

The Structures of Rubidium and Caesium Hydrogen Iminodiacetate Iminodiacetic Acids

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The structure of $\text{RbC}_8\text{H}_{13}\text{N}_2\text{O}_8$ has been determined from X-ray data obtained with a diffractometer, and refined to $R = 0.052$. The space group is $Pbcn$ with $a = 14.6444$ (15), $b = 8.6383$ (8), $c = 19.1452$ (16) Å, $Z = 8$. Iminodiacetate residues are held together by Rb^+ ions and hydrogen bonds in a three-dimensional structure. The two ligands are zwitterions and one forms an eight-membered chelate with Rb^+ . The hydrogen bonds are of the type $\text{N}-\text{H}-\text{O}$ with lengths between 2.718 (7) and 2.996 (8) Å and of the type $\text{O}-\text{H}-\text{O}$ with length 2.445 (7) Å. The cation is surrounded by nine O atoms at distances from 2.985 (5) to 3.534 (6) Å. The corresponding Cs compound is isostructural with $a = 14.9450$ (28), $b = 8.6510$ (12), $c = 19.3441$ (24) Å.

Introduction

Several acid alkali salts of oxydi-, thiodi- and iminodiacetic acid have been investigated to determine the hydrogen bonding, coordination and conformation of the ligands. Examples are Rb hydrogen oxydiacetate (Albertsson, Grenthe & Herbertsson, 1973) and Rb hydrogen thiodiacetate (Herbertsson, 1976). The structures of the acids have also been described (Herbertsson & Boman, 1973; Paul, 1967; Boman, Herbertsson & Oskarsson, 1974). In an attempt to synthesize iminodiacetates of the heavy alkali metals, crystals of composition MH_3A_2 were obtained ($\text{M}^+ = \text{Rb}^+$ or Cs^+ ; A^{2-} = the iminodiacetate ion). These compounds can be regarded as a link between the free acids and their alkali hydrogen salts.

Crystal data

Rubidium hydrogen iminodiacetate iminodiacetic acid, $\text{RbC}_8\text{H}_{13}\text{N}_2\text{O}_8$; F.W. 350.7; orthorhombic, space group $Pbcn$; $a = 14.6444$ (15), $b = 8.6383$ (8), $c = 19.1452$ (16) Å, $V = 2421.9$ Å³; $Z = 8$; $\mu(\text{Mo } K\alpha) = 43.6$ cm⁻¹; $D_m = 1.92$, $D_x = 1.923$ g cm⁻³.

Caesium hydrogen iminodiacetate iminodiacetic acid, $\text{CsC}_8\text{H}_{13}\text{N}_2\text{O}_8$; F.W. 398.1; orthorhombic, space group $Pbcn$; $a = 14.9450$ (28), $b = 8.6510$ (12), $c = 19.3441$ (24) Å, $V = 2501.0$ Å³; $Z = 8$; $D_m = 2.10$, $D_x = 2.114$ g cm⁻³.

Numbers in parentheses represent estimated standard deviations.

Experimental

Colourless crystals were obtained from solutions of iminodiacetic acid to which RbOH or CsOH had been

added until $\text{pH} = 7$. Elemental analyses gave values in good agreement with those calculated for $\text{RbC}_8\text{H}_{13}\text{N}_2\text{O}_8$ and $\text{CsC}_8\text{H}_{13}\text{N}_2\text{O}_8$. The densities were found from the loss of weight in CCl_4 . Space group $Pbcn$ from absent spectra: $h0l$, l odd; $0kl$, k odd and hko , $h + k$ odd. The cell parameters were determined from data collected with a Guinier-Hägg camera (Cu $K\alpha_1$ radiation, $\lambda = 1.54051$ Å) with Al (cubic, $a = 4.04934$ Å, 22°C) as internal standard. A single crystal of the Rb compound, $0.10 \times 0.30 \times 0.10$ mm, mounted along \mathbf{b} , was used for data collection on an automatic CAD-4 diffractometer. The radiation was $\text{Mo } K\alpha$, monochromatized by reflexion in a graphite crystal. The $\omega-2\theta$ technique was used with scan interval $\Delta\omega = 0.60 + 1.00 \tan \theta$. The background intensity was measured before and after each reflexion. All 2634 independent reflexions in the interval $4^\circ < \theta < 27^\circ$ were measured, but 1121 reflexions with $I < 2\sigma_c(I)$ were rejected in the subsequent calculations. A fast pre-scan was used to determine the scan speed at which a pre-determined minimum number of counts (3000) were received by the detector; however, no reflexion was measured for more than 180 s. The values of $\sigma_c(I)$ were based on counting statistics. The reflexions $\bar{8}2\bar{2}$, $\bar{8}20$ and $\bar{4}1\bar{2}$ were chosen as standards and the intensity of each was recorded every hour. The fluctuations were random and less than 8%. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects. The transmission factors varied between 0.635 and 0.726.

Structure determination and refinement

The Rb atom was located from a Patterson synthesis and the positions of the other non-hydrogen atoms from a difference map. Full-matrix least-squares refine-

ment minimizing $\sum w(|F_o| - |F_c|)^2$ was performed with weights $w = 1/(\sigma_c^2 + a|F_c|^2)$, with a chosen to make the average values of $w(|F_o| - |F_c|)^2$ as equal as possible in the different $|F_o|$ and $\sin\theta$ intervals. The value $a = 0.001$ was used in the last cycles of refinement.

Table 1. Atomic coordinates ($\times 10^5$; $\times 10^4$ for H)

	x	y	z
Rb ⁺	43868 (5)	29358 (9)	51597 (4)
O(11)	25070 (34)	90663 (60)	46415 (24)
O(12)	39814 (39)	92992 (67)	43735 (28)
O(13)	39990 (39)	31763 (53)	30174 (27)
O(14)	46558 (36)	48446 (62)	37466 (30)
O(21)	27235 (33)	9933 (62)	55622 (25)
O(22)	12225 (34)	12753 (64)	54164 (26)
O(23)	6418 (33)	68522 (53)	66497 (27)
O(24)	14522 (33)	52783 (57)	73277 (25)
N(11)	37513 (36)	73115 (66)	32267 (29)
N(21)	9627 (36)	26805 (64)	66437 (28)
C(11)	30759 (47)	73789 (87)	37978 (39)
C(12)	32394 (50)	86944 (85)	42951 (35)
C(13)	36951 (45)	58302 (80)	28355 (36)
C(14)	41535 (45)	45193 (84)	32445 (36)
C(21)	19208 (46)	23899 (83)	64310 (36)
C(22)	19293 (48)	14860 (85)	57287 (34)
C(23)	5694 (46)	41889 (76)	64080 (36)
C(24)	9187 (46)	55410 (80)	68292 (37)
H(11)	4372	7397	3369
H(12)	3682	8134	3023
H(13)	2502	7444	3619
H(14)	3074	6551	4118
H(15)	3064	5618	2670
H(16)	4122	6300	2451
H(21)	903	2649	7122
H(22)	646	1970	6409
H(23)	2218	3339	6317
H(24)	2254	1524	6730
H(25)	598	4330	5883
H(26)	-20	4008	6523

The convergence was checked by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. Refinement of the scale, positional, and anisotropic thermal parameters resulted in $R = 0.061$ and $R_w = 0.086$. All H atoms except that in the O—H—O bond were located in a difference map obtained from data with $\sin\theta/\lambda \leq 0.5 \text{ \AA}^{-1}$. At this stage an isotropic extinction parameter (Zachariasen, 1967) and the parameters of the H atoms found were included in the refinement. The positional parameters were fixed and the thermal parameter $B = 3.0 \text{ \AA}^2$ was chosen. The remaining H atom could not be located in the subsequent difference map. In the last cycle of refinement the shifts in the parameters were less than 5% of the estimated standard deviations. The refined value of the extinction parameter $g = 1.4(3) \times 10^4$ corresponds to a mosaic spread of $4.2''$ if the crystal is of type I and a domain size of $9.9 \times 10^{-5} \text{ cm}$ if it is of type II. The final R was 0.052 and R_w 0.069. The value of $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, where m is the number of observations and n the number of parameters varied, was 1.5. The final difference map showed no peaks higher than 0.5 e \AA^{-3} . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The positional and thermal parameters, and the r.m.s. components along the principal axes of thermal motion, are given in Tables 1 and 2.*

All computations (Oskarsson, 1973) were made on the Univac 1108 computer in Lund, Sweden.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32030 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Anisotropic thermal parameters with standard deviations ($\times 10^4$)

The form of the temperature factor is $\exp(-\beta_{11}h^2 - \dots - 2\beta_{12}hk - \dots)$. The r.m.s. components R_i ($\times 10^3 \text{ \AA}$) of thermal displacement along the ellipsoid axes are also listed.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Rb ⁺	25 (1)	104 (1)	21 (1)	2 (1)	3 (1)	9 (1)	160 (2)	179 (2)	215 (2)
O(11)	25 (2)	88 (7)	15 (2)	7 (4)	4 (2)	-9 (3)	130 (13)	177 (10)	193 (10)
O(12)	26 (3)	128 (10)	21 (2)	-13 (4)	9 (2)	-17 (3)	134 (12)	174 (12)	246 (10)
O(13)	42 (3)	48 (8)	14 (2)	7 (4)	2 (2)	-2 (3)	127 (14)	162 (11)	214 (9)
O(14)	34 (3)	73 (8)	23 (2)	8 (4)	-14 (2)	4 (3)	128 (14)	171 (11)	250 (10)
O(21)	24 (3)	98 (8)	15 (2)	10 (4)	-2 (2)	-12 (3)	139 (13)	158 (11)	208 (10)
O(22)	25 (3)	107 (9)	14 (1)	4 (4)	-2 (2)	-7 (3)	154 (12)	158 (12)	206 (10)
O(23)	27 (2)	43 (7)	19 (2)	6 (4)	-2 (2)	-2 (3)	119 (14)	170 (10)	184 (10)
O(24)	33 (3)	59 (8)	13 (1)	5 (4)	-7 (2)	-4 (3)	125 (13)	148 (12)	205 (10)
N(11)	18 (3)	42 (8)	10 (2)	2 (4)	1 (2)	2 (3)	123 (15)	123 (15)	147 (12)
N(21)	15 (2)	38 (8)	10 (2)	0 (4)	-2 (2)	-2 (3)	102 (17)	124 (15)	151 (13)
C(11)	21 (3)	67 (11)	15 (2)	7 (5)	6 (2)	-1 (4)	110 (20)	159 (17)	200 (14)
C(12)	23 (4)	54 (10)	12 (2)	-1 (5)	3 (2)	6 (4)	120 (20)	156 (17)	165 (16)
C(13)	23 (3)	40 (9)	14 (2)	0 (5)	-5 (2)	1 (4)	109 (20)	134 (18)	187 (14)
C(14)	20 (3)	60 (10)	8 (2)	3 (4)	5 (2)	5 (4)	89 (23)	142 (16)	177 (15)
C(21)	20 (3)	62 (11)	14 (2)	8 (5)	2 (2)	-16 (4)	98 (22)	145 (16)	198 (15)
C(22)	20 (3)	63 (10)	7 (2)	3 (5)	2 (2)	-4 (4)	115 (19)	138 (17)	144 (17)
C(23)	18 (3)	37 (9)	15 (2)	-5 (5)	-4 (2)	-3 (3)	88 (23)	129 (18)	186 (14)
C(24)	17 (3)	45 (10)	12 (2)	-3 (4)	4 (2)	-2 (4)	114 (19)	132 (17)	168 (15)

Description of the structure

Rb hydrogen iminodiacetate iminodiacetic acid, Fig. 1, contains two independent iminodiacetic acid residues connected *via* hydrogen bonds of the type N—H—O to form infinite aggregates along **b**. These hydrogen bonds take part in an extensive ring system also found in iminodiacetic acid (Boman, Herbertsson & Oskarsson, 1974). There are two 12-membered rings consisting of N(11)—H(11)⋯O(23)—C(24)—O(24)⋯H(12)

Table 3. Coordination distances (Å) with estimated standard deviations

The superscripts indicate transformations applied to the coordinates given in Table 1: (i) $\frac{1}{2} - x, -(\frac{1}{2} - y), z$; (ii) $x, -(1 - y), z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

Rb ⁺ —O(11 ⁱ)	3.103 (5)	Rb ⁺ —O(21)	3.057 (5)
Rb ⁺ —O(12 ⁱⁱ)	3.534 (6)	Rb ⁺ —O(22 ^{iv})	2.985 (5)
Rb ⁺ —O(12 ⁱⁱⁱ)	3.199 (6)	Rb ⁺ —O(22 ^v)	3.059 (6)
Rb ⁺ —O(14)	3.193 (6)	Rb ⁺ —O(23 ⁱ)	3.003 (5)
Rb ⁺ —O(14 ⁱⁱⁱ)	3.166 (6)		

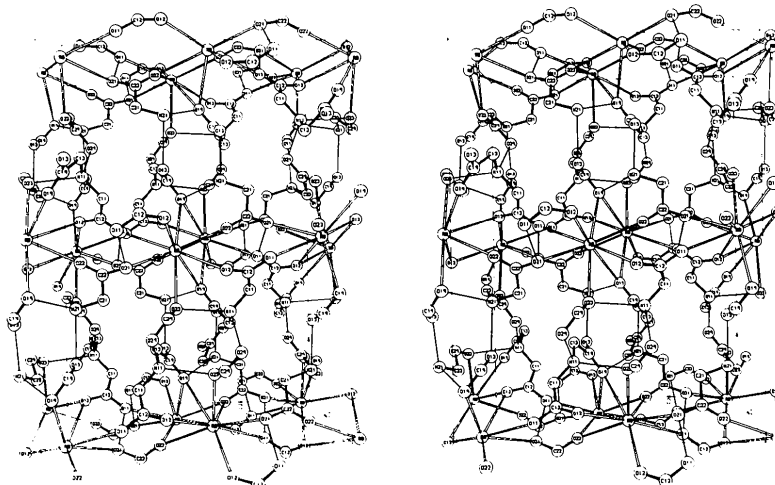


Fig. 1. A stereoscopic view of the structure of the Rb compound with the hydrogen bonds marked by thin lines. Figs. 1–3 were drawn by the program ORTEP.

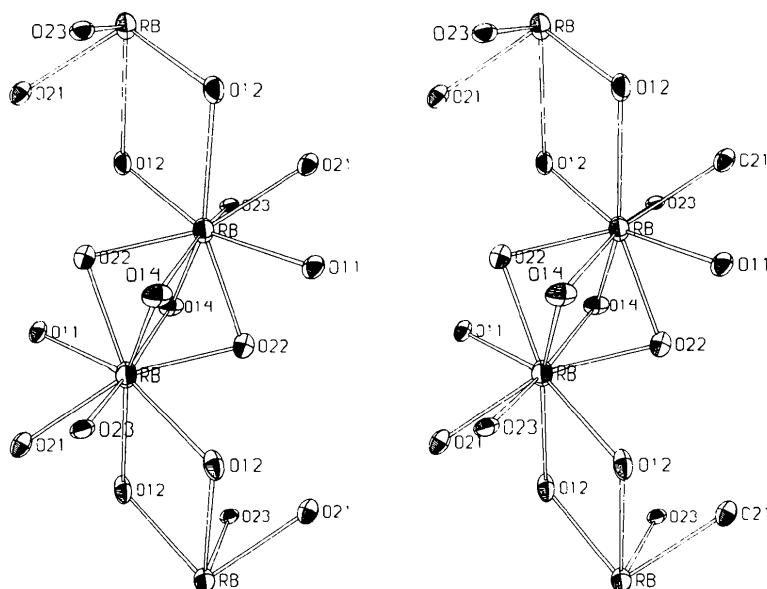


Fig. 2. The coordination around Rb⁺. The figure shows how the Rb⁺ ions are held together along **a**, pointing upwards. In Figs. 2 and 3 thermal ellipsoids were used for the non-hydrogen atoms.

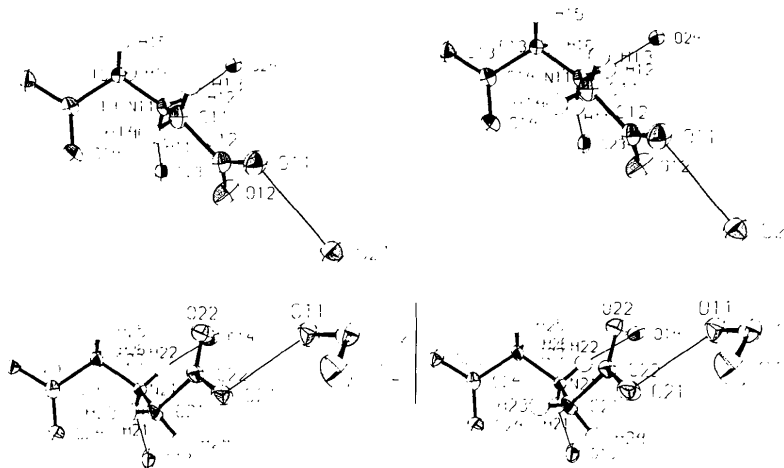


Fig. 3. The ligands with the hydrogen bonds shown as thin lines.

Table 4. *Interatomic distances (Å) and angles (°) with estimated standard deviations*

(a) Ligand 1

N(11)—C(11)	1.476 (9)	C(11)—H(13)	0.91
N(11)—C(13)	1.485 (9)	C(11)—H(14)	0.94
C(11)—C(12)	1.502 (10)	C(13)—H(15)	0.99
C(13)—C(14)	1.532 (10)	C(13)—H(16)	1.05
C(12)—O(11)	1.301 (9)	C(11)—N(11)—C(13)	111.8 (5)
C(12)—O(12)	1.215 (9)	N(11)—C(11)—C(12)	113.1 (6)
C(14)—O(13)	1.259 (9)	N(11)—C(13)—C(14)	110.8 (6)
C(14)—O(14)	1.243 (9)	C(11)—C(12)—O(11)	112.2 (6)
O(11)...O(12)	2.228 (8)	C(11)—C(12)—O(12)	123.1 (7)
O(13)...O(14)	2.225 (8)	O(11)—C(12)—O(12)	124.6 (7)
O(11)...O(13)	6.350 (8)	C(13)—C(14)—O(13)	115.2 (6)
O(12)...O(14)	4.150 (8)	C(13)—C(14)—O(14)	119.2 (6)
		O(13)—C(14)—O(14)	125.6 (7)

(b) Ligand 2

N(21)—C(21)	1.482 (9)	C(21)—H(23)	0.95
N(21)—C(23)	1.494 (9)	C(21)—H(24)	1.06
C(21)—C(22)	1.555 (10)	C(23)—H(25)	1.01
C(23)—C(24)	1.509 (10)	C(23)—H(26)	0.90
C(22)—O(21)	1.279 (9)	C(21)—N(21)—C(23)	115.4 (5)
C(22)—O(22)	1.209 (9)	N(21)—C(21)—C(22)	109.3 (5)
C(24)—O(23)	1.251 (8)	N(21)—C(23)—C(24)	112.5 (6)
C(24)—O(24)	1.254 (8)	C(21)—C(22)—O(21)	113.0 (6)
O(21)...O(22)	2.229 (7)	C(21)—C(22)—O(22)	119.8 (6)
O(23)...O(24)	2.223 (7)	O(21)—C(22)—O(22)	127.2 (6)
O(21)...O(23)	6.264 (8)	C(23)—C(24)—O(23)	116.4 (6)
O(22)...O(24)	5.047 (8)	C(23)—C(24)—O(24)	118.6 (6)
		O(23)—C(24)—O(24)	125.1 (6)

(c) Dihedral angles

N(11)—C(11)—C(12)—O(11)	-158.4
N(11)—C(11)—C(12)—O(12)	23.6
N(11)—C(13)—C(14)—O(13)	-167.8
N(11)—C(13)—C(14)—O(14)	14.3
N(21)—C(21)—C(22)—O(21)	170.3
N(21)—C(21)—C(22)—O(22)	-7.3
N(21)—C(23)—C(24)—O(23)	-177.9
N(21)—C(23)—C(24)—O(24)	2.5

Table 4 (cont.)

(d) The hydrogen bonds

N(11)...O(23)	2.871 (7)	C(11)—N(11)...O(23)	125.1 (4)
N(11)—H(11)	0.95	C(13)—N(11)...O(23)	108.2 (4)
H(11)...O(23)	1.97	C(24)—O(23)...N(11)	121.2 (4)
N(11)...O(24)	2.718 (7)	C(11)—N(11)...O(24)	111.4 (4)
N(11)—H(12)	0.82	C(13)—N(11)...O(24)	109.6 (4)
H(12)...O(24)	1.92	C(24)—O(24)...N(11)	106.0 (4)
N(21)...O(13)	2.733 (7)	C(21)—N(21)...O(13)	101.5 (4)
N(21)—H(21)	0.92	C(23)—N(21)...O(13)	122.3 (4)
H(21)...O(13)	1.86	C(14)—O(13)...N(21)	125.3 (5)
N(21)...O(14)	2.996 (8)	C(21)—N(21)...O(14)	114.4 (4)
N(21)—H(22)	0.89	C(23)—N(21)...O(14)	108.3 (4)
H(22)...O(14)	2.18	C(14)—O(14)...N(21)	91.2 (4)
O(11)...O(21)	2.445 (7)	C(12)—O(11)...O(21)	115.4 (4)
		C(22)—O(21)...O(11)	106.8 (4)

Table 5. *Deviations (Å) from the least-squares planes through the independent halves of the ligands*

The planes are defined by the atoms listed.

Plane I		Plane II	
N(11)	-0.148	N(11)	-0.092
C(11)	0.195	C(13)	0.116
C(12)	0.021	C(14)	0.007
O(11)	-0.118	O(13)	-0.072
O(12)	0.050	O(14)	0.041

Angle between planes I and II: 76°.

Plane III		Plane IV	
N(21)	0.065	N(21)	-0.016
C(21)	-0.076	C(23)	0.020
C(22)	-0.025	C(24)	0.001
O(21)	0.057	O(23)	-0.012
O(22)	-0.022	O(24)	0.007

Angle between planes III and IV: 62°.

and N(21)—H(21)···O(13)—C(14)—O(14)···H(22) together with their centrosymmetrically related atoms. The rings have atoms in common and, as a result of this, 18-membered rings are also formed. The infinite chains are cross-linked by O—H—O bonds and by the interaction between O and Rb⁺ in a three-dimensional structure. There are nine O atoms around the Rb⁺ ion, eight of them situated at distances 2.985 (5) to 3.199 (6) Å and the ninth at the considerably longer distance 3.534 (6) Å, Table 3. The cations are held together in pairs through four O atoms, and these pairs are in their turn linked parallel to **b** by two O atoms (Fig. 2). One ligand forms an eight-membered chelate by coordination of two carboxylate oxygens, O(12) and O(14), to Rb⁺. The cation takes part in six and seven-membered rings involved in the hydrogen-bond system.

The two independent iminodiacetic acid molecules have lost one proton and are connected through a bond of type O—H—O, with O—O = 2.445 (7) Å, as well as through the N—H—O bonds along **b**. The H atom in the O—H—O bond could not be located, but a neutron diffraction study is planned in order to decide if the hydrogen bond is symmetrical or not. As with monoclinic iminodiacetic acid the two ligands are zwitterions, which makes the hydrogen-bond system very complex. The negative charge is most probably spread over the carboxylate groups O(13)—C(14)—O(14) and

O(23)—C(24)—O(24). The dimensions of the other carboxyl groups indicate double bonds C(12)—O(12) and C(22)—O(22) and single bonds C(12)—O(11) and C(22)—O(21). Relevant distances and angles are listed in Table 4 and it can be seen that the main difference between the ligands involves O(12)···O(14), 4.150 (8) Å, and O(22)···O(24), 5.047 (8) Å, owing to the fact that ligand 1 forms a chelate with Rb⁺. From the dihedral angles (Table 4) and the deviations from the least-squares planes (Table 5) through the ligand-halves it is obvious that ligand 2 is the more planar.

Fig. 3 shows the ligands with hydrogen bonds.

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The Structure of Orthorhombic Cadmium Oxydiacetate Trihydrate

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The structure of orthorhombic CdO(CH₂COO)₂·3H₂O has been determined from counter data. The space group is *P*2₁2₁2₁ with *a* = 7.3934 (7), *b* = 8.8955 (10), *c* = 13.3536 (15) Å, *Z* = 4. The structure (*R* = 0.054) consists of layers of composition CdO(CH₂COO)₂·2H₂O joined by hydrogen bonds *via* water molecules. Each Cd atom coordinates seven or possibly eight O atoms. The seven closest O atoms form a pentagonal bipyramid with coordination distances between 2.27 (1) and 2.64 (1) Å and the eighth O is situated at 2.84 (1) Å. The oxydiacetate ion is twisted and the CCOCC framework has the *trans-gauche* conformation. The non-hydrogen atoms are coplanar in each of the two oxydiacetate halves with an angle of 84° between the planes. The absolute configuration has been determined.

Introduction

This work forms part of an investigation of the coordination about Cd in compounds CdA·*n*H₂O, where A²⁻ represents the oxydi-, thiodi- or iminodiacetate ion. Several structures containing these anions in dif-

ferent environments have already been determined (Albertsson, 1972; Albertsson, Grenthe & Herbertsson, 1973*a,b*; Malmberg & Oskarsson, 1973; Oskarsson, 1974; Whitlow, 1975; Herbertsson, 1976), and the present investigation should give some new information about the geometry and chelating ability of the dif-