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## Structures of the 3:1 Adducts of Cadmium(II) Bromide and of Cadmium(II) Chloride with 15-Crown-5 Ether:\* Structural Changes Induced by Radiation

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### Abstract

3CdBr<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>,  $M_r = 1036.9$ , monoclinic,  $P2_1/c$ ,  $a = 7.535$  (6),  $b = 14.452$  (17),  $c = 11.771$  (12) Å,  $\beta = 116.54$  (2)°,  $V = 1147$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.00$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 131.2$  cm<sup>-1</sup>,  $F(000) = 948$ ,  $T = 295$  K,  $R(F) = 0.036$  for 1234 reflexions [ $I \geq 3\sigma(I)$ ] and 105 variables. 3CdCl<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>, ordered structure,  $M_r = 770.2$ , monoclinic,  $P2_1$ ,  $a = 7.217$  (1),  $b = 14.235$  (2),  $c = 11.255$  (1) Å,  $\beta = 115.835$  (8)°,  $V = 1040.7$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.46$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $F(000) = 732$ ,  $T = 295$  K. 3CdCl<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>, disordered structure, second data set,  $M_r = 770.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.231$  (3),  $b = 14.331$  (21),  $c = 11.284$  (7) Å,  $\beta = 116.00$  (2)°,  $V = 1051$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.43$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\mu = 37.9$  cm<sup>-1</sup>,  $F(000) = 732$ ,  $T = 295$  K,  $R(F) = 0.035$  for 2285 reflexions [ $I > 3\sigma(I)$ ] and 105 variables. 3CdCl<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>, disordered structure, third data set,  $M_r = 770.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.236$  (4),  $b = 14.417$  (46),  $c = 11.312$  (13) Å,  $\beta = 116.05$  (5)°,  $V = 1060$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.41$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\mu = 37.6$  cm<sup>-1</sup>,  $F(000) = 732$ ,  $T = 295$  K,  $R(F) = 0.041$  for 2073 reflexions [ $I > 3\sigma(I)$ ] and 105 variables. 3CdCl<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>, disordered structure, fourth data set,  $M_r = 770.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.249$  (1),  $b = 14.521$  (19),  $c = 11.350$  (5) Å,  $\beta = 116.15$  (3)°,  $V = 1072$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.38$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\mu = 37.1$  cm<sup>-1</sup>,  $F(000) = 732$ ,  $T = 293$  K,  $R(F) = 0.054$  for 1862 reflexions [ $I > 3\sigma(I)$ ] and 105 variables. 3CdCl<sub>2</sub>·C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>, dis-

ordered structure, fifth data set,  $M_r = 770.2$ , monoclinic,  $P2_1/c$ ,  $a = 7.251$  (1),  $b = 14.560$  (19),  $c = 11.360$  (5) Å,  $\beta = 116.19$  (3)°,  $V = 1076$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.38$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\mu = 37.0$  cm<sup>-1</sup>,  $F(000) = 732$ ,  $T = 293$  K,  $R(F) = 0.060$  for 1713 reflexions [ $I > 3\sigma(I)$ ] and 105 variables. For the disordered structures, *i.e.* the bromide and data sets 2–5 for the chloride, the cell dimensions are the mean of those measured before and after the intensity measurements. The compounds are isostructural; both contain trigonal and pentagonal bipyramidally coordinated Cd atoms which are linked by halogen bridges to form sheets perpendicular to  $b$ . The Cd atom at the centre of the crown ether, which is disordered, is bonded by strong Cd—O bonds [Cd—O 2.22 (2) to 2.38 (2) Å in the bromide and 2.239 (5) to 2.404 (6) Å in the chloride]. The axial Cd—Br bonds [2.812 (3) to 2.878 (2) Å] are longer than the equatorial Cd—Br bonds [2.623 (2) to 2.640 (2) Å]. The axial Cd—Cl bonds range from 2.651 to 2.691 (1) Å and the equatorial Cd—Cl bonds from 2.508 (1) to 2.535 (1) Å. Both compounds suffer radiation damage which results in changes in the cell dimensions during data collection and, for the chloride, a phase transition occurs in which the crown becomes disordered and the space group changes from  $P2_1$  to  $P2_1/c$ .

### Introduction

The dihalides of cadmium and mercury form 1:1 complexes with 18-crown-6 ether (18C6) in which the

\* 1,4,7,10,13-Pentaoxacyclopentadecane.

Table 1. Details of data collection and refinement for  $C_{10}H_{20}O_5Cd_3X_6$  ( $X = Cl, Br$ )

X	Cl	Cl	Cl	Cl	Cl	Br
Data set	1	2	3	4	5	
Data collection						
$h_{min}$	0	0	0	0	0	0
$h_{max}$	10	10	10	10	10	10
$k_{min}$	-20	-20	-20	-20	-20	-20
$k_{max}$	0	0	20	0	0	20
$l_{min}$	-15	-15	-15	-15	-15	-16
$l_{max}$	14	14	14	14	14	14
Time/step (s)	1	1	1	1	1	2
Steps/scan	50	50	50	50	50	50
$\theta$ scan width, $B$ ( $^\circ$ )*	0.8-1.2	1.2	1.2	1.2	1.2	0.8
$(\sin\theta/\lambda)_{max}$ ( $\text{\AA}^{-1}$ )	0.702	0.703	0.702	0.702	0.702	0.700
Standard 1	0T5	0T5	015	015	015	015
Standard 2	0,T0,0	0,T0,0	080	080	080	080
Mean decay (%)	15	10	25	12	15	9
Refinement						
$N_{obs}$	3153	3037	3202	3101	3101	3328
$N[ I  > 3\sigma(I)]$	2529	2285	2073	1862	1713	1234
$R_{int}$	-	-	0.049	-	-	0.106
$trans_{min}$	0.282	0.272	0.281	0.278	0.281	0.465
$trans_{max}$	0.515	0.515	0.518	0.522	0.523	0.527
$R$	-	0.035	0.041	0.054	0.060	0.036
$wR$	-	0.044	0.046	0.061	0.068	0.032
$S$	-	1.879	2.057	2.248	2.498	0.960
$(\Delta/\sigma)_{max}$	-	0.037	0.033	0.096	0.180	0.190
$\Delta\rho_{min}$ ( $e \text{\AA}^{-3}$ )	-	-1.2 (1)	-1.0 (2)	-1.9 (2)	-2.0 (2)	-0.9 (2)
$\Delta\rho_{max}$ ( $e \text{\AA}^{-3}$ )	-	1.1 (1)	1.0 (2)	2.0 (2)	2.3 (2)	0.8 (2)
$g \times 10^{-4}$	-	0.083 (8)	0.073 (9)	0.018 (7)	0.015 (8)	0.272 (2)
$I/(corr)_{min}$	-	0.622	0.647	0.869	0.893	0.737
$\langle U \rangle_{Cd,Cl}$	-	0.040	0.049	0.055	0.059	-
$\langle U \rangle_{C,O}$	-	0.045	0.059	0.069	0.076	-
$\langle U \rangle_H$	-	0.062	0.087	0.105	0.128	-

\*  $\theta$  scan width is  $(B + 0.346\tan\theta)^\circ$ .

metal atom sits at the centre of the crown and is weakly bonded to it (Paige & Richardson, 1984; Hazell, 1988). No 1:1 complexes of cadmium dihalides with 15-crown-5 ether (15C5) seem to have been reported, but Wulfsberg & Weiss (1977) have described a 3:1 adduct of  $CdBr_2$  with 15C5 and a 1.2:1 adduct of 15C5 with  $CdI_2$ . We attempted to prepare the 1:1 and 3:1 adducts with  $CdBr_2$ , and the 1:1 adduct with  $CdCl_2$ , but in each case obtained the 3:1 adducts, the structures of which are described here. The chloride underwent a phase change (from  $P2_1$  to  $P2_1/c$ ) during data collection. Furthermore, the cell dimensions of the centrosymmetric form continued to increase during irradiation. A total of five data sets were collected at intervals, over a period of a year, in order to investigate the changes taking place as a function of time and irradiation.

## Experimental

### Preparation

$C_{10}H_{20}O_5Cd_3X_6$  ( $X = Cl, Br$ ):  $CdX_2$  was dissolved in warm ethanol, treated with triethyl orthoformate in order to dehydrate it, and the appropriate amount of 15C5 added. In the case of the bromide, crystals of the 3:1 adduct separated on standing for an hour; the chloride, however, required recrystallization from ethanol. The adducts crystallize as colourless needles, bounded by  $\{010\}$  and  $\{011\}$  and terminated by  $\{100\}$  and  $\{10\bar{1}\}$ .

### X-ray measurements

Data-collection and structure-refinement details are summarized in Table 1. Data were collected at 295 K, on a Huber diffractometer, from crystals of the bromide ( $0.14 \times 0.08 \times 0.06$  mm) and the chloride ( $0.48 \times 0.34 \times 0.19$  mm) using an  $\omega$ - $2\theta$  scan and Nb-filtered  $Mo K\alpha$  radiation, the filter being situated between the crystal and counter. Two standard reflexions were monitored every 50 reflexions. Cell dimensions were determined from the setting angles of reflexions measured with  $Mo K\alpha$  radiation ( $\lambda = 0.71073 \text{\AA}$ ) at  $2\theta, \omega, \chi, \varphi; -2\theta, -\omega, \chi, \varphi; 2\theta, \omega, 180 + \chi, \varphi$ ; and  $-2\theta, -\omega, 180 + \chi, \varphi$ . Irradiation of the crystal causes changes in the cell dimensions; the values for the disordered structures, *i.e.* the bromide and for data sets 2-5 for the chloride, are the mean of those measured before and after the intensity measurements, and the figures in parentheses are the differences divided by two. The values for the ordered phase of the chloride are those measured before collecting the first data set. The data were corrected for absorption.

The structure of the bromide was determined using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); the crown ether lies on a centre of symmetry and is thus disordered. A difference map showed maxima close to the positions calculated for H atoms. Least-squares refinement (on  $F$ ) included anisotropic  $U$  for Cd and Br, isotropic  $U$  for C and O and a common  $U_{iso}$  for

H atoms which were kept at their calculated positions with C—H = 0.95 Å, and an isotropic extinction factor,  $g$ . The weighting scheme was  $w = 1/\sigma(F)$  where  $\sigma(F) = [\sigma_{cs}(F^2) + 1.02F^2]^{1/2} - |F|$  and  $\sigma_{cs}(F^2)$  is the standard deviation of  $F^2$ . Fractional coordinates are listed in Table 2, bond distances, angles and torsion angles in Table 3.\*

During data collection of set 1 for the chloride the peak-width doubled, reflexions  $h0l$  with  $l$  odd became almost zero, *i.e.* the space group changed from  $P2_1$  to  $P2_1/c$ , and the cell dimensions changed. A second data set was measured, but the cell dimensions continued to increase. A total of five data sets were collected with a pause of 61 days between the second and third sets and of 322 days between the third and fourth sets. The data processing and refinement for sets 2–5 were carried out as for the bromide. Data set 1 was collected while the crystal was undergoing a phase transformation so that attempting to fit one model to the data was not meaningful; the data were similar to those of set 2, the  $R$  value between reflexions common to both data sets was 0.082 for 2233 reflexions with  $I > 3\sigma(I)$  suggesting that the heavy-atom framework is similar in both phases.

As with the bromide complex it was not possible to refine anisotropic thermal parameters for the C and O atoms since the disorder meant that the atomic positions were close together, leading to large correlations between the thermal and positional parameters for these atoms.

Computations were carried out on a VAX 6210 computer with the following programs: *INTEG*, based on the Nelves (1975) algorithm for integration of intensities; *DATAP* and *DSORT* (State Univ. of New York) for data processing; modified *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinement; *ORFFE* (Busing, Martin & Levy, 1964) for the geometry; *ORTEPII* (Johnson, 1976) for preparing drawings. Scattering curves used were those of Cromer & Mann (1968) for Cd, Br, Cl, O and C, and of Stewart, Davidson & Simpson (1965) for H; dispersion corrections for Cd, Br and Cl were taken from Cromer & Liberman (1970).

## Discussion

### Structure

The bromide contains two crystallographically independent Cd atoms. Cd(1) lies on a centre of symmetry and at the centre of the crown ether, which

Table 2. Fractional atomic coordinates ( $\times 10^5$  for Cd, Br and Cl,  $\times 10^4$  for C and O) and  $U_{eq}$  or  $U_{iso}$  ( $\times 10^3$  for Cd, Br and Cl,  $\times 10^3$  for C and O)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{eq}/U_{iso}$ (Å <sup>2</sup> )
15-Crown-5(CdBr <sub>2</sub> ) <sub>3</sub>				
Cd(1)	50000	50000	0	394 (7)
Cd(2)	29948 (12)	48712 (6)	56568 (8)	358 (5)
Br(1)	51071 (18)	41201 (8)	-20993 (10)	415 (7)
Br(2)	39370 (17)	39020 (8)	41030 (10)	372 (7)
Br(3)	4528 (17)	62443 (8)	48790 (12)	454 (8)
O(1)	4868 (24)	3434 (10)	570 (14)	39 (4)
C(2)	3058 (46)	3212 (22)	514 (29)	46 (9)
C(3)	1427 (37)	3579 (16)	-644 (24)	35 (6)
O(4)	1694 (22)	4598 (10)	-607 (13)	31 (3)
C(5)	385 (49)	5055 (23)	-1784 (29)	49 (10)
C(6)	1115 (40)	6078 (21)	-1534 (25)	48 (8)
O(7)	3158 (21)	6078 (10)	-1393 (13)	36 (4)
C(8)	4064 (44)	6957 (19)	-1096 (28)	46 (7)
C(9)	6247 (51)	6813 (24)	-862 (30)	53 (10)
O(10)	7148 (27)	6004 (13)	-106 (16)	63 (5)
C(11)	8850 (36)	6063 (19)	1040 (23)	37 (6)
C(12)	9641 (46)	5040 (22)	1416 (29)	44 (9)
O(13)	8104 (24)	4555 (11)	1494 (14)	43 (4)
C(14)	8295 (44)	3603 (19)	1558 (25)	46 (8)
C(15)	6572 (45)	3154 (21)	1694 (28)	57 (8)
15-Crown-5(CdCl <sub>2</sub> ) <sub>3</sub> (data set 2)				
Cd(1)	50000	50000	0	403 (3)
Cd(2)	29875 (5)	48833 (3)	56749 (3)	351 (2)
Cl(1)	50826 (19)	41868 (10)	-20945 (11)	435 (7)
Cl(2)	40823 (18)	39475 (9)	41793 (12)	388 (6)
Cl(3)	3649 (18)	61738 (10)	48892 (13)	440 (7)
O(1)	4889 (11)	3397 (5)	542 (7)	40 (2)
C(2)	2934 (19)	3146 (9)	447 (12)	44 (3)
C(3)	1392 (18)	3544 (9)	-739 (11)	43 (3)
O(4)	1628 (10)	4561 (5)	-642 (6)	35 (1)
C(5)	255 (21)	5123 (10)	-1723 (13)	41 (3)
C(6)	1060 (19)	6093 (10)	-1523 (12)	48 (3)
O(7)	3095 (12)	6101 (5)	-1424 (7)	44 (2)
C(8)	4178 (22)	6971 (10)	-992 (13)	55 (3)
C(9)	6300 (22)	6867 (10)	-845 (13)	51 (3)
O(10)	7285 (11)	6022 (5)	-78 (7)	43 (2)
C(11)	8969 (19)	6105 (9)	1160 (12)	48 (3)
C(12)	9768 (24)	5147 (11)	1591 (15)	51 (4)
O(13)	8216 (12)	4534 (6)	1611 (7)	46 (2)
C(14)	8513 (19)	3548 (9)	1675 (11)	46 (3)
C(15)	6670 (18)	3078 (8)	1703 (11)	45 (2)
15-Crown-5(CdCl <sub>2</sub> ) <sub>3</sub> (data set 3)				
Cd(1)	50000	50000	0	488 (4)
Cd(2)	29829 (6)	48856 (3)	56660 (4)	420 (3)
Cl(1)	50668 (22)	41991 (12)	-20984 (13)	525 (9)
Cl(2)	40828 (21)	39522 (10)	41828 (14)	465 (8)
Cl(3)	3657 (20)	61691 (12)	48967 (15)	526 (9)
O(1)	4898 (13)	3391 (6)	547 (8)	50 (2)
C(2)	2945 (25)	3182 (12)	391 (16)	63 (4)
C(3)	1376 (22)	3531 (10)	-753 (14)	54 (3)
O(4)	1610 (12)	4563 (6)	-638 (8)	46 (2)
C(5)	245 (26)	5139 (12)	-1703 (16)	52 (4)
C(6)	1104 (22)	6069 (11)	-1465 (14)	57 (4)
O(7)	3095 (13)	6095 (6)	-1429 (8)	52 (2)
C(8)	4168 (29)	6976 (13)	-988 (19)	77 (5)
C(9)	6345 (28)	6862 (12)	-849 (17)	67 (5)
O(10)	7313 (14)	6015 (7)	-69 (8)	58 (2)
C(11)	9004 (23)	6071 (12)	1154 (14)	61 (4)
C(12)	9769 (30)	5143 (13)	1588 (19)	63 (5)
O(13)	8205 (15)	4517 (7)	1593 (9)	62 (2)
C(14)	8562 (23)	3523 (11)	1657 (14)	63 (4)
C(15)	6651 (22)	3070 (10)	1699 (14)	57 (3)
15-Crown-5(CdCl <sub>2</sub> ) <sub>3</sub> (data set 4)				
Cd(1)	50000	50000	0	561 (6)
Cd(2)	29788 (9)	48894 (5)	56571 (6)	470 (4)
Cl(1)	50417 (35)	42198 (20)	-21046 (20)	612 (15)
Cl(2)	40858 (32)	39593 (17)	41922 (22)	526 (13)
Cl(3)	3691 (31)	61608 (19)	49094 (24)	599 (14)
O(1)	4883 (22)	3391 (10)	539 (13)	58 (3)
C(2)	2963 (42)	3174 (20)	378 (27)	74 (8)
C(3)	1364 (34)	3557 (15)	-764 (21)	57 (5)
O(4)	1608 (19)	4573 (9)	-632 (12)	52 (3)
C(5)	263 (49)	5181 (22)	-1596 (29)	73 (9)
C(6)	1067 (35)	6076 (18)	-1449 (21)	63 (6)
O(7)	3147 (21)	6091 (10)	-1391 (12)	61 (3)

\* Lists of structure factors, anisotropic thermal parameters, cell parameters, bond lengths and angles, torsion angles, and H-atom parameters derived from data sets 2–5 for the chloride have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53632 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso} (\text{Å}^2)$
C(8)	4100 (51)	6978 (22)	-998 (32)	93 (9)
C(9)	6320 (46)	6855 (20)	-866 (27)	80 (8)
O(10)	7324 (21)	6014 (10)	-55 (12)	61 (3)
C(11)	9081 (39)	6031 (20)	1187 (24)	74 (7)
C(12)	9761 (43)	5130 (20)	1671 (26)	62 (8)
O(13)	8240 (28)	4485 (13)	1587 (15)	85 (5)
C(14)	8541 (38)	3490 (18)	1631 (22)	70 (6)
C(15)	6612 (37)	3066 (17)	1674 (23)	67 (6)
15-Crown-5(CdCl <sub>2</sub> ) <sub>2</sub> (data set 5)				
Cd(1)	50000	50000	0	600 (7)
Cd(2)	29763 (10)	48907 (6)	56540 (7)	494 (5)
Cl(1)	50347 (43)	42253 (24)	-21045 (24)	654 (18)
Cl(2)	40850 (38)	39609 (21)	41931 (26)	554 (16)
Cl(3)	3736 (37)	61587 (23)	49124 (28)	637 (18)
O(1)	4871 (28)	3390 (12)	542 (16)	63 (4)
C(2)	2986 (55)	3186 (26)	377 (35)	80 (10)
C(3)	1382 (42)	3553 (19)	-735 (26)	61 (7)
O(4)	1626 (23)	4571 (11)	-642 (14)	52 (4)
C(5)	215 (52)	5169 (24)	-1583 (32)	65 (10)
C(6)	1073 (42)	6072 (23)	-1437 (25)	64 (7)
O(7)	3138 (27)	6090 (12)	-1383 (15)	68 (4)
C(8)	4146 (67)	6991 (29)	-976 (41)	105 (12)
C(9)	6344 (65)	6848 (29)	-863 (38)	98 (13)
O(10)	7340 (27)	6001 (13)	-45 (15)	68 (4)
C(11)	9090 (53)	6042 (28)	1192 (32)	91 (10)
C(12)	9668 (61)	5143 (27)	1692 (36)	82 (12)
O(13)	8280 (36)	4478 (16)	1581 (19)	94 (6)
C(14)	8521 (48)	3483 (22)	1626 (28)	77 (8)
C(15)	6598 (44)	3053 (20)	1651 (27)	67 (7)

Table 3 (cont.)

	$X = \text{Cl}$ (weighted mean)	$X = \text{Br}$
X(2)—Cd(2)—X(3 <sup>iv</sup> )	93.17 (5)	92.68 (7)
X(2 <sup>iii</sup> )—Cd(2)—X(3 <sup>iv</sup> )	170.16 (3)	172.56 (4)
Cd(2 <sup>iii</sup> )—X(1)—Cd(1)	119.49 (5)	116.96 (9)
Cd(2)—X(2)—Cd(2 <sup>iii</sup> )	95.65 (5)	93.38 (7)
Cd(2)—X(3)—Cd(2 <sup>iii</sup> )	97.48 (6)	95.72 (9)
C(2)—O(1)—Cd(1)	110.5 (5)	112 (2)
C(15)—O(1)—Cd(1)	115.1 (4)	113 (1)
C(3)—O(4)—Cd(1)	111.3 (4)	112 (1)
C(5)—O(4)—Cd(1)	110.8 (5)	111 (1)
C(6)—O(7)—Cd(1)	108.5 (5)	111 (1)
C(8)—O(7)—Cd(1)	107.9 (5)	112 (2)
C(9)—O(10)—Cd(1)	112.7 (5)	114 (2)
C(11)—O(10)—Cd(1)	110.4 (5)	112 (2)
C(12)—O(13)—Cd(1)	109.1 (5)	114 (2)
C(14)—O(13)—Cd(1)	114.3 (4)	111 (1)
C(2)—O(1)—C(15)	118.0 (6)	116 (2)
O(1)—C(2)—C(3)	111.0 (7)	111 (2)
C(2)—C(3)—O(4)	106.9 (7)	107 (2)
C(3)—O(4)—C(5)	119.6 (6)	114 (2)
O(4)—C(5)—C(6)	108.6 (7)	103 (2)
C(5)—C(6)—O(7)	111.2 (7)	107 (2)
C(6)—O(7)—C(8)	114.2 (7)	113 (2)
O(7)—C(8)—C(9)	108.3 (8)	106 (2)
C(8)—C(9)—O(10)	110.7 (8)	113 (3)
C(9)—O(10)—C(11)	121.2 (7)	122 (2)
O(10)—C(11)—C(12)	108.2 (8)	106 (2)
C(11)—C(12)—O(13)	113.7 (9)	106 (2)
C(12)—O(13)—C(14)	121.0 (8)	116 (2)
O(13)—C(14)—C(15)	107.6 (7)	111 (2)
O(1)—C(15)—C(14)	106.5 (6)	104 (2)

Table 3. Bond distances (Å), bond angles and torsion angles (°)

	$X = \text{Cl}$ (weighted mean)	$X = \text{Br}$
Cd(1)—X(1)	2.657 (1)	2.812 (3)
Cd(2)—X(2)	2.535 (1)	2.640 (2)
Cd(2)—X(3)	2.511 (2)	2.623 (2)
Cd(2)—X(1 <sup>i</sup> )	2.508 (1)	2.633 (3)
Cd(2)—X(2 <sup>iii</sup> )	2.651 (1)	2.826 (2)
Cd(2)—X(3 <sup>iv</sup> )	2.691 (1)	2.878 (2)
Cd(1)—O(1)	2.404 (6)	2.376 (15)
Cd(1)—O(4)	2.313 (5)	2.337 (14)
Cd(1)—O(7)	2.239 (5)	2.238 (15)
Cd(1)—O(10)	2.246 (5)	2.218 (18)
Cd(1)—O(13)	2.340 (5)	2.303 (16)
O(1)—C(2)	1.39 (1)	1.37 (3)
C(2)—C(3)	1.41 (1)	1.47 (4)
C(3)—O(4)	1.48 (1)	1.48 (3)
O(4)—C(5)	1.43 (1)	1.45 (3)
C(5)—C(6)	1.46 (1)	1.56 (4)
C(6)—O(7)	1.44 (1)	1.47 (3)
O(7)—C(8)	1.45 (1)	1.41 (3)
C(8)—C(9)	1.50 (1)	1.56 (4)
C(9)—O(10)	1.49 (1)	1.44 (4)
O(10)—C(11)	1.40 (1)	1.39 (3)
C(11)—C(12)	1.46 (1)	1.58 (4)
C(12)—O(13)	1.43 (1)	1.39 (3)
O(13)—C(14)	1.44 (1)	1.38 (3)
C(14)—C(15)	1.53 (1)	1.52 (4)
C(15)—O(1)	1.44 (1)	1.43 (3)
X(1)—Cd(1)—X(1 <sup>i</sup> )	180.0	180.0
X(1)—Cd(1)—O(1)	80.0 (1)	80.7 (4)
X(1)—Cd(1)—O(4)	92.0 (1)	93.7 (3)
X(1)—Cd(1)—O(7)	85.0 (1)	85.6 (4)
X(1)—Cd(1)—O(10)	87.0 (1)	86.5 (4)
X(1)—Cd(1)—O(13)	99.2 (1)	97.3 (4)
O(1)—Cd(1)—O(4)	70.7 (2)	71.1 (5)
O(4)—Cd(1)—O(7)	74.8 (2)	73.8 (5)
O(7)—Cd(1)—O(10)	75.2 (2)	74.5 (6)
O(10)—Cd(1)—O(13)	73.6 (2)	73.0 (6)
O(13)—Cd(1)—O(1)	69.6 (2)	71.0 (5)
X(3)—Cd(2)—X(1 <sup>i</sup> )	131.89 (3)	133.01 (6)
X(3)—Cd(2)—X(2)	124.76 (4)	122.68 (7)
X(3)—Cd(2)—X(2 <sup>iii</sup> )	91.09 (6)	89.86 (9)
X(3)—Cd(2)—X(3 <sup>iv</sup> )	82.52 (6)	84.28 (9)
X(1 <sup>i</sup> )—Cd(2)—X(2)	103.56 (5)	104.31 (9)
X(1 <sup>i</sup> )—Cd(2)—X(2 <sup>iii</sup> )	94.31 (4)	93.29 (7)
X(1 <sup>i</sup> )—Cd(2)—X(3 <sup>iv</sup> )	95.53 (4)	94.06 (6)
X(2)—Cd(2)—X(2 <sup>iii</sup> )	84.35 (5)	86.62 (7)

O(1)—C(2)—C(3)—O(4)	-61 (1)	-59 (3)
C(2)—C(3)—O(4)—C(5)	179 (1)	171 (2)
C(3)—O(4)—C(5)—C(6)	-167 (1)	-175 (2)
O(4)—C(5)—C(6)—O(7)	58 (1)	65 (3)
C(5)—C(6)—O(7)—C(8)	-170 (1)	-177 (2)
C(6)—O(7)—C(8)—C(9)	175 (1)	175 (2)
O(7)—C(8)—C(9)—O(10)	-49 (1)	-43 (3)
C(8)—C(9)—O(10)—C(11)	-114 (1)	-121 (3)
C(9)—O(10)—C(11)—C(12)	-173 (1)	-167 (2)
O(10)—C(11)—C(12)—O(13)	-54 (1)	-59 (3)
C(11)—C(12)—O(13)—C(14)	163 (1)	167 (2)
C(12)—O(13)—C(14)—C(15)	178 (1)	178 (2)
O(13)—C(14)—C(15)—O(1)	56 (1)	61 (3)
C(14)—C(15)—O(1)—C(2)	-173 (1)	-173 (2)
C(15)—O(1)—C(2)—C(3)	179 (1)	177 (2)

Symmetry code: (i)  $x, y, 1+z$ ; (ii)  $x, y, -1+z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $-x, 1-y, 1-z$ ; (v)  $-x, -y, -z$ .

is of necessity disordered. The coordination figure can be described as a pentagonal bipyramid with Br atoms in the axial positions (Fig. 2). Cd(2) lies at the centre of a trigonal bipyramid of Br atoms. The Cd atoms are linked by Br bridges to form infinite sheets perpendicular to  $b$  (Fig. 3).

The O atoms are strongly bonded to Cd with Cd(1)—O distances ranging from 2.218 (18) to 2.376 (15) Å. These distances are close to values normally found *e.g.* Cd—O = 2.349 (9) in Cd-Br<sub>2</sub>·2H<sub>2</sub>O (Leligny & Monier, 1978) and are quite different from those for CdBr<sub>2</sub>·18C<sub>6</sub> where Cd—O is 2.752 (3) Å. The length of the  $M$ —O bond is governed by the size of the crown, *cf.* Zn—O = 2.22 Å in Zn(H<sub>2</sub>O)<sub>2</sub>15C<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub> (Dejehet, Debuyst, Wei, Declercq & Tinant, 1987) and 2.867 (2) Å in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn18C<sub>6</sub> (Parvez, Bergstresser & Richey, 1986). The long Cd(1)—Br distance, 2.812 (3) Å, is similar to that of the axial Cd(2)—Br bonds of the trigonal bipyramid, 2.826 (2) and 2.878 (2) Å. In the trigonal bipyramid the axial bonds are longer than

the equatorial bonds, 2.623 (2) to 2.640 (2) Å,  $r_{ax}/r_{eq} = 1.08$ , although the difference is not as great as that predicted,  $r_{ax}/r_{eq} = 1.21$ , by Kepert (1982).

The conformation of the crown is  $sc^- ap ap sc^+ ap ap sc^- ac^- ap sc^- ap ap sc^+ ap ap^*$  *i.e.* one torsion angle, C(8)—C(9)—O(10)—C(11), is eclipsed. This conformation, *i.e.*  $(ap sc^+ ap ap sc^- ap)_2 ap sc^+ ac^-$  is found in 19% of the 59 15-crown-5 ethers listed in the Cambridge Structural Database (CSD) (Allen, Kennard & Taylor, 1983), and is the most common for 15C5. 45% of 15C5 ethers have conformations with the 14-angle sequence  $(ap sc^+ ap ap sc^- ap)_2 ap sc^+$  which may be compared with that for the most stable conformation of the 18C6 ethers, *i.e.*  $(ap sc^+ ap ap sc^- ap)_3$  (Uiterwijk, Harkema, van der Waal, Göbel & Nibbeling, 1983). The Cd and O atoms are not coplanar, the O atoms being 0.14 to 0.38 Å out of the plane perpendicular to Cd—Br and passing through Cd. The geometry of the crown is poorly determined because of disorder but the mean bond distances and angles, C—O 1.42 (1), C—C 1.54 (2) Å, C—C—O 107 (1) and C—O—C 116 (2)°, are similar to the expected values, C—O 1.425 (2), C—C 1.490 (4) Å, C—C—O 108.1 (2) and C—O—C 114.0 (2)°, which are the mean values found from 67 determinations listed in the CSD.

The disordered form of the chloride is isomorphous with and isostructural to the bromide. Cd(1)—Cl is 2.657 (1) Å and Cd(1)—O range from 2.246 (5)—2.404 (6) Å. In the trigonal bipyramid the axial Cd(2)—Cl distances are 2.651 (1) and 2.691 (1) Å and the equatorial Cd(2)—Cl distances range from 2.508 (1)—2.535 (1) Å giving  $r_{ax}/r_{eq} = 1.06$ . The O atoms are 0.08 to 0.42 Å out of the plane perpendicular to Cd—Cl and passing through Cd. The mean bond distances and angles in the crown

\* The notation indicates endocyclic torsion angles in the following ranges:  $sp = 0 \pm 30$ ,  $sc^+ = 60 \pm 30$ ,  $ac^+ = 120 \pm 30$ ,  $ap = 180 \pm 30$ ,  $ac^- = 240 \pm 30$ ,  $sc^- = 300 \pm 30$ °.

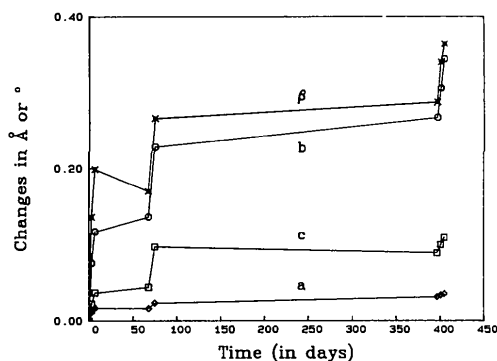


Fig. 1. Changes in cell parameters ( $\delta x = x_t - x_0$ , etc.) versus time. The e.s.d.'s of the cell parameters are:  $\sigma(a)$  0.0006–0.0011,  $\sigma(b)$  0.0014–0.0033,  $\sigma(c)$  0.0008–0.0020 Å,  $\sigma(\beta)$  0.006–0.008°.

are: C—O 1.44 (1), C—C 1.47 (2) Å, C—C—O 109 (1) and C—O—C 119 (1)°. The conformation of the crown is the same as in the bromide.

The coordination figure at Cd(2) is closer to trigonal bipyramidal than to square pyramidal; the r.m.s. deviations of the angles from the ideal angles are 6.0° for trigonal bipyramidal and 11.4° for square pyramidal for the bromide and 6.6 and 12.7° for the chloride. For both compounds Cd(2)—X(3<sup>iv</sup>) is longer than Cd(2)—X(2<sup>iii</sup>) and Cd(2)—X(2) is the longest of the equatorial bonds.

### Radiation damage

For both compounds the intensities of the standard reflexions fell, although not alarmingly, during data collection indicating radiation damage. The results of radiation damage are superficially similar to those observed when a crystal is heated (Kolontsova & Telegina, 1969). For the chloride the following effects are seen: there is an order-disorder phase transformation, the unit cell expands while the crystal is irradiated (Fig. 1), and the  $U$  values increase (Table 1). These changes are irreversible and occur only while the crystal is irradiated. The crystal, originally transparent, became semi-opaque after 18 months; by comparison crystals left in their mother liquor reacted with water from the atmosphere after a few days to give a white fluffy solid. So reaction with atmospheric water would appear to play only a minor role. The experimental arrangement was unwittingly chosen so as to give maximum absorption of X-rays by Cd; the generator was operated at 50 kV giving white radiation with maximum intensity at about 0.46 Å which is close to the  $K$  absorption edge for Cd ( $\lambda = 0.46407$  Å), and the filter was placed between the crystal and the counter. The phase transition from  $P2_1$  to  $P2_1/c$  can be explained by a disordering of the crown molecules, the heavy-atom framework being virtually unchanged. The largest changes in cell dimensions during irradiation

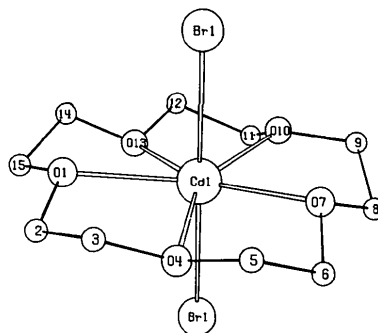


Fig. 2. Coordination of a 15-crown-5 ether to Cd(1), showing the numbering of the atoms in the crown.

were for  $\beta$  and  $b$ , the smallest was for  $a$ . These changes are reflected in an increased separation between the cadmium-halogen layers which are perpendicular to  $b$ , and a widening of the Cd(1)—Cl(1)—Cd(2<sup>ii</sup>) angle. The cell dimensions of the bromide also increased but here there was no phase transition; photographs showed no evidence for the existence of the ordered form at room temperature. The spacing between layers is larger in the bromide and so it would be easier for the crown to reorientate.

Phase changes induced by irradiation with X-rays are not common but do occur, e.g. in sodium (ethylenediaminetetraacetato)holmate(III) octahydrate where a disordering of water molecules takes place and the structure changes from monoclinic to orthorhombic (Templeton, Templeton & Zalkin, 1985), in dibromobis(1,2-diaminoethane)platinum(IV) bis(1,2-diaminoethane)platinum(II) tetrakis(perchlorate) which also changes from monoclinic to orthorhombic (Keller, Müller, Ledezma & Martin, 1985), and the EF-TU.GDP complex from *E. coli* which changes from orthorhombic to tetragonal (Kjeldgaard, 1990). In each each the changes are small and to a higher symmetry.

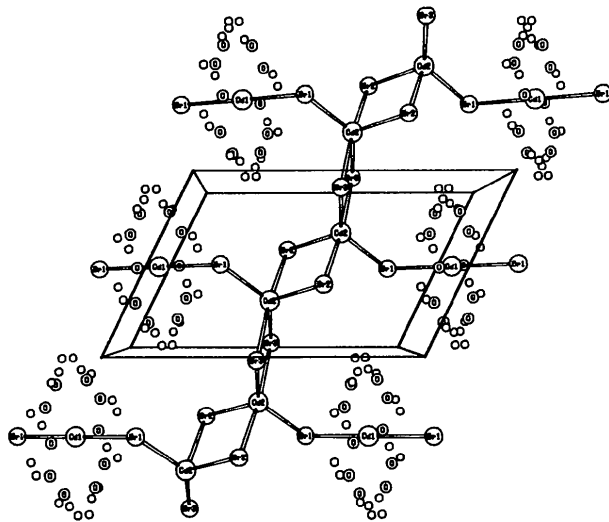


Fig. 3. A portion of one of the  $15\text{Cd}_3\text{X}_6$  layers viewed down  $b$ ;  $c$  is across the page.

Changes in cell dimensions produced by X-rays would seem to be rarer, indeed we could find no examples in the literature, the routine measurement of cell parameters both before and after data collection would require little extra work and might provide more examples.

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