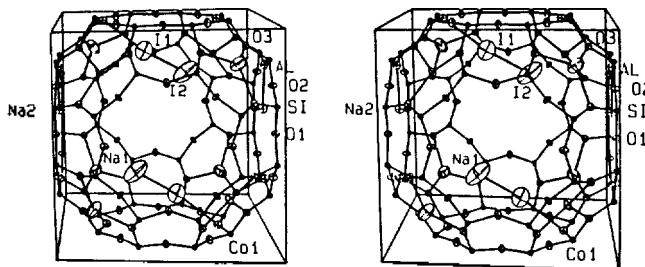A positive deviation indicates that the atom lies on the same side of the plane as the origin.



**Figure 1.** The unit cell of Co₃.₅Na₅–A·2.5I₂ is shown in stereoview. About 50% of the unit cells may have this arrangemetn. The remaining 50% may contain 4 Co²⁺ ions at Co(1), 4 Na⁺ ions at Na(1) and 3 I₂ molecules. Ellipsoids of 20% probability are shown.
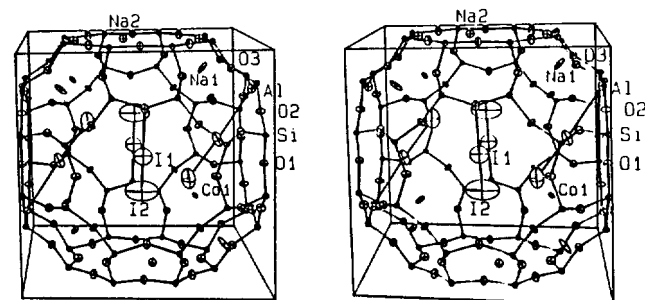


**Figure 2.** The unit cell of Co₃.₅Na₅–A·5.0I₂ is shown in stereoview. About 50% of the unit cells have this arrangement. The remaining 50% contain 4 Co²⁺ at Co(1), 4 Na⁺ ions at Na(1), and 6 I₂. Ellipsoids of 20% probability are shown.

peak at (0,0,0) with peak height of 2.0(13) eÅ⁻³ for Co₃.₅Na₅–A·2.5I₂ and one at (0.16, 0.5, 0.5) with peak height of 1.1(18) eÅ⁻³ for Co₃.₅Na₅–A·5.0I₂, respectively.

Atomic scattering factors for Co²⁺, Na⁺, O⁻, and (Si, Al)¹·⁷⁵⁺ were used[15,16]. The function describing (Si,Al)¹·⁷⁵⁺ is the mean of the Si⁰, Si⁴⁺, Al⁰ and Al³⁺ function. All scattering factors were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction[17,18]. Final position, thermal and occupancy parameters are presented in Table 1; bond angle and lengths are given in Table 3.

## Discussion

In this work, the closest approach of an iodine atom to a framework atom is that of I(1) to O(1). Furthermore, the axis of the I₂ molecule points directly at an oxygen atom, O(1) (see Figure 1, 2 and 3). Such an effect has been observed in complexes between diatomic halogen molecules and organic molecules[19]. This can be understood in terms of a degree of electron pair donation ("charge transfer") from the electronegative O(1) ion, the only crystallographic kind of ox-
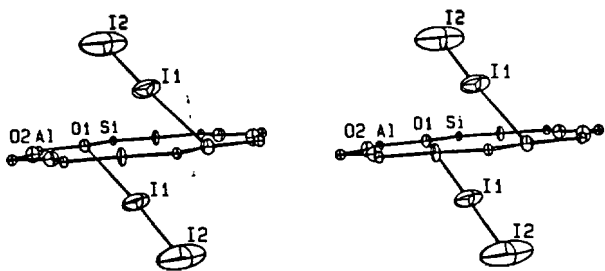
**Figure 3.** An 8-ring not containing Na(2) in the structure of $Co_{3.5}Na_5-A \cdot 5.0I_2$. Ellipsoids of 20% probability are shown.

ygen not near a cation position, toward axially electropositive region on the iodine molecule with its vacant $5p$ $\sigma^*$ antibonding molecular orbital.

The long diiodine bond, 2.72(3) Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$ and 2.76(4) Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ as compared to 2.662 Å in gas phase $I_2$[20] are a consequence of the resulted reduced bond order due to the formation of this change transfer complex (Table 2).

The nearest approach distance for I(1) to O(1) is 3.23(3) Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ and 3.48(2) Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$. These distances are less than the sum of the appropriate nonbonded van der Waals radii, 3.55 Å[21]. The bond angle of O(1)–I(1)–I(2) is ca. 175° for both structures (see Figure 3). These are also in agreement with the hypothesis of some degrees of charge transfer bonding. Such a pattern of angles and distance has been observed before in a complex between diiodine and O(1) in zeolite 5A $(Ca_4Na_4-A)^2$.

The Na$^+$ ions at Na(2) are associated with 8-ring oxygens (see Figures 1 and 2). This position is about the same as those found in other structures[22,23]. The distances between Na$^+$ ions and framework oxygens, Na(2)–O(2) = 2.50(10) Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$ and 2.68(7) Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ are longer than the sum of the ionic radii of Na$^+$ and $O^{2-}$, 2.29 Å[24]. Therefore this bond is relatively weak.

Because of the presence of 0.5 Na$^+$ ion at Na(2) in the 8-ring planes, $I_2$ molecules do not approach either side of this particular 8-ring. Therefore, in the structure of $Co_{3.5}Na_5-A \cdot 5.0I_2$, an average of five diiodine molecules per unit cell are sorbed per unit cell.

3.5 Co$^{2+}$ ions at Co(1) lie on the unit cell threefold axes, recessed into the large cavity. Each Co$^{2+}$ ion is bound to the three equivalent O(3) framework oxygen atoms of its 6-ring at a distance of ca. 2.20 Å (Table 2). The angles subtended at Co$^{2+}$ ion are 115.7(2)° for $Co_{3.5}Na_5-A \cdot 2.5I_2$ and 109.7(3)° for $Co_{3.5}Na_5-A \cdot 5.0I_2$, respectively. Each Co$^{2+}$ ion lies somewhat "above" 0.464 Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ and 0.725 Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$, respectively from its plane of three O(3) atoms (see Table 3).

The fractional occupancies observed at Na(1), Na(2) and Co(1) indicate the existence of at least two types of unit cells with regards to the cations. For example, 50% of the unit cells may have 4 Na$^+$ ions at Na(1) and 4 Co$^{2+}$ ions at Co(1). The remaining 50% would have 3 Co$^{2+}$ ions, 5 Na$^+$ ions at Na)1) and 1 Na$^+$ ion at Na)2) (see Figure 1). At Na(1), 4.5 Na$^+$ ions occupy a 3-fold-axis sites near 6-rign, and recess 0.464(13) Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ and 0.287 Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$, respectively, into the sodalite cavity from the (111) plane at O(3) (see Table 3). Each Na(1) ion is trigonally coordinated to three O(3) framework oxygens at

2.214(9) Å for $Co_{3.5}Na_5-A \cdot 2.5I_2$ and 2.11(1) Å for $Co_{3.5}Na_5-A \cdot 5.0I_2$, resectively.

Recently, the crystal structure of bromine sorption complexes of partially cobalt(II)-exchanged zeolite A have been determined[25]. In this structure, 3.5 tribromide ions are found, indicating that Co(II) has been oxidized to Co(III). The atom at one end of each is involved in a linear charge-transfer complex with a framework oxygen; and in a much weaker interaction with the opposite end atom of an adjacent tribromide ion. The latter bromine atom, is in the vicinity of a Co(II) ion. However in this work, diiodine molecule makes no significant approach to Co$^{2+}$ ions. In closest approach I-Co$^{2+}$ distance is 4.13 Å (see Figure 1 and 2).

A comparison of two crystal structures determined in this work shows that dehydrated $Co_{3.5}Na_5-A$ sorbs 2.5 iodine molecules per unit cell at 70 °C (vapor pressure of $I_2$ is 8.3 torr) within 30 minutes and 5 iodine molecule per unit cell at 80 °C (vapor pressure of $I_2$ is 14.3 torr) within 24 hours. In the structure of $Co_{3.5}Na_5-A \cdot 5.0I_2$, 0.5 Na$^+$ ion is located on 8-ring plane, and 2.5 eight-rings are free of cations. Therefore 2.5 eight-ring oxygens can accommodate 5 diiodine molecules, i.e., 2 $I_2$ per available 8-ring.

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# Spin-Rotational Relaxation Study of Molecular Reorientation of Oblate Symmetric Top Molecules with Internal Extended Rotational Diffusion

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Molecular reorientation of oblate symmetric top molecules in the presence of internal rotation is investigated and an analytic expression for the spin–rotational relaxation rate of a nucleus attached to the internal rotor is obtained as a function of the internal angular momentum correlation time. The overall reorientation of the symmetric top is treated by the anisotropic rotational diffusion and the internal rotation is assumed to undergo modified extended rotational diffusion. The result is compared with the previous work for the prolate symmetric top molecule and it is shown that both results reduce to the same expression in the spherical top limit.

## Introduction

Study of molecular reorientation in the presence of internal rotation has been carried out for many molecular systems. Theoretically, one usually adopt a certain model for the reorientation and widely employed models are rotational diffusion[1-3], jump diffusion[4-6], and extended rotational diffusion[7-12]. Experimentally[10,13], various techniques of spectroscopy such as NMR, IR, Raman, and Rayleigh light scattering are employed and these techniques can be complemented with one another to extract reliable informaiton on the molecular reorientation.

Recently, we investigated a model of a symmetric-top molecule undergoing anisotropic rotational diffusion in the presence of the extended diffusion of internal rotation[14-17]. Particularly, the effects of internal rotation of methyl group in liquid toluene which is a prolate symmetric top molecule on the $^{13}C$ nuclear dipolar and spin–rotational relaxation times were investigated[16] to evaluate the internal angular momentum correlation time which reveals the inertial effect in the internal rotation. We also carried out a similar investigation of the effect of the reorientation of oblate symmetric top molecules containing internal rotors on the $^{13}C$ nuclear dipolar relaxation time[17]. In this case, the overall reorientational correlation time expressed in terms of the internal angular momentum correlation time is quite different from the expression for prolate symmetric top molecules but reduces to the same expression in the spherical top limit.

The purpose of this work is to investigate the effect of reorientation of oblate symmetric top molecules in the presence of internal rotation on the $^{13}C$ nuclear spin–rotational relaxation time. The result can be compared with the case of

$^{13}C$ nucelar dipolar relaxation and the internal angular momentum correlation time can then be evaluated reliably.

## Theory

The spin–rotational contribution to the relaxation rate in the extreme narrowing limit is given by[18]

$$1/T_{1,SR} = \hbar^{-2} \int_0^\infty dt \left[ g_{-1,1}(t) + g_{-1,1}(t) \right] \tag{1}$$

where

$$g_{kk}(t) = \langle V_k(t) V_k(0) \rangle (-1)^k \tag{2}$$

with

$$V_k = \sum_q D_{kq}^{(1)*} A_q. \tag{3}$$

Here the rotation matrices $D^{(j)}(\Omega)$ defined by Rose[19] are employed and the angular brackets denote the ensemble average. $A_q$ in Eq. (3) appears in the spin–rotational Hamiltonian as follows[20]:

$$H_{SR}/\hbar = \sum_{k=-1}^{1} A_k I_k \tag{4}$$

where

$$I_0 = I_c, \quad I_{\pm 1} = \mp 2^{-1/2} (I_a \pm i I_b) \tag{5}$$

and

$$A_{+1} = 2^{-1/2} (C_{aa} J_a - i C_{bb} J_b) \tag{6a}$$

$$A_0 = - (C_{cc} J_c + D_a j) \tag{6b}$$

$$A_{-1} = - 2^{-1/2} (C_{aa} J_a + i C_{bb} J_b). \tag{6c}$$