

Disproportionation of an Element in a Zeolite. II. Crystal Structure of an Iodine Sorption Complex of Dehydrated Fully Cd²⁺-Exchanged Zeolite X Containing *n*-I₅[−] as I[−]–I₃⁺–I[−] and Square *cyclo*-I₄²⁺

Mee Kyung Song, Eun Young Choi, and Yang Kim*

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea

Karl Seff*

Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, Hawaii 96822-2275

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The crystal structure of an iodine sorption complex of fully dehydrated, fully Cd²⁺-exchanged zeolite X, Cd₄₆Si₁₀₀Al₉₂O₃₈₄ · 89.6I per unit cell (*a* = 24.861(8) Å), has been determined by single-crystal X-ray diffraction methods in the cubic space group *Fd* $\bar{3}$ *m* at 21(1) °C. The crystal was prepared by ion exchange in a slightly basic aqueous stream 0.05 M in Cd²⁺, followed by washing with distilled water at 80 °C. Dehydration was then done at 450 °C and 2 × 10^{−6} Torr, followed by exposure in situ to zeolitically dry iodine vapor. The structure was refined to the final error indices *R*₁ = 0.044 and *R*₂ = 0.043 with 263 reflections, for which *I* > 3σ(*I*). Forty-six Cd²⁺ ions are found at four crystallographic sites: 14 at site I at the center of the hexagonal prism (Cd–O = 2.389(5) Å), 4 at site I' in the sodalite cavity just outside the hexagonal prism (Cd–O = 2.441(8) Å), 2.4 at site II' in the sodalite cavity (Cd–O = 2.200(9) Å), and the remaining 25.6 at site II near single six-oxygen rings in the supercage (Cd–O = 2.218(7) Å). All 44.8 diiodine molecules sorbed per unit cell have disproportionated to give 12.8 *n*-I₅[−] anions with symmetry 2 and 6.4 square *cyclo*-I₄²⁺ cations. The sorption reaction ends precisely when the eight supercages per unit cell are full (12.8/2 + 6.4/4 = 8.0). In *cyclo*-I₄²⁺, I–I = 2.757(14) Å and 2.796(13) Å, and I–I–I = 90.0(5)°; each iodine atom is 3.167(10) Å from a framework oxygen (I–I···O = 159.4(4)°). In *n*-I₅[−], the central bond lengths are 2.473(14) Å and the terminal bond lengths are 2.534(13) Å, all less than 2.67 Å, the I–I distance in I₂. The central bond angle, 114.8(7)°, is indicative of I₃⁺, indicating that the terminal atoms are iodide ions. That the terminal atoms coordinate to Cd²⁺ also indicates that they are iodide ions. The 12.8 *n*-I₅[−] anions per unit cell each bridge between two site-II Cd²⁺ ions in the supercage.

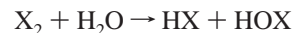
Introduction

Halogen Sorption by Zeolites. Zeolites readily sorb dihalogens by a variety of mechanisms.^{1–7} In the crystal structures of a bromine sorption complex of Ag₁₂–A² (fully dehydrated fully Ag⁺-exchanged zeolite A) and that of an iodine sorption complex of Ca₄Na₄–A,³ the dihalogen molecules interact with zeolite framework oxygens. In these structures, Br₂ and I₂ act as Lewis acids with respect to framework oxygen lone pairs. Linear O–X–X sequences, with the X₂ bond lengthened by complexation, were found in these charge–transfer complexes (O–Br–Br = 174(4)° and O–I–I = 178°).

In the crystal structures of the chlorine sorption complexes of Ag⁺-exchanged zeolite A⁴ and Eu(II)-exchanged zeolite A,⁵ chlorine gas oxidized hexasilver to AgCl and is reported to have oxidized Eu(II) to Eu(IV) (may be incorrect due to the slow hydrolysis of Eu(II) to Eu(III) in water). In the latter structure, six additional dichlorine molecules are sorbed per unit cell; these form charge–transfer complexes with framework oxygens (O–Cl–Cl = 166(2)°). When Cl₂ gas was sorbed onto a single crystal of vacuum-dehydrated Co₄Na₄–A,⁶ dichlorine coordinated to Co(II) in a bent manner. The chlorine molecule is equatorially basic with respect to the hard acid Co(II), and the dichlorine bond was reported to be lengthened by a large amount

upon complexation. However, when Br₂ gas was sorbed onto a single crystal of vacuum-dehydrated Co₄Na₄–A,⁷ a redox reaction occurred between Co(II) and Br₂ to yield Co(III) and Br₃[−] ions. Four quite asymmetric Br₃[−] ions each bridge between a Co³⁺ ion and an 8-ring framework oxygen. Only with Br₂, and with neither Cl₂ nor I₂, is Co²⁺ oxidized and X₃[−] formed.

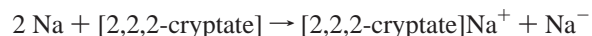
The Disproportionation of Elements. The elements chlorine and bromine disproportionate in water to give HX and HOX.



HOX disproportionates further to produce HX and HXO₃.⁸ Iodine disproportionates in water to give HI and HIO₃ directly. A much more complete discussion of the disproportionation of Cl₂, Br₂, and I₂ in the water is available.⁹ Iodine reacts similarly with triphenylphosphine or triphenylarsine to produce ϕ₃PI⁺ or ϕ₃AsI⁺, respectively, and I₃[−].¹⁰



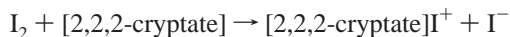
Sodium disproportionates to give Na⁺ and Na[−] using cryptates,^{11–13} organic multidentate ligands that provide a good coordination environment to cations.



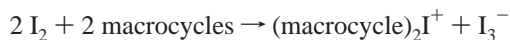
In this case, Na⁺ is captured by a cryptate molecule, leaving

* To whom correspondence should be addressed. E-mail: ykim@pusan.ac.kr; seff@hawaii.edu.

Na⁺ as the product anion. The same disproportionation reaction occurs with iodine.^{14–16}



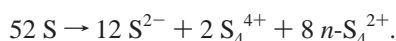
Macrocycles can do this also, forming a sandwich around the cation.¹⁷



Sometimes two different macrocycles work best.

Anaerobic bacteria that can disproportionate elemental sulfur to sulfide and sulfate have been found. The net reaction consumes water and gives hydrogen sulfide and sulfuric acid, but it does not proceed spontaneously: it is endergonic.¹⁸ It can be made exergonic by adding a substance (e.g., FeOOH, FeCO₃, MnCO₃, or MnO₂) that can coordinate to the sulfide ions and neutralize the acid.^{19–25} The actual net reaction, a feature of which is the disproportionation of elemental sulfur, is therefore one that consumes sulfur, water, and a third substance. The other disproportionations discussed above, and the one reported here, involve only the element and one other substance, water, a phosphine or an arsine, a cryptate or two macrocycles, or a zeolite.

Recently, the crystal structure of Cd₄₆–X · 52S, a sulfur sorption complex of Cd₄₆–X, was reported.²⁶ This was the first observation of the (electronic) disproportionation of an element upon sorption into zeolite. All fifty-two sulfur atoms sorbed per unit cell had disproportionated to give sulfide anions and two new tetrasulfur cations, S₄⁴⁺ and *n*-S₄²⁺, by the reaction



Each sulfide ion coordinates only to a Cd²⁺ ion to form solitary CdS molecules. S₄⁴⁺ is tetrahedral (S–S = 2.16(3) Å). Each S₄⁴⁺ atom interacts with three anionic framework oxygens (S–O = 3.379(13) Å); in that way, the anionic sodalite cavity of Cd₄₆–X hosts and stabilizes S₄⁴⁺. Each supercage hosts an electron-deficient *n*-S₄²⁺ cation that bridges covalently between two zeolite oxygens and has a predominantly ionic interaction with a sulfide ion.

This work was done to learn whether iodine would disproportionate upon sorption into Cd–X as sulfur had, to provide a second example of this phenomenon in zeolites. If this occurred, species new to chemistry might again be found.

Experimental Section

Large single crystals of sodium zeolite X, Na₉₂Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.²⁷ 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.

Cd₄₆–X was prepared by allowing an aqueous exchange solution of Cd(NO₃)₂ (Aldrich, 99.999%) and Cd(O₂CCH₃)₂ (Aldrich, 99.99%) in the molar ratio 1:1 with a total Cd²⁺ 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. (With Cd–A, this wash had been found necessary to remove occluded material, perhaps Cd(OH)₂.)²⁸ The Pyrex-tube extension of the crystal-containing capillary was sealed onto to a vacuum system, and the crystal was fully dehydrated by increasing the temperature (ca. 25 °C/h) to 450 °C at a constant pressure of 2 × 10^{–6} Torr. The system was maintained at this state for 48 h. After cooling to room temperature, the crystal was seen to be colorless.

TABLE 1: Experimental and Structure Refinement Data

Cd ₄₆ Si ₁₀₀ Al ₉₂ O ₃₈₄ · 89.6I	
color	violet
ρ _{calcd} (gcm ^{–3})	2.106
μ (mm ^{–1})	4.08
ion exchange T(°C)/t(days)	21/3
data collection T(°C)	21
scan technique	ω–2θ
scan speed (deg/min)	0.25–0.31
scan width (deg)	0.80 + 0.344 tan θ
radiation (Mo Kα) λ ₁ (Å)	0.70930
λ ₂ (Å)	0.71359
space group	<i>Fd</i> $\bar{3}$ <i>m</i>
unit cell constant, <i>a</i> (Å)	24.861(8)
2θ range for <i>a</i> (deg)	14–22
no. of reflections for <i>a</i>	25
2θ range in data collection (deg)	3 < 2θ < 50
no. of reflections gathered	1362
no. of unique reflections (<i>m</i>)	690
no. of reflections (<i>I</i> > 3σ(<i>I</i>))	263
(<i>I</i> > 0)	495
no. of parameters (<i>s</i>)	68
data/parameter ratio (<i>m/s</i>)	7.3
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>I</i> > 3σ(<i>I</i>))	0.044/0.043
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>I</i> > 0)	0.116/0.044
goodness of fit ^c (<i>I</i> > 3σ(<i>I</i>)/ <i>I</i> > 0)	1.80/1.26

^a *R*₁ = Σ|*F*_o–|*F*_c||/Σ|*F*_o|. ^b *wR*₂ = (Σ*w*(*F*_o–|*F*_c|)²/Σ*wF*_o²)^{1/2}. ^c Goodness of fit = (Σ*w*(*F*_o–|*F*_c|)²/(*m*–*s*))^{1/2}.

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 iodine under vacuum. This iodine 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 was exposed to iodine vapor at 20 °C for 23 h. The vapor pressure of iodine at 20 °C is ca. 0.3 Torr.²⁹ After the residual iodine was condensed away from the crystal, the crystal was seen to have become violet.

The cubic space group *Fd* $\bar{3}$ was initially chosen because most crystals from this synthesis batch, regardless of subsequent chemical treatment, have been refined successfully with *Fd* $\bar{3}$.³⁰ However, *Fd* $\bar{3}$ was rejected and the space group *Fd* $\bar{3}$ *m* was chosen because only an insignificant difference was seen in least-squares refinement between the mean Al–O and Si–O distances. The error indexes did not increase when the space group was changed to *Fd* $\bar{3}$ *m*. The near zero difference between mean Al–O and Si–O distances indicates that the Si/Al composition at both the Si and Al positions is essentially the same as that for the entire crystal: the long-range Si/Al ordering has been lost.³⁰ This can occur most easily if antidomains have formed.³¹

The cubic unit cell constant is *a* = 24.861(8) Å. Diffraction data were collected with an automated Enraf–Nonius four-circle computer-controlled CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. 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 2θ < 50°, *l* > *h*, and *k* > *h* were recorded. Of the 690 unique reflections examined, only the 263 reflections for which *I* > 3σ(*I*) were used in subsequent structure determination. (More data were used in the final refinement; vide infra.) Calculations were performed with the structure determination program package, *MolEN*.³²

An absorption correction was made empirically using a ψ scan.³³ This correction had little effect on the final *R* indices. Table 1 provides a summary of the experimental data.

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}	varied	occupancy varied with constraints	fixed
(Si,Al)	192(i)		-538(1)	1224(1)	359(1)	225(14)	106(13)	161(13)	-37(13)	-32(12)	-23(13)			192
O(1)	96(h)		-1074(2)	1074(2)	0	237(32)	237(32)	381(59)	75(39)	-33(34)	-33(34)			96
O(2)	96(g)		-27(3)	-27(3)	1472(3)	162(25)	162(25)	271(49)	164(40)	-49(31)	-49(31)			96
O(3)	96(g)		-642(2)	-642(2)	313(3)	283(33)	283(33)	320(58)	-16(47)	81(32)	81(32)			96
O(4)	96(g)		1691(2)	1691(2)	3145(3)	335(35)	335(35)	267(57)	-17(48)	85(36)	65(36)			96
Cd(1)	16(c)	I	0	0	0	152(7)	152(7)	152(7)	-9(8)	-9(8)	-9(8)	14.2(1)	14.1(1)	14.0
Cd(2)	32(e)	II	2309(1)	2309(1)	2309(1)	219(5)	219(5)	219(5)	102(7)	102(7)	102(7)	27.1(2)	26.0(1)	25.6
Cd(3)	32(e)	II'	2059(6)	2059(6)	2059(6)	210(66)						2.4(2)	2.0(1)	2.4
Cd(4)	32(e)	I'	668(7)	668(7)	806(62)	806(62)	806(62)	452(80)	452(80)	452(80)	4.2(2)	3.9(1)	4.0	
I(1)	192(i)		1885(4)	2961(4)	4820(4)	1557(93)	2310(128)	1693(134)	-267(69)	-174(74)	-881(94)	27.3(4)	26.0(1)	25.6
I(2)	32(e)		2956(1)	2956(1)	2956(1)	2099(20)	2099(20)	2099(20)	-837(14)	-837(14)	-837(14)	26.3(3)	26.0(1)	25.6
I(3)	192(i)		2919(4)	3863(5)	2492(6)	3544(142)	2101(107)	1520(85)	-908(81)	-134(120)	-563(94)	25.4(3)	26.0(1)	25.6
I(4)	48(f)		1957(6)	3750	3750	851(112)	5267(185)	5267(185)	0	0	-975(290)	10.8(3)	13.0(1)	12.8

^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 $B_{iso} = 8\pi^2 U_{iso}$.

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 $Mn_{28}Cs_{36}X$.³⁴ Isotropic refinement converged to $R_1 = 0.55$ and $wR_2 = 0.66$.

A Fourier difference electron-density function yielded three strong peaks at (0.0, 0.0, 0.0), (0.232, 0.232, 0.232), and (0.347, 0.347, 0.347) with heights of 23.1, 11.5, and 10.5 $e\text{\AA}^{-3}$, respectively. The isotropic refinement of the framework atoms and these peaks as Cd^{2+} ions at Cd(1) and Cd(2) and iodine atoms at I(2) converged to $R_1 = 0.18$ and $wR_2 = 0.24$, respectively. (Cd^{2+} ions can be distinguished from I atoms by their close approaches to framework oxygens.)

A subsequent difference Fourier synthesis revealed four more peaks at (0.179, 0.179, 0.179), (0.187, 0.297, 0.482), (0.255, 0.263, 0.400), and (0.196, 0.375, 0.375) with heights of 3.7, 3.3, 3.1, and 3.0 $e\text{\AA}^{-3}$, respectively. Inclusion of these peaks in isotropic least-squares refinement as Cd^{2+} ions at Cd(3) and iodine atoms at I(1), I(3), and I(4), respectively, lowered the error indices to $R_1 = 0.100$ and $wR_2 = 0.098$. From the next difference Fourier synthesis, a peak of height 1.4 $e\text{\AA}^{-3}$ was found at (0.067, 0.067, 0.067). Inclusion of this peak as Cd^{2+} at Cd(4) lowered the error indices to $R_1 = 0.094$ and $wR_2 = 0.089$. The anisotropic refinement of all framework atoms, Cd^{2+} ions, and iodine atoms, except Cd(4), which was refined isotropically, converged to $R_1 = 0.042$ and $wR_2 = 0.040$. The refined occupancies of Cd(2), I(1), I(2), I(3), and I(4) were 27.1(2), 27.3(4), 26.3(3), 25.4(3), and 10.8(3), respectively. The occupancies of Cd(2), I(1), I(2), and I(3) were nearly equal, and were constrained to be equal. By the requirement of neutrality, and the avoidance of impossibly close interatomic distances (vide infra), the occupancies at all Cd and I positions were fixed at the values shown in Table 2. The final error indices with 263 reflections for which $I > 3\sigma(I)$ are $R_1 = 0.044$ and $R_2 = 0.043$. The final refinement, the results of which are shown in Table 2, was done using the 495 reflections for which $I > 0$ to make better use of the diffraction data: $R_1 = 0.116$, $R_2 = 0.045$. This allowed the esds to decrease by about 30% of their former values. This result and additional refinement data are given in Table 1. Atomic scattering factors^{35,36} for (Si,Al)^{1.75+}, O²⁻, I⁰, and Cd²⁺ were used. The function describing (Si,Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. All scattering factors were modified to account for anomalous dispersion.³⁷ The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

TABLE 3: Selected Interatomic Distances (Å), Angles (deg), and a Torsion Angle^a

(Si,Al)-O(1)	1.645(3)	O(1)-(Si,Al)-O(2)	112.3(2)
(Si,Al)-O(2)	1.707(5)	O(1)-(Si,Al)-O(3)	107.3(3)
(Si,Al)-O(3)	1.703(6)	O(1)-(Si,Al)-O(4)	112.8(2)
(Si,Al)-O(4)	1.635(5)	O(2)-(Si,Al)-O(3)	107.1(3)
Mean	1.673	O(2)-(Si,Al)-O(4)	104.4(4)
Cd(1)-O(3)	2.389(5)	O(3)-(Si,Al)-O(4)	111.9(2)
Cd(2)-O(2)	2.218(7)	(Si,Al)-O(1)-(Si,Al)	131.4(3)
Cd(3)-O(2)	2.200(9)	(Si,Al)-O(2)-(Si,Al)	134.9(4)
Cd(4)-O(3)	2.441(8)	(Si,Al)-O(3)-(Si,Al)	111.9(4)
Cd(2)-I(2)	2.783(2)	(Si,Al)-O(4)-(Si,Al)	115.4(3)
I(2)-I(3)	2.534(13)	O(3)-Cd(1)-O(3)	89.3(2)/90.7(2)/ 180.(0)
I(3)-I(4)	2.473(14)	O(2)-Cd(2)-O(2)	113.5(2)
I(1)-I(1)	2.757(14)/2.796(13)	O(2)-Cd(3)-O(2)	114.9(2)
I(1)-O(1)	3.167(10)	O(3)-Cd(4)-O(3)	86.93(14)
		O(2)-Cd(2)-I(2)	105.10(13)
		Cd(2)-I(2)-I(3)	103.3(3)
		I(2)-I(3)-I(4)	96.6(4)
		I(3)-I(4)-I(3)	114.8(7)
		O(1)-I(1)-I(1)	159.4(4)
		I(1)-I(1)-I(1)	90.0(5)
		I(1)-I(1)-I(1)-I(1)	0

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

Results and Discussion

Zeolite X. Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The cuboctahedron (14-hedron with 24 vertexes), known as the sodalite cavity or β cage, may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Figure 1). The Si and Al atoms occupy the vertexes of these polyhedra. 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. (An n -ring is composed of n O and n T (Si or Al) atoms.) The oxygen atoms lie approximately midway between each pair of Si and Al atoms but are displaced from those points to be closer to Si and 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

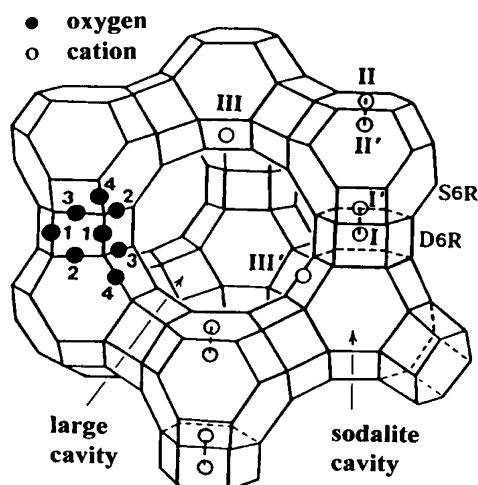


Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The numbers 1 to 4 indicate the four nonequivalent oxygen atoms. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that a silicon atom substitutes for aluminum at about 4% of the Al positions. For the crystal studied here, this is true only in the short range; long-range order is absent (refs 30 and 31). Extraframework cation positions are labeled with Roman numerals.

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 single six-ring (S6R) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a sodalite four-ring (on a 2-fold axis), and III' on the inner surface of the supercage somewhat or substantially off that 2-fold axis.

Cd²⁺ Ions. Forty-six Cd²⁺ ions are found at four crystallographic sites: I, II, I', and II' (see Table 2). In contrast, Cd²⁺ ions occupied only two sites, I (fully) and II, in fully dehydrated Cd₄₆-X,³⁸ so a substantial rearrangement of Cd²⁺ ions has occurred upon iodine sorption. Of the 46 Cd²⁺ ions per unit cell, 6.4 have moved into the sodalite cavities.

Eighteen Cd²⁺ ions occupy sites I and I'. The 14 at Cd(1) occupy the octahedral site I (see Figure 2). The Cd(1)–O(3) distance, 2.389(5) Å, is just a little longer than the sum of the corresponding conventional ionic radii,³⁹ 0.97 + 1.32 = 2.29 Å, indicating a reasonably good fit. The distance between the neighboring positions I and I' is only 2.88 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 $2 \times 2.88 = 5.76$ 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

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

	position	site	displacement
at O(3) ^a	Cd(1)	I	1.40
	Cd(4)	I'	−1.48
at O(2) ^b	Cd(2)	II	0.58
	Cd(3)	II'	−0.50
	I(2)		3.36

^a The positive deviation at Cd(1) indicates that it lies within a D6R. The negative deviation at Cd(4) indicates that it is in the sodalite cavity.

^b Positive deviations indicate that the ion lies in the supercage. The negative deviation indicates that Cd(3) is in the sodalite cavity.

those sites per unit cell. Four Cd²⁺ ions are found at site I', Cd(4), so $n(I) + n(I')/2 = 14 + 4/2 = 16$. Therefore, each D6R either has a Cd²⁺ ion at its center or two just outside. Each Cd(4) ion extends substantially, 1.48 Å, out of the D6R (into the sodalite unit) from its three-O(3) plane (see Figure 2 and Table 4), because of Cd²⁺–Cd²⁺ repulsion through the D6R.

Site II (Cd(2) in the supercage) is occupied by 25.6 Cd²⁺ ions. As compared to the site-II position in dehydrated Cd₄₆-X,³⁸ each Cd²⁺ ion at Cd(2) has moved 0.39 Å further into the supercage from its six-ring plane to coordinate to an iodide ion (a terminal atom of *n*-I₅[−], vide infra) at I(2). Correspondingly, the Cd(2)–O(2) bond has increased from 2.16(1)³⁸ to 2.218(7) Å, closer to the sum of the corresponding conventional ionic radii,³⁹ 2.29 Å. The O(2)–Cd(2)–O(2) bond angle has decreased from a near trigonal planar value of 119.2(5)° in empty Cd₄₆-X³⁸ to 113.5(2)°, closer to tetrahedral.

The remaining 2.4 Cd²⁺ ions are at site II', at Cd(3). Each is recessed 0.50 Å into the sodalite cavity from the S6R plane at O(2). The Cd(3)–O(2) distance, 2.200(9) Å, is again a little less than the sum of the conventional ionic radii,³⁹ 2.29 Å, because of three-coordination. The O(2)–Cd(3)–O(2) bond angle is 114.9(2)°.

Iodine Atoms and Ions. Iodine atoms and ions are found at four sites: 25.6 each at I(1), I(2), and I(3), and 25.6/2 = 12.8 at I(4) in the supercage. The assignment of local structure and charge to these 89.6 iodine atoms or ions in their four fractionally filled equipoints must meet the requirement that the total charge of the sorbed iodine species sum to zero. This is necessary because the structure shows that no oxidation nor reduction of the Cd²⁺ ions has occurred, nor would it have been expected.

Iodide Ions. Among the four iodine positions, only the one at I(2) is close to a Cd²⁺ ion, Cd(2)–I(2) = 2.783(2) Å (see Figure 3). This distance is much shorter than the sum of the ionic radius of Cd²⁺ and the van der Waals radius⁴⁰ of an I atom, 0.97 + 2.15 = 3.12 Å; it is also much shorter than the

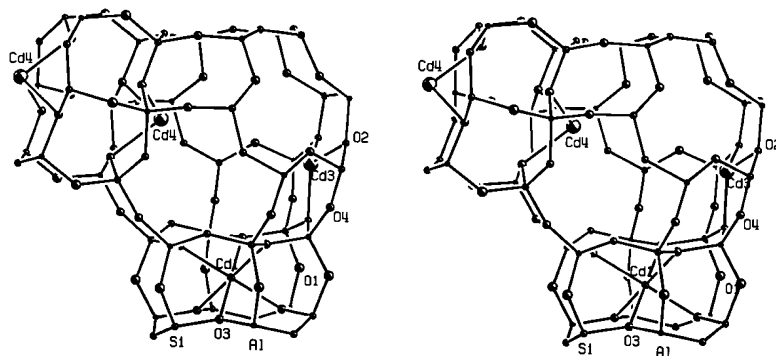


Figure 2. Stereoview of a sodalite cavity with two attached double six-rings in Cd₄₆-X · 89.6I. One Cd²⁺ ion at Cd(1) (site I), one at Cd(3) (site II'), and two at Cd(4) (site I') are shown. Ellipsoids of 20% probability are used.

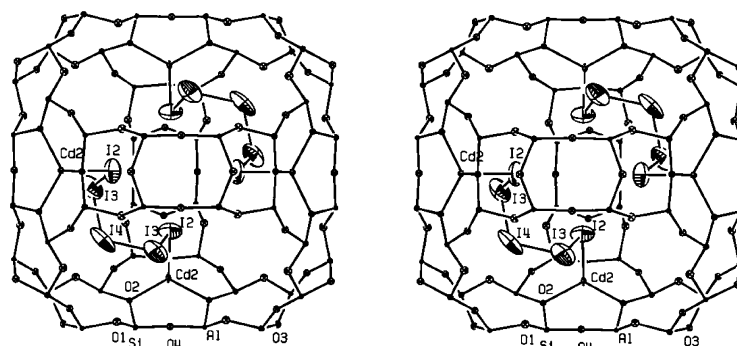


Figure 3. Stereoview of a supercage in $\text{Cd}_{46}\text{-X} \cdot 89.6\text{I}$ with four Cd^{2+} ions at $\text{Cd}(2)$ and two $n\text{-I}_5^-$ anions. Each $n\text{-I}_5^-$ anion, $\text{I}(2)\text{--I}(3)\text{--I}(4)\text{--I}(3)\text{--I}(2)$, bridges between two Cd^{2+} ions at $\text{Cd}(2)$ (site II). Each Cd^{2+} ion at $\text{Cd}(2)$ coordinates to three framework oxygens at $\text{O}(2)$ and to a terminal $\text{I}(2)$ ion. Up to 80% (6.4/8) of the supercages have this arrangement. Ellipsoids of 20% probability are used.

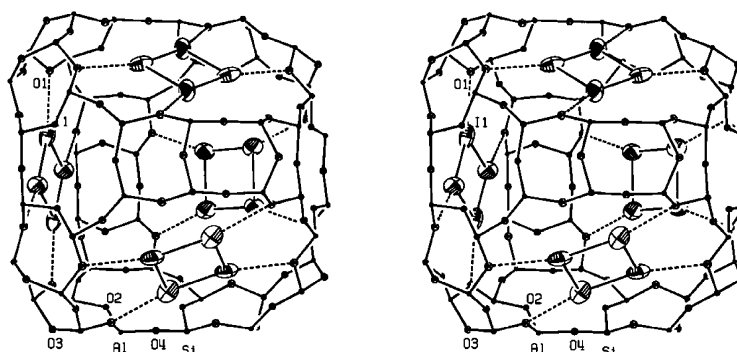


Figure 4. Stereoview of a supercage in $\text{Cd}_{46}\text{-X} \cdot 89.6\text{I}$ with four cyclo-I_4^{2+} ions in its four 12-rings. Each atom of each I_4^{2+} cation interacts both ionically and covalently with an $\text{O}(1)$ framework oxygen. Up to 20% of the supercages may have this particular arrangement. Supercages with one $n\text{-I}_5^-$ and two cyclo-I_4^{2+} ions are likely to occur also. Ellipsoids of 20% probability are used.

sum of the Cd^{2+} and I^- radii, $0.97 + 2.20 = 3.17 \text{ \AA}$. This indicates a strong ionic interaction with substantial covalent character between Cd^{2+} and an $\text{I}(2)$ anion. (The $\text{I}(2)$ anions are the terminal atoms of $n\text{-I}_5^-$ (vide infra).) For comparison, the $\text{Cd}^{2+}\text{--I}^-$ bond distance in solid CdI_2 is 2.55 \AA .⁴¹ $\text{Cd}(2)$ and $\text{I}(2)$ are both on 3-fold axes, and those positions are nearly full (25.6 per 32 equipoints). Each iodide anion at $\text{I}(2)$ completes (with three framework oxygens) a tetrahedron about each Cd^{2+} ion at $\text{Cd}(2)$.

I_3^+ Cations. The $\text{I}(3)\text{--I}(4)$ distance is $2.473(14) \text{ \AA}$, the $\text{I}(3)\text{--I}(4)\text{--I}(3)$ bond angle is $114.8(7)^\circ$, and $\text{I}(4)$ approaches no atom other than $\text{I}(3)$ closely (see Table 3). This indicates that these three atoms are bonded together in a bent manner. The two $\text{I}(3)$ atoms of this I_3 cluster approach two $\text{I}(2)$ anions closely ($\text{I}(2)\text{--I}(3) = 2.534(13) \text{ \AA}$), indicating that this I_3 is a cation. To obey Lewis's rules, it should be I_3^+ . I_3^+ has eight electrons around each iodine, so the electron pairs are tetrahedral and the ion is bent (see Figure 3).

From the study of $\text{I}_3\text{SO}_3\text{F}$,⁴² I_3AlCl_4 ,⁴³ I_3AsF_6 ,⁴⁴ and I_3SbF_6 ,⁴⁵ the structure of I_3^+ is well established. The bent structure of I_3^+ (I--I--I ca. 102°)⁴⁶ was learned by X-ray crystallography⁴⁶ and by Raman^{45,47} and NQR⁴³ spectroscopies. I_3^+ is isostructural with other 20-electron species such as XY_2^+ (an interhalogen cation), SCl_2 , and Te_3^{2-} .

$n\text{-I}_5^-$ Anions. The bent I_3^+ cation has, at each end, a strong, perhaps predominantly ionic, interaction with I^- at $\text{I}(2)$ (see Figure 3). The $\text{I}(2)\cdots\text{I}(3)\text{--I}(4)\text{--I}(3)\cdots\text{I}(2)$ sequence, $\text{I}^-\text{--I}_3^+\text{--I}^-$, can be viewed as the polyatomic iodine anion, $n\text{-I}_5^-$. $\text{I}(4)$ occupies a special position (see Table 2) with point symmetry $mm2$, which is the symmetry of I_3^+ . The symmetry of $n\text{-I}_5^-$ is 2 (see Figure 3).

Various structures have been reported for $n\text{-I}_5^-$. It appears in each case as an assemblage of I^- or I_3^- ions with I_2 molecules,

as $\text{I}_2\cdots\text{I}^-\cdots\text{I}_2$, $\text{I}_3^-\cdots\text{I}_2$, or infinite chains.⁴⁸ The I_3^- ion is linear with two I--I distances (ca. 2.8 to 3.1 \AA), both greater than that in the I_2 molecule (2.67 \AA).⁴⁸ $\text{I--I}\cdots\text{I}$ is also generally close to linear with a much longer $\text{I}\cdots\text{I}$ distance. In contrast, the $\text{I}(2)\text{--I}(3)\text{--I}(4)$ bond angle in this work, $96.6(4)^\circ$, is far from linear, and both the $\text{I}(2)\text{--I}(3)$ and $\text{I}(3)\text{--I}(4)$ distances are shorter (Table 3) than that in I_2 . This indicates that this $n\text{-I}_5^-$ ion is quite unlike those previously reported.

cyclo-I_4^{2+} Cations. With 12.8 I_5^- ions per unit cell, the remaining iodine species (at $\text{I}(1)$) must have in total a $12.8+$ charge to achieve charge balance. The 25.6 iodine atoms at $\text{I}(1)$ are close to framework oxygens ($\text{I}(1)\text{--O}(1) = 3.167(10) \text{ \AA}$), indicating that $\text{I}(1)$ is positive. $\text{I}(1)\text{--I}(1) = 2.757(14) \text{ \AA}$ and $\text{I}(1)\text{--I}(1)\text{--O}(1) = 159.4(4)^\circ$ suggest that I_2^+ may exist, forming a near linear charge-transfer complex with a framework oxygen. The I_2^+ cation may be viewed as an I_2 molecule that has lost one electron from a π^* orbital. However the I_2^+ bond length seen here is about 0.2 \AA longer than that in some other I_2^+ complexes.⁴⁸ This can be attributed to electron-pair delocalization from a framework oxygen into a σ^* orbital on I_2^+ , but it could also be because each iodine atom bonds to two iodine atoms instead of one. Cotton and Wilkinson⁴⁹ discuss I_2^+ and indicate that rectangular dimers, I_4^{2+} , sometimes form. This is reasonable because I_2^+ is an odd ion.

The $\text{I}(1)$ atoms occupy 12-rings with $\text{I}(1)\text{--I}(1) = 2.757(14)$ and $2.796(13) \text{ \AA}$, $\text{I}(1)\text{--I}(1)\text{--I}(1) = 90.0(5)^\circ$, and $\text{I}(1)\text{--I}(1)\text{--O}(1) = 0^\circ$. The cyclo-I_4^{2+} ion would have, within esds, a square-planar geometry (see Figure 4). Although it is possible that 12.8 I_2^+ ions occupy the 16 12-rings per unit cell, $6.4 \text{ cyclo-I}_4^{2+}$ ions seem far more likely. Because it occupies a site of symmetry $\bar{3}$, some distortion is to be expected. The hypothetical cation cyclo-I_4^{4+} would have an octet of electrons about each atom. Square-planar cyclo-I_4^{2+} would have two more electrons

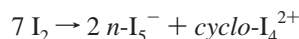
fully delocalized in the lowest π^* orbital, causing its I—I bond to be longer.

Iodine sorption and disproportionation has proceeded until any further sorption in the same positions would have led to unacceptably close contacts. The 12.8 $n\text{-I}_5^-$ anions and 6.4 cyclo-I_4^{2+} cations require, respectively, $12.8/2 = 6.4$ supercages (see Figure 3) + $6.4/4 = 1.6$ supercages (see Figure 4). The sum, $6.4 + 1.6 = 8$, is the number of supercages per unit cell. From this, it can be seen that there are not enough 8-rings for I_2^+ ions, so cyclo-I_4^{2+} must exist. It is likely that some supercages will contain one $n\text{-I}_5^-$ and two cyclo-I_4^{2+} ions; the cyclo-I_4^{2+} cations need not be as segregated as shown in Figure 4.

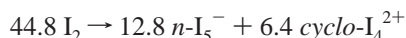
When a zeolite causes a sorbate to disproportionate to form cations and anions, it is behaving as a solid electrolyte.⁵⁰ The classical demonstration of this in a zeolite was the sorption of NO into dehydrated Na—Y to give, among other products, NO^+ and NO^- .⁵¹ The present work is another example of the disproportionation of a sorbate upon sorption into a zeolite, and the second for the sorption of an element.

Conclusions

This work shows that iodine, like sulfur, disproportionates upon sorption into $\text{Cd}_{46}\text{—X}$. The net reaction within the zeolite upon the sorption of iodine is



Per unit cell, the reaction is



This constitutes the electronic disproportionation of an element upon sorption into a zeolite. The primary driving forces for this reaction are the strong bonds formed between Cd^{2+} and the terminal iodides of $n\text{-I}_5^-$, coupled with the need for the 3-coordinate Cd^{2+} ions to increase their coordination numbers. Also important is the ability of the anionic zeolite to provide a hospitable environment for the cyclo-I_4^{2+} cations, as it had for the polyatomic sulfur cations²⁶ and as cryptate molecules had for Na^+ and I^+ cations.^{11–16}

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

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