Co^{2+} 이온과 TI^+ 이온으로 이온교환된 제올라이트 X, Co13TI66 − X를 탈수한 결정구조

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Crystal Structure of Dehydrated Co^{2+} and TI^+ − Exchanged Zeolite X, Co13TI66 − X

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요 약

Co^{2+} 이온과 TI^+ 이온으로 치환한 제올라이트 X(Co13Tl66Al92Si100O384 ; $a = 24.617(1)$ Å)를 탈수한 구조를 21 ℃에서 입방공간군 $Fd\bar{3}$을 사용하여 단결정 X-선 회절법으로 해석하고 정밀화하였다. 이 결정은 $Co(NO_3)_2$와 $Tl(NO_3)_2$의 농도가 각각 0.025 M 되도록 만든 혼합용액을 이용하여 흐름법으로 이온교환하여 만들었다. 이 결정은 380℃에서 2×10^{-6} Torr 하에서 2일간 진공 탈수하였다. Full − matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 257 개의 독립반사를 사용하여 최종오차인자를 $R_1 = 0.067, R_2 = 0.064$까지 정밀화시켰다. 이 구조에서 Co^{2+} 이온과 TI^+ 이온은 서로 다른 4개의 결정학적 자리에 위치하고 있었다. 13개의 Co^{2+} 이온은 이중 6 − 산소 고리(D6R)의 중심에 위치하였고(자리 I ; Co − O = 2.26(3) Å, O − Co − O = 91(1)°), 6개의 Tl^+ 이온은 D6R의 맞은편에 있는 소다라이트 동공

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에 있는 자리 I'에 위치하였고(Tl－O＝2.67(3)Å, O－Tl－O＝73(1)°), 30개의 Tl⁺ 이온은
큰 동공에 있는 자리 II에 위치하였다(Tl－O＝2.56(2) Å, and O－Tl－O＝89(1)°). 6개의
Tl⁺ 이온은 가장 가까운 산소 평면에서 소다라이트 동공쪽으로 1.95 Å 들어간 자리에 위치
하였고 30개의 Tl⁺ 이온은 가장 가까운 산소 평면에서 큰 동공쪽으로 1.50 Å 들어간 자리
에 위치하였다. 30 개의 Tl⁺ 이온은 큰 동공에 있는 자리 III에 위치하고 있었다(Tl－O＝
2.79(3) Å and O－Tl－O＝68.6(8)°).

Abstract

The crystal structure of dehydrated Co^{2+} and Tl^+- exchanged zeolite X, stoichiometry $Co_{13}Tl_{66}-X(Co_{13}Tl_{66}Al_{92}Si_{100}O_{384})$ per unit cell(a＝24.617(1) Å), has been determined from three－dimensional X－ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group $Fd\bar{3}$ at 21(1) ℃. The crystal was prepared by ion exchange in a flowing stream using a solution 0.025M each in $Co(NO_3)_2$ and $Tl(NO_3)$. The crystal was then dehydrated at 380℃ and 2×10^{-6} Torr for two days. The structure was refined to the final error indices, R_1＝ 0.067 and R_2＝0.064 with 257 reflections, for which $I>3\sigma(I)$. Co^{2+} ions and Tl^+ ions are located at the four different crystallographic sites : thirteen Co^{2+} ions are located at the center of the double six ring(site I ; Co－O＝2.26(3) Å, O－Co－O＝91(1)°), six Tl^+ ions lie at site I', in the sodalite cavity opposite double six rings(Tl－O＝2.67(3)Å, O－Tl－O＝73(1)°) and another thirty Tl^+ ions are located at the site II in the supercage(Tl－O＝2.56(2) Å, and O－Tl－O＝89(1)°). Six Tl^+ ions are recessed $ca.$ 1.95 Å into the sodalite cavity from oxygen plane and thirty Tl^+ ions are recessed 1.50 Å into the supercage from the three oxygen plane, respectively. Thirty Tl^+ ions lie at the site III in the supercage(Tl－O＝2.79(3) Å and O－Tl－O＝68.6(8)°).

Ⅰ. Introduction

The zeolite X of isomorph of the mineral faujasite has an open, negatively charged framework. The exchangeable cations can be located on various sites. Some of these sites, in the large cages, are easily accessible, while others are located in the dense cages. The limited dimensions of the apertures which control access to these small cavities are frequently given as a factor limiting the ion exchange[1,2].

Cation substitution into zeolite X is one of the methods of modification of their physical

and chemical properties, so the problem of reactivity and located of multivalent – exchanged ions is of interest from both theoretical and practical points of view. The distribution and coordination of various cations in the framework of faujasite – type zeolites have been widely investigated and reviewed[3].

Zeolites have been the subject of numerous investigations because of their importance in adsorption and catalysis. Accordingly, a variety of reactions have been strudied over transition metal exchanged zeolites. For example, the dehydrogenation of alkanes[4], the conversion of alcohols to aldehydes and ketones[5], and the oxidation of n – hexane to carboxylic acids[6-9] have been conducted over A – and X – type zeolites containing Cr(II), Mn(II), Fe(II), Co(II), or Ni(II) ions. Intrazeolitic transition metal complexes have also been characterized spectroscopically. By means of reflectance spectroscopy, Klier and Ralek[10,11] studied complexes of Co(II) and Ni(II) with H_2O, NH_3, N_2O, and cyclopropane in A – type zeolite systems. Also, Boudart et al[12]., employing Mössbauer spectroscopy, examined Fe(II) complexes of several small molecules such as N_2, O_2, CO, pyridine, CS_2, and alcohols in Y – type zeolites. Gallezot and Lmelik[13-15] present X – ray powder data which show that Ni(II) and Co(II) prefer I whereas Cu(II) prefers I' in dehydrated Y zeolites.

Recently single – crystal X – ray studies on hydrated and dehydrated chabazite[16,17] and heulandite[18], exchanged under controlled conditions with mono – and di – valent cations, have shown that the extra – framework structure, especially the cation distribution, may be rationalized, to a large extent, in terms of the size, charge and electronic nature of the exchanged cation. In addition, these studies have shown that the comparison of the electron density maps of the same zeolite, exchanged with different cations, may be useful in determining sites of cations and possibly the approximate ratio of two different cations at the same site[18].

The present study has been initiated to investigate the cation positions in zeolite X. Because the ionic radii of Co^{2+} and Tl^+ ion are quite different, precise and reliable crystallographic determination should be easy to achieve. The present work is preliminary to later studies of crystal structures of $Co_{46-x}Tl_{2x}$ – X absorbed with other guest molecules.

II. Experimental Section

Large single crystals of sodium zeolite X, stoichiometry $Na_{92}Al_{92}Si_{100}O_{384}$, were prepared in St. Petersburg, Russia[19]. One of these, a colorless octahedron about 0.2 mm in cross – section was lodged in a fine Pyrex capillary.

$Co_{13}Tl_{66}$ – X was prepared using an exchange solution in which mole ratio $Co(NO_3)_2$ and $Tl(NO_3)$ was 1 : 1 with total concentration of 0.05 M. Ion exchange was accomplished by flow methods ; the solution was allowed to flow past each crystal at a velocity of approximately 1.5 cm/s for 5 days at 24(1) ℃. The hydrated crystal was dehydrated at 380 ℃ and 2×10^{-6} Torr for 2 days.

After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal has become red.

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an automated Enraf – Nonius four – circle computer controlled CAD – 4 diffractometer equipped with a pulse – height analyzer and a graphite monochromator, using Mo Kα radiation(Kα_1, λ=0.70930 Å, Kα_2, λ=0.71359 Å). The unit cell constants at 21(1) ℃ determined by least – squares refinement of 25 intense reflections for which 14° $<2\theta<24°$ are a=24.617(1) Å.

The $\omega - 2\theta$ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 and 0.34 deg min^{-1} in ω. 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 collection. The intensities of all lattice points for which $2\theta<60°$ were recorded.

Of the 1150 reflections examined, only the 257 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

The intensities were corrected for Lorentz and polarization effects ; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, GENESIS, PROCESS and WEIGHT[20].

An absorption correction(μR=0.865, ρ_{cal}=2.860g/cm^3 and $F(000)$=11319) was made empirically using a Ψ scan[21]. The calculated transmission coefficients ranged from 0.971 to 0.982. This correction had little effect on the final R indices.

Ⅲ. Structure Determination

Full – matrix least – squares refinement of dehydrated $Co_{13}Tl_{66}$ – X was initiated with atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated Ca_{46} – X[22]. Initial isotropic refinement of the framework atoms converged to an R_1 index, (Σ |F_o – |F_c||)/ΣF_o) of 0.64 and a weighted R_2 index, (Σ w(F_o – |F_c|)^2/

$\Sigma wF_0^2)^{1/2}$ of 0.71.

A initial difference Fourier function showed the positions of Tl⁺ ions at Tl(2), (0.251, 0.251, 0.251) with peak height 21.86 eÅ^{-3} Co²⁺ ions at Co(1), (0.0, 0.0, 0.0) with peak height 12.44 eÅ^{-3} and Tl⁺ ions at Tl(2), (0.41, 0.125, 0.125) with peak height 8.61 eÅ^{-3}. These were stable in least – squares refinement. Anisotropic refinement of framework atoms and isotropic refinement of Tl(1), Co(1) and Tl(2) converged to $R_1 = 0.123$ and $R_2 = 0.134$ with occupancies of 13.4(4), 29.8(2), and 29.7(3), respectively(see Table I)

It is not so difficult to distinguish Co²⁺ from Tl⁺ ions for several reasons. First, their ionic radii are different, Co²⁺ = 0.72 Å and Tl⁺ = 1.47 Å, and their atomic scattering factors are also different, 25 e⁻ for Co²⁺ vs. 80 e⁻ for Tl⁺[23]. Secondly, the approach distances between those ions and zeolite oxide ions in the previous dehydrated Co₄₁Na₁₀ – X[24](see Table I and II) and Tl₉₂ – X[25] have been determined and are indicative. Finally, the requirement that 92 monovalent metal ion(or 46 divalent metal ion) per unit cell be found do not allow the major positions to refine to acceptable occupancies with the alternative assignment of ionic identities

From a successive difference Fourier, one peak was found at (0.074, 0.074, 0.074), height = 8.08 eÅ^{-3}, which refined as Tl(1). Simultaneous positional occupancy, and isotropic thermal parameter refinement converged to the error indices $R_1 = 0.066$ and $R_2 = 0.062$. The occupancy numbers of Tl(1), Co(1), Tl(2), and Tl(3) were reset and fixed as in the last column of Table I.

All shifts in the final cycles of least – squares refinement were less than 0.1% of their

Table 1. Positional, Thermal[a], and Occupancy Parameters

Atom	Wyc. Pos.	x	y	z	β_{11}[b] B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[c] varied	fixed
Si	96(g)	−516(5)	1224(7)	347(5)	3(2)	5(2)	3(2)	−5(5)	2(5)	−4(5)		96
Al	96(g)	−538(5)	360(6)	1223(7)	−0(2)[d]	8(3)	2(2)	−2(5)	−1(6)	−5(5)		96
O(1)	96(g)	−1060(10)	50(20)	1060(10)	15(8)	1(5)	7(6)	20(10)	−0(10)	−20(10)		96
O(2)	96(g)	−20(2)	−50(20)	1510(10)	9(5)	16(6)	8(5)	30(10)	−20(20)	−10(20)		96
O(3)	96(g)	−290(10)	620(10)	610(10)	14(7)	1(6)	10(7)	20(10)	−10(10)	10(10)		96
O(4)	96(g)	−679(9)	820(10)	1720(10)	−3(5)[d]	11(6)	−6(4)[d]	−2(10)	−7(8)	12(8)		96
Co(1)	16(c)	0	0	0	3(1)	3(1)	3(1)	−2(4)	−2(4)	−2(4)	13.4(4)	13
T(1)	32(e)	768(6)	768(6)	768(6)	10(2)	10(2)	10(2)	3(5)	3(5)	3(5)	6.3(5)	6
T(2)	32(e)	2545(1)	2545(1)	2545(1)	8(1)	8(1)	8(1)	−1(1)	−1(1)	−1(1)	29.8(2)	30
T(3)	48(f)	4115(3)	1250	1250	5(1)	63(4)	84(4)	0	0	−42(6)	29.7(3)	30

[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[− $\beta_{11}h^2 + \beta_{22}K^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$)].
[c] Occupancy factors are given as the number of atoms or ions per unit cell.
[d] This physically unacceptable value was increased by 1σ in the preparation of Figures 2 and 3.

corresponding standard deviations. The final error indices converged to $R_1 = 0.067$ and $R_2 = 0.064$. The final difference function was featureless except for a peak at (0.345, 0.914, 0.672) of height 1.28 e Å^{-3}. This peak was not within bonding distance of any other atom, and was not considered further.

All crystallographic calcuations were done using the MolEN(a structure determination package programs supplied by Enraf–Nonius). The full–matrix least–squares program used minimized $\Sigma w(F_o - |F_c|)^2$; the weight(w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[26,27] for Si, Al, O$^-$, and Co^{2+}, and Tl$^+$ were used. All scattering factors were modified to account for anomalous dispersion[28]. The final structural parameters and selected interatomic distances and angles are presented in Tables I and II, respectively.

Table II. Selected Interatomic Distances(Å) and Angles(deg)[a]

Framework	Co13Tl66 – X
Si – O(1)	1.71(2)
Si – O(2)	1.62(4)
Si – O(3)	1.71(4)
Si – O(4)	1.59(3)
average	**1.66(3)**
Al – O(1)	1.55(4)
Al – O(2)	1.77(5)
Al – O(3)	1.75(4)
Al – O(4)	1.71(3)
average	**1.70(4)**
Co(1) – O(3)	2.26(3)
Tl(1) – O(3)	2.67(3)
Tl(2) – O(2)	2.56(2)
Tl(1) – O(1)	3.30(4)
Tl(4) – O(4)	2.79(3)
O(1) – Si – O(2)	110(2)
O(1) – Si – O(3)	105(2)
O(1) – Si – O(4)	110(2)
O(2) – Si – O(3)	111(2)
O(2) – Si – O(4)	104(2)
O(3) – Si – O(4)	116(2)
O(1) – Al – O(2)	114(2)
O(1) – Al – O(3)	104(2)
O(1) – Al – O(4)	110(2)
O(2) – Al – O(3)	108(2)
O(2) – Al – O(4)	104(2)
O(3) – Al – O(4)	117(2)
Si – O(1) – Al	133(2)
Si – O(2) – Al	130(2)
Si – O(3) – Al	122(2)
Si – O(4) – Al	153(2)
O(3) – Co(1) – O(3)	91(1)
O(3) – Tl(1) – O(3)	73(1)
O(2) – Tl(2) – O(2)	89(1)
O(1) – Tl(3) – O(1)	131.0(8)
O(4) – Tl(3) – O(4)	68.6(8)

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

IV. Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The polyhedron with 14 vertices known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Fig. 1). These β–cages are connected tetrahedrally at 6–rings by bridging oxygens to give double 6–rings(D6R's, hexagonal prisms), and, concomitantly, an interconnected set of large cavities(supercages) accessible in three dimensions through 12–ring(24–membered) windows. The Si and Al atoms occupy the vertices of

Table III. Deviations(Å) of Cations from 6 – Ring Planes

	Co₁₃Tl₆₆ – X
at O(3)ᵃ	
Co(1)	– 1.32(1)
Tl(1)	1.95(1)
at O(2)ᵇ	
Tl(2)	1.50(1)

ᵃA negative deviation indicates that the atom lies in the D6R.

ᵃA positive deviation indicates that the atom lies in the sodalite unit.

ᵇA positive deviation indicates that the atom lies in the supercage.

these polyhedra. The oxygen atoms lie approximately half – way between each pair of Si and Al atoms, but are displaced from those points to give near tetrahedral angles about Si and Al.

There are exchangeable cations which balance the negative charge of the aluminosilicate framework located within cavities. The exchanged cations can be located on various sites ; site I in a hexagonal prism (double 6 – ring), site I′ near the single 6 – ring entrance to a hexagonal prism in the sodalite(β) cavity, II′ inside the sodalite cavity near the single

Table IV. Distribution of Nonframework Atoms over Sites

	Sites	Occupancy
Co(1)	I	13
Tl(1)	I′	6
Tl(2)	II	30
Tl(3)	III	30
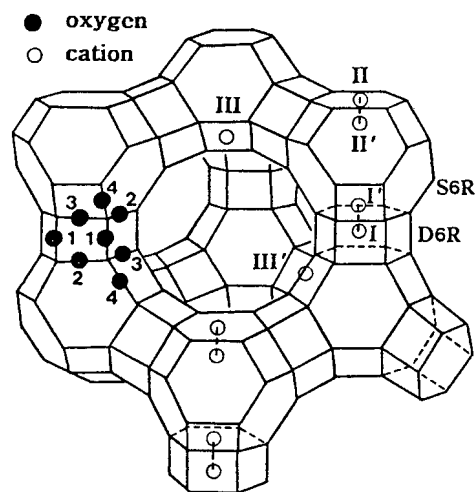
Fig. 1. A stylized drawing of the framework structure of zeolite X.

Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

6 – ring(S6R) entrances to the large(α) cavity, II in the supercages adjacent to S6R, III in supercage opposite O(3) and O(4) ring of 4 – ring, and III′ somewhat off III(off the twofold axis)(see Fig. 1).

In this structure, thirteen Co²⁺ ions occupy only one crystallographic site and about sixty – six Tl⁺ ions are found at three such sites. The Co²⁺ ions at Co(1) lie at site I, at the centers of the double six – oxygen rings(D6R′s). Each Co²⁺ ion at Co(1) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.26(3), which is longer than the sum of the ionic radii of Co²⁺ and O²⁻, $0.72 + 1.32 = 2.04$ Å [23]. This distance is very similar to the distance of the previous Co²⁺ ions in the structure of Co₄₁Na₁₀ – X [24].

Fig. 2. A stereoview of sodalite cavity of dehydrated Co13Tl66 – X. One Co^{2+} ion at Co(1) lies at site I and four Tl$^+$ ions at Tl(2) lie at site II. About 56% of the sodalite cavities may have this arrangement. About 25% may have only three Tl$^+$ ions at Tl(2). Remaining about 19% two Tl$^+$ ions at Tl(1) and four Tl$^+$ ions at Tl(2). Ellipsoids of 20% probability are shown.

The Tl$^+$ ions at Tl(1)(see Fig. 1) lie at site I′, in the sodalite cavity opposite double – six – rings(D6R′s). This is 32 – fold position, but it is occupied by only 6 Tl$^+$ ions. Each Tl$^+$ ion coordinates at 2.67(3) Å to three O(3) framework oxygens, and is recessed *ca.* 1.95 Å into the sodalite cavity from their plane. For comparison, the sum of ionic radii of Tl$^+$ and O^{2-}, 1.47+1.32=2.79 Å[23]. Also 30 Tl$^+$ ions at Tl(2) lie at site II and are recessed 1.50 Å into the supercage from the single 6 – ring plane at O(2). Each these Tl$^+$ ions coordinates to three O(2) oxygens at 2.56(2) Å, somewhat less than the sum of Tl$^+$ and O^{2-} radii, 2.79 Å. The angle subtended at Tl(2), O(2) – Tl(2) – O(2) is 89(1)°.

Thirteen Co^{2+} ions at Co(1) are occupied at site I, the center of double six ring. The positions of Tl$^+$ ions at Tl(1) are close to site I. Therefore, if site I is occupied by a Co^{2+} ion, the two adjacent site I′, the position of Tl$^+$ ion at Tl(1) are not occupied because of electrostatic repulsive force of cations.

Thirty Tl$^+$ ions at Tl(3) lie in the supercage at site III. This is 48 – fold positions, but this is occupied by only 30 ions(see Fig. 1 and 2). The Tl$^+$ ions at Tl(3) are coordinated to framework oxygens, Tl(3) – O(1)=3.30(4) Å and Tl(3) – O(4)=2.79(3) Å. For comparison the sum of the corresponding ionic radii is 1.47+1.32=2.79 Å[23].

Recently the crystal structures of dehydrated Ca46 – X[22], Cd46 – X[29], Sr46 – X[30], Mn46 – X[30], Mg46 – X[30], Ba46 – X[31], and Ca32K28 – X[22] have been determined. The divalent cations, Ca^{2+}, Cd^{2+}, Sr^{2+}, and Mn^{2+} ions are located at two different sites of high occupancies : sixteen at site I and thirty at site II. In the crystal structures of the Ba46 – X and Mg46 – X, Ba^{2+} and Mg^{2+} ions are located at the three different sites ; fourteen at site I, two at site I′, and thirty at site II. In the crystal structure of Ca32K28 – X, smaller Ca^{2+} ions occupy the smaller pore site(16 at site I and 12 at site III). Therefore, the present structure is in

Co^{2+} 이온과 Tl$^+$ 이온으로 이온교환된 제올라이트 X, Co$_{13}$Tl$_{66}$ - X를 탈수한 결정구조
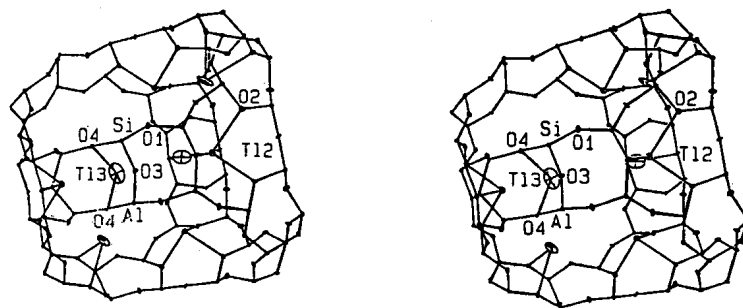
Fig. 3. A stereoview of large cavity of dehydrated Co$_{13}$Tl$_{66}$ - X.
Four Tl$^+$ ions at Tl(2) lie at site I and four Tl$^+$ ions at Tl(2) lie at site II. About 50% of the large cavities may have this arrangement. About 25% may have three Tl$^+$ ions at Tl(2) and four Tl$^+$ ions at Tl(2). Remaining about 25% four Tl$^+$ ions at Tl(2) and three Tl$^+$ ions at Tl(3). Ellipsoids of 20% probability are shown.

good agreement with the previous works.

In summary, the smaller and more highly charged Co^{2+} ions fill the site I position, affirming that Co^{2+} ions prefer site I. The large Tl$^+$ ions, which are less able to balance the anionic charge of the zeolite framework because of their larger size and smaller charge, avoid D6R's and finish filling sites I' and II, with the remainder going to the least suitable cation site in the structure, site III. In this structure all Co^{2+} and Tl$^+$ ions are located in sites I, I', II, and III. The Co^{2+} ions are not found in the sites II and III.

Acknowledgement

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Supplementary Table.
Observed and calculated structure factors for dehydrated Co₁₃Tl₆₆ - X.

Values of 10*Fobs and 10*Fcalc

Page 1

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
0	0	4	5547	5395	92	1	7	19	8104	7844	249
0	0	8	24016	25489	83	1	9	9	4966	5449	197
0	0	12	15627	15213	117	1	9	19	7655	7487	258
0	0	16	18657	18795	140	1	9	25	3813	4305	571
0	0	20	9514	9239	222	1	11	11	17777	17443	138
0	0	24	14895	15235	223	1	11	13	2985	3179	436
0	0	32	5280	6967	668	1	11	15	4974	5641	306
0	2	2	9509	10873	56	1	13	17	4924	5771	363
0	2	18	3788	3264	357	1	15	19	4680	5967	433
0	4	4	29504	29989	76	1	17	21	5308	4832	427
0	4	8	21814	20753	91	1	23	23	6285	6107	550
0	4	12	13064	13459	124	2	2	2	16931	17533	53
0	4	16	18273	17868	142	2	2	4	4916	5467	115
0	4	20	10575	10499	226	2	2	6	17725	18196	78
0	4	24	5680	4942	384	2	2	8	15917	14801	93
0	4	28	5849	5931	467	2	2	10	17982	18062	103
0	6	6	6029	5651	142	2	2	12	10763	10383	129
0	6	10	7734	7747	146	2	2	14	12381	12201	139
0	6	22	3651	3808	492	2	2	18	8051	7559	224
0	6	26	4278	4546	509	2	2	22	8767	8385	241
0	8	8	27148	24855	105	2	2	26	4283	3761	507
0	8	12	17396	18242	131	2	4	6	2754	2670	243
0	8	16	9463	9235	202	2	4	14	4207	4232	262
0	8	20	18303	18071	185	2	6	6	15303	14820	94
0	8	24	5987	6209	378	2	6	10	12872	13191	121
0	8	28	4883	4627	521	2	6	12	2726	2791	325
0	8	32	5741	5125	565	2	6	14	7815	8733	185
0	10	10	15868	15642	133	2	6	18	8577	8169	220
0	10	22	3778	3131	489	2	6	22	6660	5918	313
0	12	12	26379	25462	144	2	8	8	2823	1997	279
0	12	16	10754	10948	216	2	8	18	3206	3137	492
0	12	20	6453	6565	340	2	10	10	13008	12936	138
0	12	24	4692	3895	476	2	10	14	9957	9725	179
0	12	28	9801	10005	357	2	10	18	8907	9018	236
0	14	26	5070	4387	523	2	10	20	5100	4354	372
0	16	16	4449	4802	424	2	10	22	4720	4942	439
0	16	20	7583	7246	328	2	10	28	4485	4163	585
0	16	24	5918	6303	447	2	14	14	6453	5803	281
0	16	28	5851	6065	580	2	14	18	7621	7219	275
0	20	20	5891	7087	450	3	3	3	7234	6789	96
0	20	24	5262	5330	611	3	3	5	7545	8859	112
0	22	22	8586	9962	420	3	3	7	15303	15306	92
1	1	1	16177	15151	40	3	3	15	8006	8144	185
1	1	3	5308	5883	85	3	5	7	7807	8419	120
1	1	7	4549	4646	157	3	5	9	7086	7148	139
1	1	9	11020	10593	105	3	5	11	2567	2854	311
1	1	17	4359	4537	338	3	5	15	4671	3970	269
1	1	19	7731	8535	236	3	5	19	4277	4292	374
1	1	21	8798	9277	243	3	5	21	4566	5031	393
1	1	23	5113	4242	377	3	7	9	2434	1755	332
1	3	3	2801	2777	158	3	7	11	9734	9185	140
1	3	9	5860	5505	149	3	7	13	5447	3969	212
1	3	13	5280	4646	191	3	7	19	4429	4699	385
1	3	15	6037	5647	211	3	7	23	7234	7665	317
1	3	17	4466	4519	312	3	9	11	2737	2609	357
1	3	23	4823	5032	421	3	9	13	3710	3410	310
1	5	5	11396	11317	91	3	9	17	8009	8892	237
1	5	15	6206	6233	217	3	11	13	3322	1160	362
1	5	17	3583	3082	379	3	11	19	7235	6886	293
1	5	21	3196	1085	483	3	13	15	3165	3017	458
1	7	7	8816	9151	120	3	15	19	5690	5181	381
1	7	9	3944	3164	226	4	4	4	9954	9472	97
1	7	15	5653	5460	234	4	4	8	24033	24668	94

장세복·박상윤·김 양

Values of 10*Fobs and 10*Fcalc

H	K	L	Fobs	Fcalc	SigF
4	4	12	21654	21929	117
4	4	16	10863	10787	180
4	4	18	3432	5080	414
4	4	20	7277	7274	268
4	4	24	9699	10396	261
4	4	28	4292	4306	586
4	4	32	5753	5742	583
4	6	6	6633	6799	134
4	6	8	3504	4210	218
4	6	10	3800	3032	244
4	6	14	6218	6804	216
4	8	8	11857	12600	125
4	8	12	12142	11741	147
4	8	16	10747	10933	185
4	8	20	9865	10161	237
4	8	24	5492	5955	435
4	8	28	8060	7379	388
4	10	14	3481	3596	398
4	10	26	4627	3280	502
4	12	12	13936	15065	164
4	12	16	6935	6898	274
4	12	20	11043	11182	241
4	12	24	6226	6694	398
4	12	32	5256	3660	672
4	14	14	3885	4415	424
4	16	16	11047	11561	230
4	16	20	8105	8628	320
4	20	20	5033	4429	508
5	5	5	20360	18421	90
5	5	7	4424	6115	183
5	5	9	6453	5880	155
5	5	11	5596	5384	191
5	5	17	11953	13147	188
5	5	19	3415	3268	461
5	5	21	3339	3803	490
5	7	7	3400	1437	218
5	7	15	4386	4819	312
5	7	19	3530	3266	462
5	7	23	6024	5582	354
5	9	13	4468	4733	284
5	9	17	4977	4482	351
5	9	25	5128	5871	467
5	11	17	4236	4239	407
5	11	23	3824	3487	555
5	11	27	5626	4928	476
5	13	13	3588	4098	384
5	13	21	4693	3131	444
5	15	15	3684	3779	451
5	15	19	4271	4799	486
5	17	29	5368	5543	626
6	6	6	5500	5122	151
6	6	10	13503	13508	124
6	6	12	7139	6657	190
6	6	14	7452	6969	198
6	6	16	14068	13724	175
6	6	18	8653	8663	247
6	6	28	5505	5219	503
6	8	14	6041	5795	250
6	10	10	11691	11664	150
6	10	14	10037	10131	195
6	10	16	3260	2293	471
6	10	18	6807	7227	295
6	16	18	5068	5134	391
6	18	18	4609	4617	480
7	7	7	16012	15075	116
7	7	9	5933	5726	180
7	7	11	5457	5464	224
7	7	15	4682	5132	320
7	7	19	5115	4698	343
7	7	27	4351	2841	587
7	9	9	3380	2847	305
7	9	15	3990	2690	365
7	9	21	4048	3767	462
7	11	11	7448	7417	217
7	11	15	8410	8588	242
7	11	23	5186	3631	424
7	15	15	6031	6570	341
7	15	27	4733	4256	606
7	17	17	5768	5281	387
7	19	19	6662	7789	415
8	8	8	17829	17201	124
8	8	12	23008	22904	137
8	8	16	13091	12302	185
8	8	20	8579	8328	268
8	8	24	7541	7572	352
8	10	10	3922	2741	302
8	10	18	3976	4208	422
8	12	12	6081	6346	267
8	12	16	11720	11898	211
8	12	20	7580	7558	304
8	12	28	5022	4358	614
8	16	16	7545	8585	297
8	18	22	3919	3193	591
9	9	9	13066	12286	148
9	9	11	6106	5021	228
9	11	11	3208	3914	425
9	11	17	4494	3585	380
9	13	13	9784	9217	225
9	15	15	4490	4759	420
9	17	21	4822	4600	534
9	19	23	5215	3933	594
9	21	21	4599	5096	625
10	10	10	9975	10207	188
10	10	14	8396	8478	238
10	10	22	5826	6707	420
10	12	22	5592	5595	428
10	14	14	6691	7318	302
10	14	18	5945	4924	364
10	18	22	4604	3852	618
11	11	11	5198	4888	309
11	11	17	5123	3600	372
11	11	19	5715	6080	379
11	11	21	5184	4741	456
11	11	23	7818	7851	375
11	15	15	7343	6460	299
11	19	19	6223	5954	445
12	12	12	8860	8731	244
12	12	16	9705	9834	253
12	12	20	6013	6412	411
12	12	24	7600	7796	401
12	14	14	3992	3858	452
12	16	16	8357	9043	324
12	16	20	5447	5813	483
12	18	18	4284	2363	537
12	20	20	8863	8801	383
13	13	21	3989	4023	600
14	14	14	4327	3751	461
14	18	18	5321	4123	506
15	15	15	6142	6105	376
16	20	20	6030	5957	565
17	17	17	10221	11418	336