JOURNAL OF SOLID STATE CHEMISTRY 37, 133–139 (1981)

The Crystal Structures of α- and β-CdUO$_4$

TOSHIYUKI YAMASHITA, TAKEO FUJINO, NORIO MASAKI, AND HIROAKI TAGAWA*

Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, 319-11, Japan

Received April 21, 1980; in revised form August 4, 1980

The structural parameters of α- and β-CdUO$_4$ crystals are determined by X-ray powder diffraction technique. α-CdUO$_4$ is rhombohedral and cell parameters are $a = 6.233(3)$ Å and $\alpha = 36.12(5)°$. β-CdUO$_4$ crystallizes in a C-centered orthorhombic cell with $a = 7.023(4)$, $b = 6.849(3)$, $c = 3.514(2)$ Å. The space groups are $R\bar{3}m$ for α-CdUO$_4$ and $Cmmm$ for β-CdUO$_4$. α-CdUO$_4$: 1U in (000), 1Cd in (1/2 1/2 1/2), 2O(1) in $\pm(uuu)$, 2O(2) in $\pm(vvv)$; $u = 0.113$, $v = 0.350$, $Z = 1$. β-CdUO$_4$: 2U in (000; 1/2 1/2 0), 2Cd in (1/2 0 1/2; 0 1/2 1/2), 4O(1) in (0, $\pm y$, 0; 1/2, 1/2 $\pm y$, 0), 4O(2) in ($\pm x$, 0, 1/2; 1/2 $\pm x$, 1/2, 1/2); $x = 0.159$, $y = 0.278$, $Z = 2$. β-CdUO$_4$ contains collinear uranyl UO$_2^{2+}$ groups with a U–O(1) distance of 1.91 Å, located either along or parallel to the c axis whereas the U–O(1) bond length in α-CdUO$_4$ is 1.98 Å which is longer than the usual uranyl bond length.

Introduction

In the early work by Ippolitova *et al.* (*1*), α-CdUO$_4$ was found to be formed by the reaction of CdO and U$_3$O$_8$ (Cd/U = 1) in air at 570°C. Ippolitova *et al.* reported that this α phase transformed into β-CdUO$_4$ at 720°C and that the β-CdUO$_4$ decomposed into oxygen-deficient CdUO$_{4-x}$ above 925°C. According to them, α-CdUO$_4$ is hexagonal and its crystal structure is isomorphous with CaUO$_4$, the cell parameters being $a = 3.865(3)$ and $c = 17.44(2)$ Å. On the other hand, β-CdUO$_4$ is face-centered orthorhombic with the lattice parameters $a = 7.024(2)$, $b = 6.850(3)$, and $c = 3.526(5)$ Å. They have also reported that the high temperature phase CdUO$_{4-x}$ crystallizes into an oxygen-deficient structure of CaUO$_4$-type of which cell parameters are $a = 3.904(3)$ and $c = 17.52(2)$ Å in hexagonal indexing.

The structure analysis of the nonstoichiometric CdUO$_{4-x}$ has been determined by Reshetov and Kovba (*2*) by means of the X-ray powder diffractometry. They used the sample with composition CdUO$_{3.63}$ and showed that it could be indexed also in a rhombohedral system with the space group $R\bar{3}m$ and that the oxygen parameters in $R\bar{3}m$ were given as $u = 0.110$ and $v = 0.335$. Since there have been no reports of the structural determination of the stoichiometric α-CdUO$_4$, this is the first aim of this paper.

The crystal structure of β-CdUO$_4$ has been studied by Kovba *et al.* (*3*) by X-ray diffraction using powder sample and single crystal. Their final proposed structure was $Pbam$ with 2U in (a), 2Cd in (d), 4O(1) in (g) with $x = 0.05$ and $y = 0.275$, 4O(2) in (h) with $x = -0.175$ and $y = 0.08$.

---

* Present address: Institute of Environmental Science and Technology, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama, 240, Japan.

0022-4596/81/050133-07$02.00/0

However, the systematic absence of general *hkl* reflections was in conflict with the extinction rule for *Pbam*, and the least-squares calculations for our intensity data did not converge into reasonably small *R* indexes. The analysis of the crystal structure of the β-$CdUO_4$ is the second aim of this paper.

We have investigated the α to β phase transformation of strontium monouranate, $SrUO_4$, where an anomalous oxygen nonstoichiometry change was observed around the transition temperature (*4*, *5*). The α-$SrUO_4$ is rhombohedral and its crystal structure is isomorphous with α-$CdUO_4$. According to our X-ray diffraction study (*6*), the U–O(1) distance in α-$SrUO_4$ was between 2.04 and 2.08 Å which is longer than the usual uranyl bond length of 1.7 to 1.9 Å. Since similar compositional anomaly was recently observed also in the α to β phase transformation of cadmium monouranate (*7*), comparison of the detailed structure of α- and β-$CdUO_4$ to those of α- and β-$SrUO_4$ is worthwhile.

Experimental

α-$CdUO_4$ was prepared by heating an intimate mixture of CdO and $UO_3 \cdot 2H_2O$ with Cd to U atomic ratio of unity at 520°C in air for 40 hr. The product was orange-red and had the composition of $CdUO_{3.988}$ by thermogravimetric analysis. β-$CdUO_4$ was prepared by heating the mixture of CdO and U_3O_8 in air at 850°C for 10 hr. The product was yellow, the composition being $CdUO_{3.983}$.

The X-ray diffraction study on these samples was performed with a Rigaku-Denki Geigerflex 2182D1 type diffractometer using Cu*Kα* radiation monochromatized with curved pyrolytic graphite placed in front of the NaI(T1) scintillation detector. The integrated intensities of 42 and 47 reflections, in the range of $10° \leqq 2\theta \leqq 120°$, were recorded for α- and β-$CdUO_4$, respectively. To eliminate systematic errors in obtained diffraction angles, the observed data were corrected with those of rhombohedral α-$SrUO_4$ as standard (*6*). Lattice parameters were calculated by least-squares method on FACOM 230-75 for the diffraction angles in the range of $80° \leqq 2\theta \leqq 120°$.

TABLE I

CRYSTAL DATA

α-$CdUO_4$

	Ippolitova *et al.* (*1*)	Reshetov and Kovba (*2*)	Present work
Composition		$CdUO_{3.63}$	$CdUO_{3.988}$
a(hex) (Å)	3.865(3)	3.904(4)	3.864(3)
c(hex) (Å)	17.44(2)	17.54(1)	17.46(1)
c/*a* (hex)	4.51(2)	4.49(1)	4.52(1)
a(rhomb) (Å)	6.227(6)	6.266(3)	6.233(3)
α(rhomb) (deg)	36.16(6)	36.30(3)	36.12(5)
d(calc) (g/cm^3)	9.21	8.79	9.13

β-$CdUO_4$

	Ippolitova *et al.* (*1*)	Present work
Composition		$CdUO_{3.983}$
a (Å)	7.024(2)	7.023(4)
b (Å)	6.850(3)	6.849(3)
c (Å)	3.526(5)	3.514(2)
d(calc) (g/cm^3)	8.19	8.13

The crystal data are tabulated in Table I together with those by Ippolitova *et al.* (*1*) and, Reshetov and Kovba (*2*). The observed and calculated $Q(= 1/d^2)$ for α-$CdUO_4$ are given in the second and the third columns of Table II, respectively. The *Q* values for β-$CdUO_4$ are shown in Table III.

Structure Analysis

1. Structure of α-CdUO₄

All reflections of the combination of *hkl* were observed for rhombohedral α-$CdUO_4$ in the whole 2θ range of the experiments of which the diffraction pattern was closely related to that of the α-$SrUO_4$ (*6*). Thus, we

TABLE II

OBSERVED AND CALCULATED Q VALUES AND INTENSITIES FOR α-$CdUO_4$[a]

$h\ k\ l$	Q_{obs}	Q_{calc}	I_{obs}	I_{calc}
1 1 1	0.0299	0.0295	12.05	11.16
1 0 0	0.0930	0.0926	9.58	7.66
1 1 0	0.1029	0.1024	60.89	64.18
2 2 2	0.1188	0.1181	20.80	20.09
2 1 1	0.1423	0.1418	27.86	27.00
2 2 1	0.1720	0.1713	2.31	1.51
3 2 2	0.2506	0.2500	1.52	1.21
3 3 3	0.2554	0.2657	0.959	1.29
1 0 $\bar{1}$	0.2684	0.2679	21.42	23.48
2 1 0 3 3 2	0.2999	0.2974 0.2992	21.04	20.61
1 1 $\bar{1}$	0.3616	0.3604	2.08	1.27
2 0 0	0.3706	0.3703	9.46	9.11
3 2 1	0.3865	0.3860	18.61	18.60
2 2 0	0.4101	0.4096	6.52	5.59
4 3 3	0.4180	0.4173	8.30	7.15
3 1 1	0.4396	0.4392	0.789	0.547
4 4 4	0.4731	0.4724	2.00	1.90
4 4 3	0.4870	0.4862	1.01	0.992
3 3 1	0.5189	0.5179	0.437	0.501
4 3 2	0.5339	0.5336	1.68	2.38
4 2 2	0.5674	0.5671	4.87	5.17
2 0 $\bar{1}$	0.6289	0.6283	1.09	1.13
2 1 $\bar{1}$	0.6382	0.6381	6.41	6.84
5 4 4	0.6475	0.6437	0.625	0.208
3 1 0	0.6776	0.6775	4.63	4.75
4 4 2	0.6854	0.6852	3.55	2.95
3 2 0	0.7075	0.7070	0.695	0.633
5 5 4	0.7330	0.7322	3.22	2.78
5 5 5 5 4 3	0.7406	0.7381 0.7402	5.21	5.32
5 3 3	0.7538	0.7541	0.634	0.531
4 2 1	0.7864	0.7858	0.720	0.625
2 $\bar{1}$ $\bar{1}$	0.8033	0.8036	2.97	3.19
2 2 $\bar{1}$ 3 0 0 4 3 1	0.8349	0.8331 0.8331 0.8350	6.50	6.29
5 5 3 3 3 0 4 1 1	0.9213	0.9115 0.9217 0.9217	4.15	4.45
6 5 5	0.9299	0.9290	3.02	1.90
5 3 2	0.9528	0.9531	4.19	3.75
6 4 4 6 5 4	0.9999	1.0001 1.0059	2.59	2.49
5 4 2	1.0218	1.0219	0.847	0.837
6 6 5	1.0383	1.0373	0.488	0.578
6 6 6	1.0633	1.0628	0.913	0.659
4 4 1 5 2 2 2 0 $\bar{2}$	1.0707	1.0693 1.0693 1.0715	1.82	3.42
3 1 $\bar{1}$	1.1000	1.1010	0.564	0.782

[a] I_{obs} are integrated observed intensities in arbitrary units. $Q = 1/d^2$ are in $Å^{-2}$.

made the structure analysis on the basis of space group $R\bar{3}m$. The atomic positions were 1U in (000), 1Cd in (1/2 1/2 1/2), 2O(1) in $\pm(uuu)$ and 2O(2) in $\pm(vvv)$. To determine two unknown oxygen parameters, u and v, the peaks in two scans of different gains were recorded. One was for larger peaks and the other for smaller ones. The whole integrated intensities were collected by adjusting the former peak areas to the latter by means of several common peaks with middle heights.

To know the initial value of the oxygen parameters, a difference Fourier synthesis was made along the body-diagonal axis using the equation $\rho(x) = \Sigma Am \cdot \cos(2\pi mx)$, where the sum was taken for $m = h + k + l$ and x was the distance along the axis. The factor Am is expressed as $Am = c|F_{obs}| - |f_U + f_{Cd} \cos(\pi m)|$ where c is the adjustable parameter expressed as $c = \Sigma|F_{calc}|/\Sigma|F_{obs}|$. Atomic scattering factors for U^{6+} were those from International Tables for X-ray Crystallography (*8*), and the factors for Cd^{2+} were obtained from Cromer and Waber (*9*). These were used with anomalous dispersion corrections (*10*). The electron-density curve for oxygen with $0 \leqq m \leqq 18$ is shown in Fig. 1. The first maximum seen at $x = 0.114$ is assigned to O(1) and the second one at $x = 0.356$ to O(2). Refinement was carried out by minimizing the reliability index of $R = \Sigma w|I_{obs} - I_{calc}|/\Sigma wI_{obs}$, as a function of the oxygen parameters and temperature factors for cadmium and uranium. The weight, w, was regarded as $w = I_{obs}^{-1}$ for $I_{obs} \geqq 10 \cdot I_{obs(min)}$ and $w = 1$ for $I_{obs} <$

TABLE III

OBSERVED AND CALCULATED Q VALUES AND INTENSITIES FOR β-$CdUO_4$[a]

$h\ k\ l$	Q_{obs}	Q_{calc}	I_{obs}	I_{calc}
1 1 0	0.0420	0.0416	6.56	6.83
0 0 1 2 0 0	0.0815	0.0810 0.0811	19.95	17.58
0 2 0	0.0857	0.0853	12.51	13.54
1 1 1	0.1229	0.1226	27.14	27.95
2 0 1	0.1626	0.1621	2.87	2.39
0 2 1 2 2 0	0.1670	0.1662 0.1664	7.97	8.10
3 1 0	0.2046	0.2038	0.393	0.300
1 3 0	0.2128	0.2121	1.16	1.34
2 2 1	0.2480	0.2473	0.965	0.849
3 1 1	0.2855	0.2848	12.17	11.36
1 3 1	0.2938	0.2931	9.05	9.30
0 0 2 4 0 0	0.3243	0.3239 0.3244	5.26	4.88
0 4 0	0.3417	0.3411	2.15	2.44
1 1 2	0.3659	0.3655	0.781	0.838
2 0 2 4 0 1 0 2 2 4 2 0	0.4053 0.4095	0.4050 0.4054 0.4092 0.4097	8.33	8.37
0 4 1 2 4 0	0.4228	0.4220 0.4222	2.72	2.96
3 3 1	0.4559	0.4553	5.33	5.64
2 2 2 4 2 1	0.4906	0.4903 0.4907	3.28	3.58
2 4 1	0.5037	0.5031	0.703	0.705
3 1 2 5 1 0	0.5278	0.5277 0.5282	0.532	0.453
1 3 2	0.5364	0.5360	0.563	0.612
5 1 1	0.6098	0.6092	2.79	2.58
1 5 1	0.6347	0.6342	2.13	2.12
4 0 2	0.6486	0.6483	1.53	1.31
0 4 2 4 4 0	0.6653	0.6650 0.6655	2.74	2.72
3 3 2 5 3 0	0.6986	0.6982 0.6987	0.437	0.431
0 0 3 6 0 0 4 2 2	0.7310 0.7340	0.7288 0.7299 0.7336	2.75	2.39
2 4 2 4 4 1	0.7464	0.7461 0.7465	2.20	2.55
0 6 0 1 1 3	0.7702	0.7674 0.7704	2.34	2.28
5 3 1	0.7803	0.7797	1.75	1.97
3 5 1	0.7967	0.7964	1.74	1.91
2 0 3 6 0 1 0 2 3 6 2 0	0.8159	0.8099 0.8109 0.8140 0.8152	1.38	1.28
0 6 1 2 6 0	0.8489	0.8484 0.8485	0.921	1.08
5 1 2 2 6 1 3 1 3	0.9323	0.8521 0.9295 0.9326	1.89	1.96
1 3 3	0.9406	0.9409	1.65	1.56
4 4 2	0.9895	0.9894	1.32	1.53
4 0 3 6 0 2	1.0540	1.0532 1.0538	1.08	1.10
1 7 0 0 4 3 6 4 0	1.0707	1.0648 1.0698 1.0710	1.07	1.17
0 6 2 4 6 0 7 1 1 3 3 3	1.0916 1.0963 1.1028	1.0913 1.0918 1.0958 1.1031	4.67	4.48
5 5 1	1.1212	1.1208	1.31	1.29
4 2 3 6 2 2	1.1392	1.1384 1.1391	1.65	1.69
1 7 1 2 4 3 6 4 1	1.1459	1.1458 1.1509 1.1520	2.30	2.08
2 6 2 4 6 1	1.1724	1.1724 1.1728	1.47	1.58

[a] I_{obs} are integrated observed intensities in arbitrary units. $Q = 1/d^2$ are in Å^{-2}.

$10 \cdot I_{\text{obs(min)}}$. Atomic scattering factors for O^{2-} were those from Tokonami (*11*), and as the initial u and v values for successive approximations of the least-squares calculations, those by the $\rho(x)$ synthesis were used. At first, the temperature effect was not taken into account. In this case, the minimum R was 0.102 at $u = 0.110$ and $v = 0.352$. However, if isotropic temperature factors for U^{6+} and Cd^{2+} were taken as the variables, the minimum R was reduced to 0.080 at $u = 0.113$, $v = 0.350$; $B_U = 0.248$ and $B_{Cd} = 0.639$.

The integrated observed intensities, I_{obs}, and the calculated intensities, I_{calc}, at this minimum are shown in the fourth and the fifth columns of Table II, respectively. In Table IV, the computed values of the oxy-

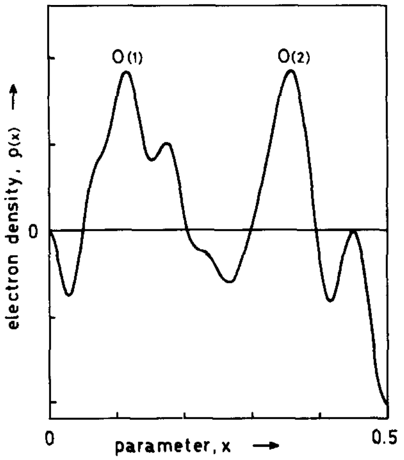

FIG. 1. The electron-density distribution along the body-diagonal axis due to oxygen atoms.

gen parameters and the isotropic temperature factors are tabulated together with the R value and the interatomic distances.

2. *Structure of β-$CdUO_4$*

The observed peaks all satisfied the condition $h + k = 2n$, which strongly suggests the C centered lattice. However, we first reexamined the space group *Pbam* of Kovba *et al.* (*3*), because it was thought that there might be the case that the intensities of diffraction peaks other than $h + k = 2n$ were accidentally too weak to be observed. The minimization of the R index was carried out by setting the atomic positions according to Kovba *et al.* (*3*), but the iterated computation of successive approximation did not converge. Moreover, I_{calc} obtianed by using the oxygen parameters of Kovba *et al.* (*3*) showed that (211) and (120) reflections which were $h + k \neq 2n$ should be strong enough to be observed. From these results, the possibility of *Pbam* was ruled out.

Because of the limitation of the powder diffraction technique, we could not try two-dimensional Fourier synthesis. Then, the problem that has to be solved, in this case, is to find out the atomic arrangement that conforms with C centered orthorhombic symmetry, under the guidance of the R index. The smallest R value was obtained for *Cmmm* with the atomic positions as follows: 2U in (000; 1/2 1/2 0), 2Cd in (1/2 0 1/2; 0 1/2 1/2), 4O(1) in (0 $\pm y$ 0; 1/2 1/2 $\pm y$ 0), 4O(2) in ($\pm x$ 0 1/2; 1/2 $\pm x$ 1/2 1/2). This space group is that which Kovba *et al.* (*3*) have reported as the possible alternative of the β-$CdUO_4$ structure. The oxygen parameters, x and y, and the isotropic temperature factors, B_U and B_{Cd}, were determined by minimizing the R index by the least-squares calculations in a way similar with that for α-$CdUO_4$. The obtained minimum R value was 0.066 with the correction of the temperature effect.

The integrated observed intensities, I_{obs}, and the calculated intensities, I_{calc}, at the minimum R are indicated in the fourth and the fifth columns of Table III, respectively. The computed values of the oxygen parameters and the isotropic temperature factors are shown in Table IV together with the R value and the interatomic distances.

Discussion of the Structure

Our cell parameters on α-$CdUO_{3.988}$ are well in accord with those by Ippolitova *et al.* (*1*). However, our a and c values in

TABLE IV

OXYGEN PARAMETERS, R FACTORS, TEMPERATURE FACTORS, AND INTERATOMIC DISTANCES OF α- AND β-$CdUO_4$

	α-$CdUO_4$	β-$CdUO_4$
Composition	$CdUO_{3.988}$	$CdUO_{3.983}$
Space group	$R\bar{3}m$	*Cmmm*
O(1)	$u = 0.113$	$y = 0.278$
O(2)	$v = 0.350$	$x = 0.159$
B_U (Å^2)	0.248	0.051
B_{Cd}	0.639	0.227
R factor	0.080	0.066
U–O(1) (Å)	1.98	1.91
U–O(2)	2.25	2.08
Cd–O(1)	2.42	2.32
Cd–O(2)	2.61	2.40
O(1)–O(1)	2.91	3.04
O(1)–O(2)	2.79	2.82
O(2)–O(2)	2.31	2.23

hexagonal indexing are remarkably smaller than those by Reshetov and Kovba (*2*) on α-$CdUO_{3.63}$. The difference can be considered as caused from oxygen nonstoichiometry of the compound. The lattice parameters will be $a = 3.863 + 0.1117x$ and $c = 17.46 + 0.2235x$ in Å for α-$CdUO_{4-x}$ provided that the dependence on nonstoichiometry is linear.

The crystal structure of α-$CdUO_4$ is isomorphous with those of $CaUO_4$ (*12, 13*) and α- and γ-$SrUO_4$ (*6*), where a uranium atom is surrounded by eight oxygen atoms which form a distorted hexahedron. Two of these oxygen atoms, O(1), which are on the body diagonal axis of the rhombohedral cell or along the *c* axis of the hexagonal cell one above and the other below the uranium atom are located closer to the uranium. Three of remaining six oxygen atoms, O(2), are on the plane 0.29 Å above and another three are on the plane 0.29 Å below the uranium atoms. These planes are normal to the body diagonal axis which is an inversion triad. Cadmium atoms are located between hexagonal layers binding them together. The oxygen around the cadmium atom is, however, made up of six O(1) atoms and two O(2) atoms. Arrangements are similar to those around the uranium atom if O(1) and O(2) are interchanged.

In $CaUO_4$ crystal which is typical of this structure, the U–O(1) distance is known to be short enough to form so-called uranyl bond. However, the distance for α-$CdUO_4$ by our data is 1.98 Å which is somewhat longer than the usual uranyl bond length which lies in the range of 1.7 and 1.9 Å. In this situation, infrared spectra were taken by the Nujol method. The data showed that the absorption peak was at 620 cm^{-1} which was shifted to the long wave side from the position of the antisymmetric stretching vibration of the uranyl bond, 700 to 900 cm^{-1}. From the equation relating the force constant, *K*, and the bond length, *R*, with $K = (181.0/R)^{1/6}$ by Ohwada (*14*), the U–O(1) distance was found to be 1.96 Å which is in good agreement with the X-ray results.

The isotropic temperature factors are 0.248 and 0.639 for uranium and cadmium atoms, respectively. These values may be compared with those of $CaUO_4$ where the factors are 0.297 for uranium atoms and 0.542 for calcium atoms by means of the neutron powder diffraction analysis (*13*).

The crystal structure of β-$CdUO_4$ is determined to be orthorhombic with space group *Cmmm*. A three-dimensional view of the atomic arrangements is shown in Fig. 2. Around each uranium atom, two O(1) atoms and four O(2) atoms are situated forming a distorted octahedron. The four O(2) atoms occupy a rectangular position on the plane normal to the *b* axis containing the uranium atoms, and the two O(1) atoms are located on the line normal to this plane forming the uranyl group. The collinearity of the uranyl group, O(1)–U–O(1), is required form the space group symmetry.

The U–O(1) bond length of the β-$CdUO_4$ is 1.91 Å. This value agrees well with the values of 1.92 and 1.91 Å for $MgUO_4$ (*16*) and $CaUO_4$ (*12*), respectively. The infrared spectra corresponding to the antisymmetric stretching vibration of the uranyl bond at 700 cm^{-1} led to the bond length 1.88 Å which supports the X-ray value. The U–O(2) distance by the present investigation is 2.08 Å. Since this distance is usually in

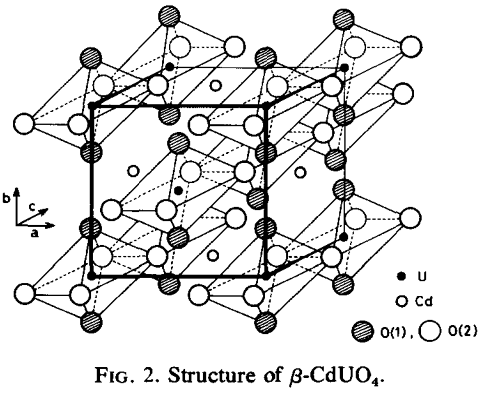

FIG. 2. Structure of β-$CdUO_4$.

the range of 2.2 and 2.3 Å in most monouranates, the U–O(2) bond seems to be stronger in β-$CdUO_4$.

As is seen in Fig. 2, the $(UO_2)O_4$ octahedra in β-$CdUO_4$ are chained endlessly along the c axis by sharing edges of the O(2) atoms. The shared O(2)–O(2) edge is 2.23 Å while the unshared O(2)–O(2) edge is 3.51 Å. Cadmium atoms are located at the center of the octahedra formed by four O(1) atoms and two O(2) atoms, and bind the uranyl chains together.

The arrangement of the $(UO_2)O_4$ octahedra in this crystal is similar to that of $MgUO_4$ (*16*) where the space group is *Iman*. The difference is that in β-$CdUO_4$ the shared O(2)–O(2) edge of $(UO_2)O_4$ octahedra is in the plane formed by a and b axes while in $MgUO_4$ it is not. As a result, $c/2$ of $MgUO_4$ becomes c of β-$CdUO_4$ forming a C centered lattice. The smaller cell parameters in $MgUO_4$ (*16*) (a = 6.520, b = 6.595, c = 6.924 Å) may be because of the smaller ionic radius of Mg^{2+} than Cd^{2+}.

It is seen from Table IV that the interatomic distances between metal and oxygen atoms of β-$CdUO_4$ are shorter than those of α-$CdUO_4$. This fact shows that the metal–oxygen bonds of β-$CdUO_4$ are stronger than those of α-$CdUO_4$, which is in accord with the smaller temperature factors obtained for β-$CdUO_4$: $B_U = 0.051$ and $B_{Cd} = 0.227$.

Here, the results with $CdUO_4$ can be compared with those of $SrUO_4$ in which phase transformation from α to β phases is similar to that of $CdUO_4$ (*7*). The crystal structure of α-$CdUO_4$ is isomorphous with that of α-$SrUO_4$, but the U–O(1) distances are 1.98 and 2.07 Å for α-$CdUO_4$ and α-$SrUO_4$, respectively. It should be noted that the crystal structure of β-$CdUO_4$ is different from that of β-$SrUO_4$ where the space group is *Pbcm* (*15*). Although the infinite chains of $(UO_2)O_4$ octahedra are parallel to each other along the c axis in β-$CdUO_4$, the distorted octahedra in β-$SrUO_4$ share the corners to form infinite two-dimensional sheets in the plane with the b and c axes. Because the U–O(1) distances are 1.91 and 1.85 Å for β-$CdUO_4$ and β-$SrUO_4$ (*15*), respectively, these values are both regarded as forming the uranyl bond.

Acknowledgments

The authors thank Dr. K. Ohwada for infrared absorption analyses.

References

1. E. A. Ippolitova, I. P. Simanov, L. M. Kovba, G. P. Polunina, and I. A. Bereznikova, DEG-INF Ser. 145 (1961).
2. K. V. Reshetov and L. M. Kovba, *J. Struct. Chem.* **7**, 589 (1966).
3. L. M. Kovba, G. P. Polunina, E. A. Ippolitova, Yu. P. Simanov, and V. I. Spitsyn, *Russ. J. Phys. Chem.* **35**, 350 (1961).
4. H. Tagawa and T. Fujino, *Inorg. Nucl. Chem. Lett.* **13**, 489 (1977).
5. H. Tagawa and T. Fujino, *J. Inorg. Nucl. Chem.* **40**, 2033 (1978).
6. T. Fujino, N. Masaki, and H. Tagawa, *Z. Krist.* **145**, 299 (1977).
7. H. Tagawa and T. Fujino, *Inorg. Nucl. Chem. Lett.* **16**, 91 (1980).
8. J. A. Ibers, D. H. Templeton, B. K. Vainshtein, G. E. Bacon, and K. Lonsdale, "International Tables for X-ray Crystallography," Vol. III, p. 206. Kynoch Press, Birmingham (1962).
9. D. T. Cromer and J. T. Waber, *Acta Crystallogr.* **18**, 104 (1965).
10. D. T. Cromer, *Acta Crystallogr.* **18**, 17 (1965).
11. M. Tokonami, *Acta Crystallogr.* **19**, 486 (1965).
12. W. H. Zachariasen, *Acta Crystallogr.* **1**, 281 (1948).
13. B. O. Loopstra and H. M. Rietveld, *Acta Crystallogr.* **B25**, 787 (1969).
14. K. Ohwada, "Study on Infrared Spectra of Uranium Compounds." Thesis, The University of Tokyo, Tokyo (1977).
15. J. O. Sawyer, *J. Inorg. Nucl. Chem.* **34**, 3268 (1972).
16. W. H. Zachariasen, *Acta Crystallogr.* **7**, 788 (1954).