

IV). Atomic coordinates are given in Table 1.* Bond lengths and bond angles are listed in Table 2. The main details of the structure are shown in Fig. 1.

Discussion. The structure contains columns of water-bridged Na^+ ions arranged parallel to **a** and centred at $0, \frac{1}{2}, 0$ and $0, 0, \frac{1}{2}$. Within the columns, centrosymmetric pairs of Na^+ ions are bridged by two water molecules; the symmetry-independent water molecules link alternate pairs of bridged Na^+ ions along the columns with $\text{Na}^+\cdots\text{O}$ in the range 2.357 (2)–2.475 (1) Å. The glutarate residue is hydrogen bonded to one of the bridging water molecules [$\text{O}(W1)\cdots\text{H}\cdots\text{O}$ 2.844 (2) and 2.865 (2) Å] such that opposite ends of each residue join to the same water molecule forming ten-membered rings (Fig. 1). In addition, the carbonyl O atoms of each glutarate residue bond to two different Na^+ ions [$\text{Na}^+\cdots\text{O}(3)$ 2.334 (2) and $\text{Na}^+\cdots\text{O}(2)$ 2.469 (1) Å] rendering

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53578 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

each Na^+ ion six-coordinate. Adjacent $\text{Na}^+\text{--H}_2\text{O}$ columns are linked through glutarate residues both by these $\text{Na}^+\cdots\text{O}$ (carbonyl) contacts and by hydrogen bonds to the $\text{O}(W2)$ water molecules [$\text{O}(1)\cdots\text{H}\cdots\text{O}(W2)$ 2.819 (2), $\text{O}(3)\cdots\text{H}\cdots\text{O}(W2)$ 2.816 (2) Å]. The glutarate residues [$^-\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2\text{H}$] are linked into infinite chains along **c** by very short asymmetric hydrogen bonds [$\text{O}(1)\cdots\text{O}(4)$ 2.410 (2), $\text{O}(1)\cdots\text{H}(11)$ 1.07 (4), $\text{H}(11)\cdots\text{O}(4)$ 1.35 (4) Å]. This is the shortest intermolecular hydrogen bond so far reported in acid salts and is amongst the shortest $\text{O}\cdots\text{H}\cdots\text{O}$ bonds yet found. It is all the more remarkable that the bond appears to be asymmetric.

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Structure of a 4:1 Adduct of Cadmium(II) Chloride with 15-Crown-5 Ether

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Abstract. Cadmium(II) chloride–1,4,7,10,13-pentaoxacyclopentadecane–water 4/1/1, $\text{C}_{10}\text{H}_{20}\text{Cd}_4\text{Cl}_8\text{O}_5\cdot\text{H}_2\text{O}$, $M_r = 971.55$, orthorhombic, *Pnma*, $a = 10.224$ (2), $b = 11.353$ (2), $c = 25.146$ (6) Å, $V = 2919$ (1) Å³, $Z = 4$, $D_x = 2.211$ Mg m⁻³, $\text{Mo } K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 3.63$ mm⁻¹, $F(000) = 1832$, $T = 295$ K, $R(F) = 0.056$ for 1009 reflexions [$I > 3\sigma(I)$] and 137 variables. The structure contains double chains built of CdCl_6 and $\text{CdCl}_5\text{H}_2\text{O}$ octahedra each sharing three edges. Adjacent unshared Cl atoms are linked by Cd atoms which are themselves coordinated to crown-ether molecules. Cd–Cl distances are 2.535 (7) to 2.586 (7) Å for Cl atoms which are shared between two Cd atoms and 2.629 (7) to 2.759 (6) Å for those shared by three.

Introduction. The dihalides of cadmium form a variety of complexes with 15-crown-5 ether (15C5) (Wulfsberg & Weiss, 1977; Hazell & Hazell, 1990).

During the recrystallization from ethanol of the 3:1 adduct of CdCl_2 with 15C5, a batch of needle-shaped crystals with a different morphology from that of the 3:1 complex were obtained. These crystals have been studied by X-ray diffraction and shown to be a 4:1 adduct which also contained water.

Experimental. $\text{Cd}_4\text{Cl}_8\cdot 15\text{C}_5\cdot\text{H}_2\text{O}$ was obtained from an ethanolic solution of 15C5 and CdCl_2 which in spite of the addition of triethyl orthoformate was not completely dry. The crystals were needles elongated in the **b** direction and bounded by {101} and {001}. A crystal, $0.05 \times 0.14 \times 0.31$ mm, was mounted on a Huber diffractometer. Cell dimensions were determined from the setting angles of 30 reflexions with $15 < 2\theta < 27^\circ$ measured with $\text{Mo } K\alpha$ radiation at $2\theta, \omega, \chi, \varphi$; $-2\theta, -\omega, \chi, \varphi$; $2\theta, \omega, 180 + \chi, \varphi$ and $-2\theta, -\omega, 180 + \chi, \varphi$. Intensities were measured out to $(\sin\theta/\lambda)_{\text{max}} = 0.595$ Å⁻¹ using an ω - 2θ scan and

Table 1. Fractional coordinates ($\times 10^4$ for Cd and Cl; $\times 10^3$ for C and O) and U_{eq} ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cd(1)	250 (2)	834 (2)	5696 (1)	48 (1)
Cd(2)	-157 (3)	2500	4305 (1)	49 (2)
Cd(3)	3764 (3)	2500	6369 (1)	52 (2)
Cl(1)	1484 (8)	2500	5135 (3)	42 (6)
Cl(2)	-1441 (6)	839 (6)	4841 (2)	53 (4)
Cl(3)	965 (7)	831 (6)	3805 (2)	60 (5)
Cl(4)	-1133 (11)	2500	6084 (3)	49 (6)
Cl(5)	2063 (6)	878 (6)	6408 (2)	59 (4)
O(water)	-198 (3)	250	364 (2)	53 (21)
O(1)	394 (3)	250	737 (1)	61 (20)
C(2)	445 (5)	141 (3)	759 (1)	319 (73)
C(3)	518 (5)	70 (4)	727 (2)	210 (47)
O(4)	521 (2)	95 (2)	674 (1)	76 (15)
C(5)	582 (4)	24 (4)	644 (2)	127 (35)
C(6)	569 (4)	40 (4)	588 (2)	119 (34)
O(7)	481 (2)	131 (3)	568 (1)	54 (13)
C(8)	540 (4)	198 (2)	525 (1)	208 (43)

Table 2. Bond distances (\AA), angles and torsion angles ($^\circ$) [O(water) is abbreviated to O(w)]

Cd(1)—Cl(1)	2.676 (6)	Cd(1)—Cl(2)	2.759 (6)	Cd(1)—Cl(2')	2.629 (7)
Cd(1)—Cl(3')	2.586 (7)	Cd(1)—Cl(4)	2.556 (7)	Cd(1)—Cl(5)	2.578 (6)
Cd(2)—Cl(1)	2.678 (9)	Cd(2)—Cl(2)	2.665 (7)	Cd(2)—Cl(3)	2.546 (7)
Cd(2)—O(w)	2.50 (4)	Cd(3)—Cl(5)	2.535 (7)	Cd(3)—O(1)	2.53 (2)
Cd(3)—O(4)	2.48 (2)	Cd(3)—O(7)	2.44 (2)	O(1)—C(2)	1.45 (3)
C(2)—C(3)	1.36 (5)	C(3)—O(4)	1.37 (4)	O(4)—C(5)	1.27 (4)
C(5)—C(6)	1.43 (5)	C(6)—O(7)	1.47 (5)	O(7)—C(8)	1.45 (4)
C(8)—C(8')	1.18 (7)				
Cl(1)—Cd(1)—Cl(2)	83.3 (2)	Cl(5)—Cd(3)—Cl(5')	93.2 (3)		
Cl(2)—Cd(1)—Cl(1)	91.2 (2)	O(1)—Cd(3)—Cl(5)	90.6 (5)		
Cl(2)—Cd(1)—Cl(2)	83.8 (2)	O(4)—Cd(3)—Cl(5)	83.1 (5)		
Cl(3)—Cd(1)—Cl(1)	177.2 (2)	O(7)—Cd(3)—Cl(5)	85.7 (6)		
Cl(3)—Cd(1)—Cl(2)	94.5 (2)	O(4)—Cd(3)—O(1)	65.2 (7)		
Cl(3)—Cd(1)—Cl(2')	86.8 (2)	O(7)—Cd(3)—O(4)	67.4 (8)		
Cl(4)—Cd(1)—Cl(1)	86.5 (2)	O(7)—Cd(3)—O(7')	67.1 (13)		
Cl(4)—Cd(1)—Cl(2)	87.1 (3)	Cd(1)—Cl(1)—Cd(1')	90.0 (3)		
Cl(4)—Cd(1)—Cl(2')	170.8 (3)	Cd(1)—Cl(1)—Cd(2)	96.7 (2)		
Cl(4)—Cd(1)—Cl(3')	95.2 (2)	Cd(1)—Cl(2)—Cd(2)	91.3 (2)		
Cl(4)—Cd(1)—Cl(5)	96.8 (3)	Cd(1)—Cl(2)—Cd(1)	96.2 (2)		
Cl(5)—Cd(1)—Cl(1)	90.8 (2)	Cd(2)—Cl(2)—Cd(1)	95.0 (2)		
Cl(5)—Cd(1)—Cl(2)	172.7 (2)	Cd(2)—Cl(3)—Cd(1')	95.1 (2)		
Cl(5)—Cd(1)—Cl(2')	92.2 (2)	Cd(1)—Cl(4)—Cd(1')	95.5 (4)		
Cl(5)—Cd(1)—Cl(3')	91.3 (2)	Cd(3)—Cl(5)—Cd(1)	118.7 (3)		
O(w)—Cd(2)—Cl(1)	170.7 (9)	C(2)—O(1)—C(2')	117 (4)		
O(w)—Cd(2)—Cl(2)	88.3 (6)	O(1)—C(2)—C(3)	119 (3)		
O(w)—Cd(2)—Cl(3)	90.3 (6)	C(2)—C(3)—O(4)	117 (4)		
Cl(2)—Cd(2)—Cl(1)	85.1 (2)	C(3)—O(4)—C(5)	117 (3)		
Cl(2)—Cd(2)—Cl(2')	90.1 (3)	O(4)—C(5)—C(6)	117 (4)		
Cl(3)—Cd(2)—Cl(1)	95.9 (2)	C(5)—C(6)—O(7)	119 (3)		
Cl(3)—Cd(2)—Cl(2)	86.8 (2)	C(6)—O(7)—C(8)	112 (3)		
Cl(3)—Cd(2)—Cl(2')	176.7 (2)	C(7)—C(8)—C(8')	122 (2)		
Cl(3)—Cd(2)—Cl(3')	96.2 (3)				
C(2')—O(1)—C(2)—C(3)	-113 (4)	O(4)—C(5)—C(6)—O(7)	-4 (7)		
O(1)—C(2)—C(3)—O(4)	-11 (8)	C(5)—C(6)—O(7)—C(8)	136 (4)		
C(2)—C(3)—O(4)—C(5)	-175 (5)	C(6)—O(7)—C(8)—C(8')	-130 (2)		
C(3)—O(4)—C(5)—C(6)	171 (5)	O(7)—C(8)—C(8')—O(7')	0		

Symmetry code: (i) $-x, -y, 1-z$; (ii) $x, 0.5-y, z$.

Nb-filtered Mo $K\alpha$ radiation, 2θ -scan width ($1.6 + 0.692 \tan \theta$) $^\circ$, divided into 50 steps, 1 s step^{-1} . Reflexions with $0 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 29$ were measured giving 2722 independent reflexions of which 1010 had $I > 3\sigma_{cs}(I)$. Reflexions 0,0,14 and 334 were monitored every 50 reflexions, their intensi-

ties fell by 23% during the data collection. The data were corrected for the fall off in intensity and for absorption, the minimum and maximum transmission factors were 0.58 and 0.82. The structure was determined using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least-squares refinement (on F) was carried out with anisotropic atomic displacements parameters for Cd, Cl, O and C: H atoms were not included. An isotropic extinction factor converged to $g = 0.48 (7) \times 10^{-4}$, corresponding to a minimum value of $I/I_{corrected}$ of 0.644. The weighting scheme was $w = 1/\sigma(F)$ where $\sigma(F) = [\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|$ and $\sigma_{cs}(F^2)$ is the standard deviation of F^2 . The final results are $R = 0.056$, $wR = 0.073$, $S = 1.91$, $(\Delta/\sigma)_{max} = 0.01$, $\Delta\rho = -1.0 (2)$ to $1.4 (2) \text{ e \AA}^{-3}$. Fractional coordinates are listed in Table 1, * bond distances, angles and torsion angles in Table 2. Computations were carried out on a VAX 6210 computer with the following programs: INTEG – based on the Nelmes (1975) algorithm for integration of intensities; DATAP and DSORT (State University of New York) – data processing; modified ORFLS (Busing, Martin & Levy, 1962) – least-squares refinement; ORFFE (Busing, Martin & Levy, 1964) – geometry; ORTEPII (Johnson, 1976) – drawings. Scattering curves those of Cromer & Mann (1968) for Cd, Cl, O and C.

Discussion. The structure contains double chains built of (CdCl_6) and $[\text{CdCl}_5(\text{H}_2\text{O})]$ octahedra which share three edges, cf. $(\text{NH}_4)\text{CdCl}_3$ (Brasseur & Pauling, 1938). Adjacent unshared Cl atoms are linked by Cd atoms which are themselves coordinated to crown-ether molecules (Fig. 1).

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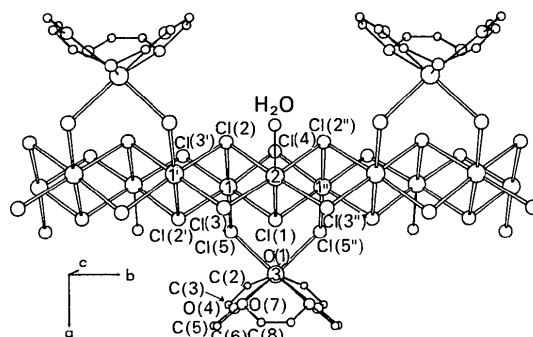
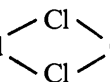


Fig. 1. A perspective drawing showing the numbering of the atoms. Symmetry code: (i) $-x, -y, 1-z$; (ii) $x, \frac{1}{2}-y, z$. Atomic symbols are omitted for Cd, O(1) is hidden behind Cd(3).

Cd—Cl distances fall into two categories; for Cl atoms which are shared between two Cd atoms Cd—Cl ranges from 2.535 (7) to 2.586 (7) Å and for those which are shared by three Cd atoms Cd—Cl ranges from 2.629 (7) to 2.759 (6) Å. Cd—O(water) is 2.50 (4) Å which is longer than the Cd—O(water) distances of 2.356 (4) Å found in Cd₂NiCl₆·12H₂O (Leclaire & Borel, 1980*a*) and 2.328 (4) Å in Cd₄NiCl₁₀·10H₂O (Leclaire & Borel, 1980*b*). There is no Cl—O(water) distance less than 3.5 Å so the water molecule is assumed not to form hydrogen bonds to Cl atoms. The (CdCl₆) and [CdCl₅(H₂O)] octahedra are distorted so that all Cl—Cd—Cl

angles in Cd  Cd units are less than 90° [83.3 (2) to 86.8 (2)°].

The structure was solved and refined assuming the space group *Pnma* which implies that the crown is on a mirror plane. The unusual geometry of the crown, e.g. the abnormally short C(8)—C(8ⁱⁱ) distance, and especially the unusual torsion angles, notably all O—C—C—O being close to zero, suggest that the crown is disordered. This is also indicated by the large 'thermal' parameters. Attempts at untangling the disorder by replacing the anisotropic atoms by pairs of isotropic atoms and trying to fit two crowns to these new positions were unsuccessful. The 3:1 adduct of CdCl₂ with 15C5 exhibits a radiation-induced phase transition (Hazell, Hazell, Holm & Krogh, 1991) where the crown becomes disordered and the structure becomes centrosymmetric, a similar effect could occur in the 4:1 complex, which also suffers from radiation damage, but the change here from *Pn2₁a* to *Pnma* would not be as easy to detect since the space-group absences would remain unchanged. Also there was no broadening of the peaks as was observed for the 3:1 adduct.

The O atoms of the crown ether are strongly bonded to Cd, the Cd—O distances range from 2.44 (2) to 2.53 (2) Å, which is longer than those in the 3:1 adduct of CdCl₂ and 15C5 [2.22 (2) to 2.38 (2) Å] where the cadmium is at the centre of the crown (Hazell, Hazell, Holm & Krogh, 1991) but considerably shorter than those in the 18-crown-6 compound (Paige & Richardson, 1984).

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Structures of *trans*-[TcCl₄{P(CH₃)(C₆H₅)₂}₂], [TcCl₄{P(C₂H₅)₃}₂] and [P(C₂H₅)₃H][TcCl₅{P(C₂H₅)₃}]

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Abstract. *trans*-Tetrachlorobis(methyldiphenylphosphine)technetium, (I), *M_r* = 641.16, triclinic, *P* $\bar{1}$, *a* =

8.991 (5), *b* = 9.603 (4), *c* = 9.750 (6) Å, α = 66.67 (4), β = 88.65 (4), γ = 62.80 (4)°, *V* = 674.6 (6) Å³, *Z* = 1, *D_x* = 1.573 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 1.04 mm⁻¹, *F*(000) = 323, *T* =

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