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The Crystal Structure of Rubidium Hydrogen Oxydiacetate. A Comparison of Crystallographically Independent Oxydiacetate Ions

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In a study of the hydrogen-bond system in the alkali hydrogen salts of oxydiacetic acid the crystal and molecular structures of $RbHO(CH_2COO)_2$ have been determined from X-ray intensities collected with a four-circle diffractometer. The crystals are tetragonal, space group $I\bar{4}2d$, with $a=8\cdot4814$ (2), $c=18\cdot0985$ (9) Å, $Z=8$. The structure has been refined to $R=0\cdot028$, $R_w=0\cdot054$. It is built up of infinite chains of oxydiacetate ions linked by short, symmetric hydrogen bonds. The chains are cross-linked by rubidium ions. The hydrogen–oxygen distance in the hydrogen bond is 1·23 Å and the oxygen–oxygen distance 2·45 (1) Å. The molecular structures of a number of oxydiacetate residues determined in various alkali hydrogen oxydiacetates and tris(oxydiacetato)lanthanoidate(III) complexes by X-ray and neutron single-crystal diffractometry are compared by half-normal probability plots.

Introduction

In a previous communication the X-ray structure determinations of the isostructural sodium and potassium hydrogen oxydiacetates (NaHOXY and KHOXY) have been described (Albertsson, Grenthe & Herbertsson, 1973). As is often the case with acid salts of simple symmetric dicarboxylic acids, these structures contain infinite chains of hydrogen-bonded dicarboxylate residues. Speakman (1972) has recently reviewed the crystal structures of a number of acid dicarboxylate salts. Normally the linking hydrogen bond lies across an element of twofold crystallographic symmetry. In NaHOXY and KHOXY there is no such symmetry element between the oxydiacetate ions and the hydrogen bond is asymmetric with oxygen–oxygen distances of 2·462 (3)* and 2·480 (2) Å, respectively.

This paper reports the X-ray structure of rubidium hydrogen oxydiacetate (RbHOXY) which also contains infinite chains of hydrogen-bonded oxydiacetate ions but with twofold axes between the dicarboxylate residues of the chain. KHOXY and RbHOXY have also been studied by single-crystal neutron diffractometry to make a more thorough comparison of the two types of structures. The results will be described in a subsequent paper (Albertsson & Grenthe, 1973).

The aim of the present investigation was to obtain accurate dimensions for the oxydiacetate ion. In this paper various crystallographically independent hydrogen oxydiacetate and oxydiacetate ions are compared by the method of half-normal probability plots (De Camp, 1973; Abrahams & Keve, 1971).

Experimental

Colourless crystals, tabular **c**, of RbHOXY were prepared by slow evaporation at room temperature of an aqueous solution of equimolar amounts of oxydiacetic acid and rubidium hydroxide. The composition of the crystals was checked by elemental analysis of C and H. Oscillation and Weissenberg photographs showed that RbHOXY crystallizes in the Laue class $4/mmm$ with the reflexions hkl: $h+k+l\neq 2n$ and hhl: $2h+l\neq 4n$ systematically absent. Possible space groups are thus $I4_1md$ and $I\bar{4}2d$ (Nos. 109 and 122, respectively). The lattice constants were improved by least-squares refinement from the powder pattern obtained at room temperature with a Guinier–Hägg camera of radius 4·00 cm. Cu $K\alpha$ radiation was used with aluminium ($a=4\cdot04934$ Å) as internal standard. The density D_m was determined by the displacement method in benzene.

Caesium and thallium(I) hydrogen oxydiacetates are isostructural with RbHOXY. Their crystal data have been determined in the same way.

Crystal data

(1) Rubidium hydrogen oxydiacetate, $RbC_4H_5O_5$; F.W. 218·6. Tetragonal; space group $I\bar{4}2d$; $a=8\cdot4814$ (2), $c=18\cdot0985$ (9) Å, $V=1301\cdot9$ Å^3; $Z=8$; $D_m=2\cdot25$, $D_x=2\cdot230$ g cm^{-3}.

(2) Caesium hydrogen oxydiacetate, $CsH_4H_5O_5$; F.W. 266·0. $a=8\cdot8095$ (4), $c=18\cdot1120$ (12) Å, $V=1405\cdot6$ Å^3; $D_m=2\cdot52$, $D_x=2\cdot514$ g cm^{-3}.

(3) Thallium(I) hydrogen oxydiacetate, $TlC_4H_5O_5$; F.W. 337·5. $a=8\cdot4668$ (2), $c=18\cdot1180$ (7) Å, $V=1298\cdot8$ Å^3; $D_m=3\cdot49$, $D_x=3\cdot451$ g cm^{-3}.

The layers $0kl$–$7kl$ of RbHOXY were recorded by the non-integrated Weissenberg multiple-film tech-

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* Estimated standard deviations referring to the least significant digits are given in parentheses.

nique with Ni-filtered Cu radiation. The intensities of 348 independent reflexions were estimated visually, and, after correction for Lorentz and polarization effects, were used to solve the structure.

The refinement of the model thus obtained was based on diffractometer data. A crystal, tabular **c**, with dimensions $0{\cdot}18\times0{\cdot}18\times0{\cdot}06$ mm and bounded by the faces $\{100\}$ and $\{001\}$ was arbitrarily mounted on the computer controlled four-circle diffractometer CAD-4 (manufactured by Enraf–Nonius, Delft, Holland) equipped with a graphite monochromator. Cu $K\alpha$ radiation was employed ($\lambda=1{\cdot}54178$ Å) with a take-off angle of 5°. The intensities were recorded with the ω–2θ scan technique. The scan interval varied as $\omega=1{\cdot}00+0{\cdot}15\tan\theta$ where the term $0{\cdot}15\tan\theta$ is a correction for the α_1–α_2 separation. The aperture of the scintillation detector, which is situated 173 mm from the crystal, was 4×4 mm^2. A fast pre-scan was used to determine a scan speed at which a predetermined minimum number of counts (3000) were received by the detector. The background was measured for $\frac{1}{4}$ of the scan time at each end of the interval. The intensities of 1468 reflexions were recorded with repeated scans. The investigated reciprocal region consists of all reflexions with $5\le\theta<30°$ and the reflexions with positive h, k, and l and $h\le k$ for $30\le\theta<70°$. Owing to a ratemeter failure, 63 reflexions had to be excluded because they did not obey the condition $(I_1-I_2)^2\le 8(I_1+I_2)$ after three attempts, where I_1 and I_2 are the intensities in two successive scans of a reflexion. Another 52 reflexions with $I<2\sigma_C(I)$ were judged to be insignificantly different from the background and were also excluded. The values of $\sigma_C(I)$ are based on counting statistics. To check the stability of the crystal and electronics, two reference reflexions (204 and 004) were measured at regular intervals during the data collection. No variation in their intensities was detected.

The values of I and $\sigma_C(I)$ were corrected for Lorentz, polarization, and absorption effects. The expression $p=(1+\cos^2 2\theta_M\cos^2 2\theta)/(1+\cos^2 2\theta_M)$ with $\theta_M=13{\cdot}3°$ was used in the correction of the polarization effects. The linear absorption coefficients is $113{\cdot}5$ cm^{-1} and the transmission factor evaluated by numerical integration varied in the interval $0{\cdot}197$–$0{\cdot}512$.

Structure determination and refinement

The choice of the space group for RbHOXY is based on symmetry considerations assuming the structure to be built up of hydrogen oxydiacetate chains running in the **c** direction. In $I\bar{4}2d$ the eight ether oxygen atoms in a unit cell can be placed on twofold axes making the two halves of each oxydiacetate ion equivalent. The molecules in each chain are then also related by twofold axes and the chains by the fourfold inversion axes. In the space group $I4_1md$, all the non-hydrogen atoms of the oxydiacetate ion would have to be located in the four planes $x=0$, $\frac{1}{2}$ and $y=0$, $\frac{1}{2}$ [positions 8(b)] to avoid assumptions about a statistical distribution of this ion in the structure. The rubidium ions were located on the lines $x=y=0$; $x=0$, $y=\frac{1}{2}$; $x=\frac{1}{2}$, $y=0$; and $x=y=\frac{1}{2}$ in the three-dimensional vector map. The subsequent difference map showed positions near the plane $y=\frac{1}{4}$ for all non-hydrogen atoms of the oxydiacetate ion. All the following calculations have therefore been carried out in the space group $I\bar{4}2d$.

336 non-zero reflexions with h, k, and l positive and $h\le k$ were used in the first series of refinements. The function minimized was $\sum w(|F_o|-|F_c|)^2$. Each reflexion was given a weight w inversely proportional to the estimated variance of the observation $w^{-1}=\sigma^2(|F_o|)=\sigma_C^2(|F_o|^2)/4|F_o|^2+C_1|F_o|^2+C_2$, where C_1 and C_2 are adjustable constants. The convergence was followed by the conventional R and the weighted R defined by $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. With $C_1=9\,.\,10^{-4}$, $C_2=0$, and anisotropic temperature factors assigned to all the non-hydrogen atoms, $R=0{\cdot}039$ and $R_w=0{\cdot}065$ were obtained. The values of C_1 and C_2 were varied until a good fit was obtained with $C_1=16\,.\,10^{-4}$ and $C_2=5{\cdot}0$ resulting in $R=0{\cdot}036$ and $R_w=0{\cdot}051$. A difference map revealed approximate positions for the hydrogen atoms.

All 1468 values of $|F_o|^2$ and $\sigma_C(|F_o|^2)$ were sorted in groups of equivalent reflexions and the mean values within each group calculated to give a new set of independent data containing 353 non-zero values of $|F_o|$. The positional parameters for the hydrogen atoms were included in the refinement with fixed temperature factors $B=5$ Å^2. The standard deviations of the parameters were fairly large and the shifts oscillated about one standard deviation in each cycle of refinement. Hence, no accurate hydrogen parameters could be obtained. As the neutron diffraction study of the structure had been completed (Albertsson & Grenthe, 1973) the positional parameters for the hydrogen atoms were taken from that work. They were not varied in the following calculations. With $C_1=16\,.\,10^{-4}$ and $C_2=8{\cdot}0$ the average value of $w(|F_o|-|F_c|)^2$ in different $|F_o|$ and $\sin\theta$ intervals was fairly constant. The final agreement indices were $R=0{\cdot}028$ and $R_w=0{\cdot}054$. Inclusion of an isotropic extinction correction (Zachariasen, 1967) gave no improvement and only two reflexions appeared to be affected. A final difference map was featureless.

Table 1. *Atomic coordinates for* RbHOXY *with standard deviations* ($\times10^4$)

	x	y	z
Rb	0	0	1162 (1)
O(1)	2492 (10)	2500	1250
O(2)	1010 (6)	2559 (8)	−40 (3)
O(3)	3244 (7)	2607 (9)	−671 (3)
C(1)	3440 (9)	2568 (13)	609 (4)
C(2)	2387 (14)	2612 (15)	−64 (8)
H(1)	2500	2676	−1250
H(2)	4241	1550	580
H(3)	4174	3631	609

The atomic coordinates with their estimated standard deviations are listed in Table 1. The thermal parameters and the root-mean-square components of thermal displacement along the principal axes of the ellipsoids of vibration are given in Table 2. The observed and calculated structure factors are listed in

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

The form of the temperature factor is exp $(-\beta_{11}h^2 - \ldots 2\beta_{12}hk - \ldots)$. The root-mean square-components R_i with standard deviations ($\times 10^3$ Å) 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	94 (1)	110 (2)	25 (1)	9 (2)	0	0	182 (2)	202 (2)	204 (2)
O(1)	77 (9)	135 (11)	12 (2)	0	0	−7 (4)	139 (12)	168 (9)	224 (9)
O(2)	100 (8)	168 (10)	19 (1)	1 (8)	−5 (3)	−1 (4)	170 (8)	196 (8)	247 (7)
O(3)	133 (9)	133 (10)	16 (2)	21 (10)	15 (3)	1 (4)	146 (9)	208 (9)	242 (9)
C(1)	89 (11)	131 (12)	14 (2)	0 (12)	7 (4)	−5 (5)	140 (13)	187 (11)	220 (10)
C(2)	82 (11)	71 (11)	18 (3)	11 (11)	−2 (7)	−6 (5)	149 (15)	169 (19)	188 (16)

Table 3. *Observed and calculated structure factors*

The reflexions are sorted in groups with *h* and *k* constant. In each group $10|F_o|$ and $10|F_c|$ are given after the running index *l*.

H= 0 K= 0		
4	1284	1351
8	1890	2044
12	530	514
16	1580	1626
20	192	205
H= 0 K= 1		
1	1312	1305
3	905	860
5	1106	1134
7	1219	1162
9	1514	1510
11	58	64
13	818	849
15	53	35
17	527	520
19	180	176
21	302	302
H= 0 K= 2		
0	543	470
2	63	29
4	2548	2602
6	66	21
8	1443	1438
10	71	70
12	1213	1232
14	91	92
16	165	159
18	64	58
20	202	213
H= 0 K= 3		
1	1619	1624
3	715	716
5	1496	1495
7	52	25
9	780	787
11	353	350
17	599	617
19	120	107
21	338	324
H= 0 K= 4		
0	2904	2947
2	129	136
4	1674	1684
6	53	47
8	1677	1687
10	57	44
12	773	754
14	102	107
16	771	774
20	251	249
H= 0 K= 5		
1	473	472
3	981	989
5	910	931
7	351	372
9	695	714
11	196	194
13	771	764
15	162	174
17	317	326
19	37	15
H= 0 K= 6		
0	546	549
2	100	87
4	1487	1514
6	63	45
8	373	343
12	812	810
16	76	85
H= 0 K= 7		
1	554	551
3	468	448
5	636	621
7	273	247
9	580	600
11	134	135
13	404	404
15	69	68
H= 0 K= 8		
0	1277	1280
2	132	132
4	673	657
6	56	30
8	866	878
10	56	38
12	372	361
H= 0 K= 9		
3	232	228
5	418	419
7	191	209
9	360	353
H= 0 K= 10		
0	307	310
4	501	498
H= 1 K= 1		
2	363	352
6	1052	1027
10	872	861
14	886	869
18	612	616
H= 1 K= 2		
1	1301	1318
3	1167	1155
5	1697	1714
7	735	683
9	928	929
11	508	513
15	44	50
17	548	552
19	125	81
21	355	346
H= 1 K= 3		
0	1302	1251
2	216	230
4	600	571
6	715	712
8	52	16
10	807	840
12	289	287
14	707	723
16	350	332
18	542	538
20	84	85
H= 1 K= 4		
1	1036	1045
3	721	677
5	815	823
7	673	674
9	1002	1027
11	72	85
13	658	658
15	162	169
17	458	453
19	155	154
H= 1 K= 5		
0	733	748
2	241	248
4	120	124
6	582	592
8	383	383
10	536	526
14	574	566
16	283	285
18	441	444
H= 1 K= 6		
1	623	646
3	535	536
5	814	813
7	181	137
9	575	567
11	174	175
13	517	515
15	50	37
17	375	376
H= 1 K= 7		
0	241	245
2	169	173
4	80	69
6	293	302
8	316	339
10	426	431
12	49	29
14	420	433
16	117	121
H= 1 K= 8		
1	478	501
3	327	335
5	435	440
7	272	257
9	500	491
11	82	91
13	363	361
H= 1 K= 9		
0	139	133
2	142	138
4	96	79
6	233	241
10	235	239
H= 1 K= 10		
1	303	295
3	213	217
5	306	311
H= 2 K= 2		
0	3716	3874
4	2309	2268
8	1549	1531
12	955	967
16	890	907
20	334	337
H= 2 K= 3		
1	756	771
3	939	925
5	927	917
7	994	1004
9	1161	1197
11	253	265
13	794	796
15	163	153
17	406	402
19	119	115
H= 2 K= 4		
0	1337	1346
2	50	39
4	1301	1313
6	65	73
8	935	952
10	104	91
12	714	664
14	60	59
16	328	343
18	38	44
H= 2 K= 5		
1	1037	1036
3	319	343
5	829	855
7	469	473
9	824	816
11	194	176
13	430	436
17	433	441
H= 2 K= 6		
0	1617	1607
2	104	116
4	989	993
6	87	91
8	1355	1354
10	97	97
12	533	520
16	488	477
H= 2 K= 7		
1	608	613
3	397	393
5	559	552
7	328	310
9	482	495
11	113	120
13	427	439
15	92	81
H= 2 K= 8		
0	575	559
4	813	809
8	406	404
10	93	112
12	430	432
H= 2 K= 9		
1	277	278
3	371	370
5	385	395
7	189	190
9	379	381
H= 2 K= 10		
0	677	661
2	98	96
H= 3 K= 3		
2	343	353
6	718	726
10	631	620
14	586	572
18	510	512
H= 3 K= 4		
1	966	982
3	598	605
5	1048	1067
7	177	180
9	671	662
11	255	251
13	560	548
15	161	162
17	442	451
H= 3 K= 5		
0	122	117
2	151	141
4	148	146
6	361	370
8	340	332
10	522	543
14	534	540
16	67	54
18	382	373
H= 3 K= 6		
1	505	502
3	510	490
5	565	547
7	385	390
9	629	617
11	61	27
13	501	508
H= 3 K= 7		
2	188	188
4	176	177
6	359	364
8	291	278
10	333	330
14	370	368
H= 3 K= 8		
1	483	481
3	284	277
5	465	476
7	110	84
9	360	367
11	114	109
H= 3 K= 9		
0	36	13
2	101	93
6	141	146
H= 4 K= 4		
0	1276	1289
4	1479	1542
8	1344	1343
12	795	791
16	332	324
H= 4 K= 5		
1	556	543
3	683	664
5	703	683
7	326	289
9	537	543
11	133	133
13	570	574
15	176	167
17	330	328
H= 4 K= 6		
0	954	954
2	70	51
4	1011	976
8	255	256
10	79	82
12	530	533
14	40	35
H= 4 K= 7		
1	343	341
3	382	377
5	529	526
7	277	264
9	523	541
11	129	118
13	344	351
H= 4 K= 8		
0	779	787
2	112	111
4	634	632
6	38	29
8	759	750
10	43	55
H= 4 K= 9		
1	415	415
5	328	330
H= 5 K= 5		
2	243	235
6	392	380
10	410	411
14	371	375
H= 5 K= 6		
1	548	534
3	243	237
5	490	489
7	244	239
9	546	558
11	59	64
13	307	311
H= 5 K= 7		
2	98	103
6	230	234
10	276	287
12	44	33
H= 5 K= 8		
1	279	293
3	316	326
5	368	365
7	134	138
9	274	292
H= 5 K= 9		
0	51	38
2	107	117
H= 6 K= 6		
0	872	866
4	564	573
8	1074	1059
12	309	314
H= 6 K= 7		
1	429	427
3	276	272
5	370	381
7	122	123
9	264	262
H= 6 K= 8		
0	450	451
2	30	37
4	570	576
H= 7 K= 7		
2	125	124

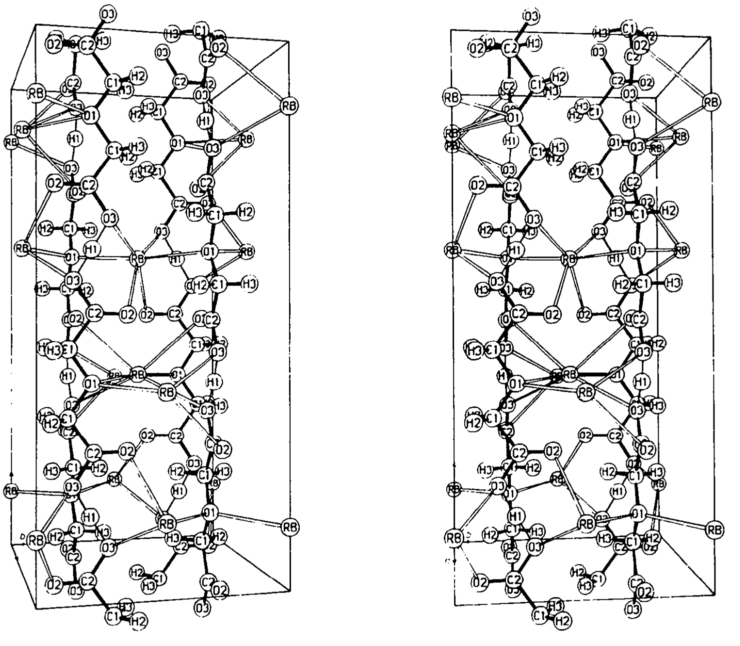

Fig. 1. A stereoscopic pair of drawings showing the content of a unit cell of RbHOXY.

Table 3. The atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The calculations were performed on the UNIVAC 1108 computer in Lund. A short account of the program system used is given by Oskarsson (1973).

Description of the structure

The structure is shown in Fig. 1. The oxydiacetate residues are linked in infinite chains by short hydrogen bonds across twofold axes. The chains run in the **c** direction along the four lines $x=y=\frac{1}{4}$; $x=\frac{1}{4}$, $y=\frac{3}{4}$; $x=\frac{3}{4}$, $y=\frac{1}{4}$; and $x=y=\frac{3}{4}$ with the non-hydrogen atoms located near the planes $y=\frac{1}{4}$, $x=\frac{1}{4}$; $x=\frac{3}{4}$, and $y=\frac{3}{4}$, respectively. The chains are crosslinked by rubidium ions. In NaHOXY and KHOXY all the oxydiacetate planes are parallel but in RbHOXY there are two perpendicular sets of parallel planes.

There is a twofold crystallographic symmetry in the oxydiacetate residue in RbHOXY with the ether oxygen atom on a twofold axis. The ion is shown in Fig. 2. Its interatomic distances and angles are given in Table 4. Distances from the least-squares planes through the non-hydrogen atoms are given in Table 5. Within the limits of error these atoms are coplanar, which means that the oxydiacetate residue has very nearly *mm* symmetry.

Table 4. *Selected interatomic distances and angles for the ligand in* RbHOXY

O(1)–C(1)	1·413 (8) Å	C(1)–O(1)–C(1^{i})	110·7 (8)°
C(1)–C(2)	1·511 (14)	O(1)–C(1)–C(2)	109·1 (8)
C(2)–O(2)	1·170 (13)	C(1)–C(2)–O(2)	124·0 (13)
C(2)–O(3)	1·317 (16)	C(1)–C(2)–O(3)	110·2 (9)
O(1)–O(2)	2·652 (6)	O(2)–C(2)–O(3)	125·7 (11)
C(1)–H(2)	1·10	H(2)–C(1)–H(3)	107·1
C(1)–H(3)	1·10		

Table 5. *Deviations from the least-squares planes through the non-hydrogen atoms for the ligand in* RbHOXY

The lower signs refer to the superscripted atoms. The angle between the ligand halves is 1°.

Whole ligand		Independent ligand-half	
O(1)	0·000 Å	O(1)	0·11 Å
C(1), C(1^{i})	∓0·023	C(1)	0·005
C(2), C(2^{i})	∓0·025	C(2)	0·016
O(2), O(2^{i})	±0·019	O(2)	−0·008
O(3), O(3^{i})	±0·012	O(3)	−0·025

Table 6. *The hydrogen bond in* RbHOXY

O(3)···O(3^{ii})	2·448 (12) Å
O(3)—H(1)	1·23
O(3)—H(1)–O(3^{ii})	174·5°
C(2)—O(3)–H(1)	115·4

The results obtained for the hydrogen bond are given in Table 6. Again it should be pointed out that the hydrogen atoms have been placed in the positions obtained in the neutron diffraction study. The hydrogen bond is short, the distance O(3)–O(3^{ii})* being 2·45 (1) Å. It is slightly bent and the hydrogen atom is most probably situated on the twofold axis between the bonded oxydiacetates. The donor and acceptor C–O–H angles are then equal with the value 115°, which is the same as found in NaHOXY and KHOXY.

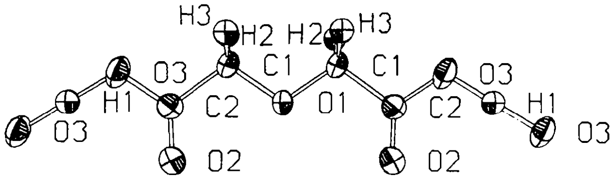

Fig. 2. The oxydiacetate residue and the hydrogen bond. The thermal ellipsoids for the non-hydrogen atoms are scaled to include 50% probability.

The alkali metal ion in NaHOXY and KHOXY is surrounded by seven oxygen atoms forming a penta-

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* For superscripted atoms, see legend to Table 7.

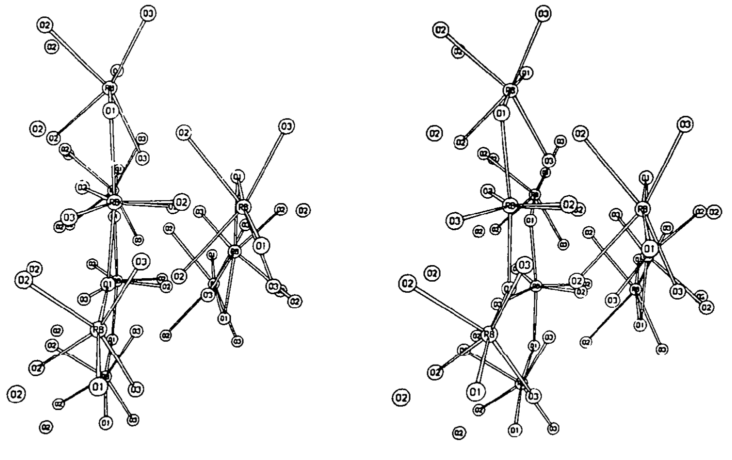
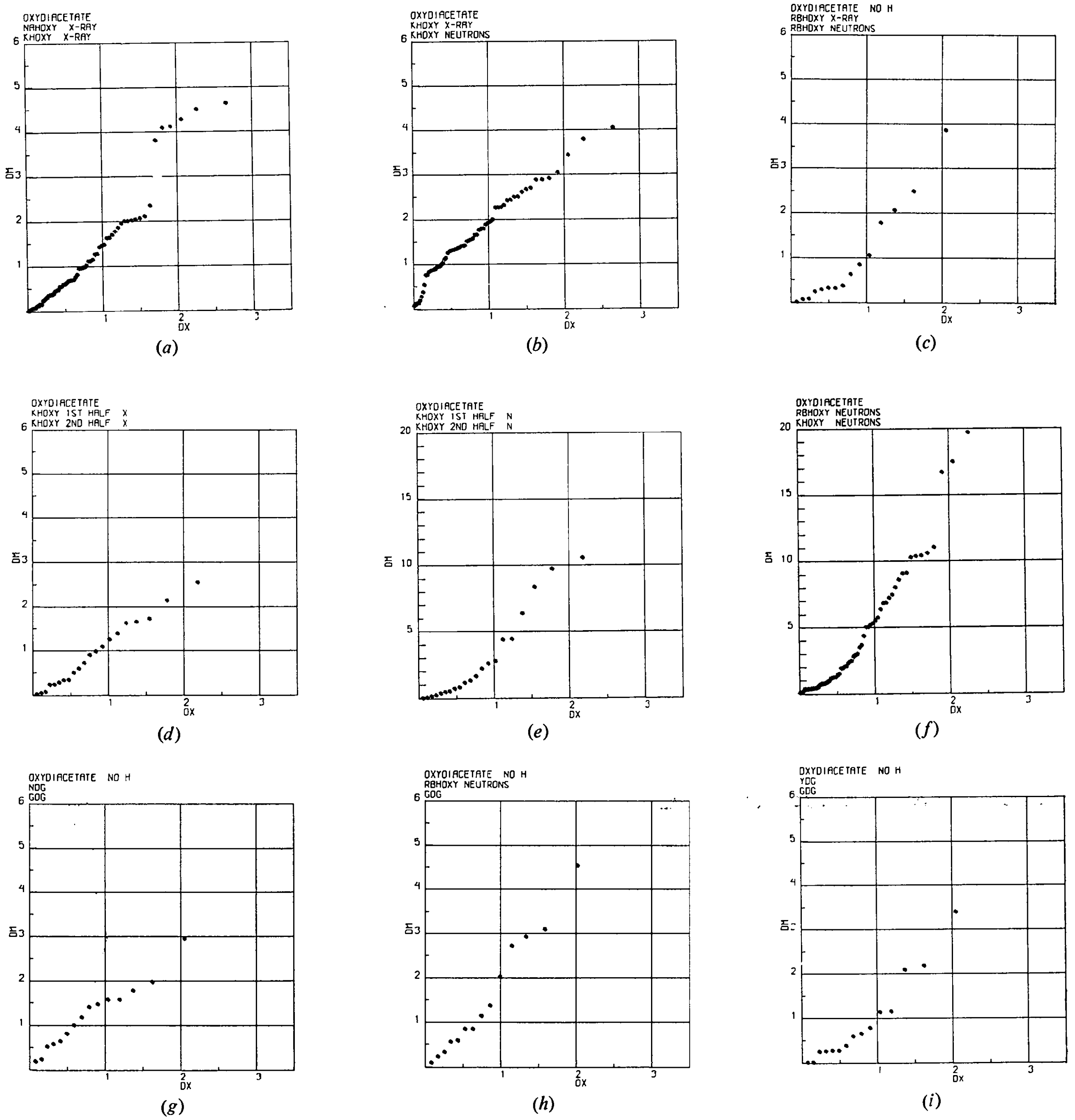


Fig. 3. A stereoscopic pair of drawings showing the chains of octahedra around the rubidium ions.

gonal bipyramid. In RbHOXY the rubidium ion has eight oxygen neighbours (Table 7). The six nearest form a distorted octahedron with the remaining two oxygen atoms outside two adjacent triangular faces of the polyhedron (Figs. 1 and 3). By sharing of the O(1) corners, the octahedra are connected in infinite chains running in the **a** and **b** directions along the lines $x=0$, $z=\frac{1}{8}$; $y=\frac{1}{2}$, $z=\frac{3}{8}$; $x=\frac{1}{2}$, $z=\frac{5}{8}$; and $y=0$, $z=\frac{7}{8}$ (Fig. 3). This type of crosslinking agrees with the fact that the spacing in the **c** direction is very little affected by the cation in the series RbHOXY, CsHOXY, and TlHOXY, while that in the **a** and **b** directions varies



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

(*g*) (*h*) (*i*)

Fig. 4. Half-normal probability plots of independent molecular geometries of the oxydiacetate ion. The compared crystal structures are given above each plot. The following four members are given for each plot: the number of values included, the number of points with $\delta m_i < 2·50$, the slope of the least-squares line through the latter points, and the intercept of the least-squares line on the ordinate. (*a*) 64, 58, 1·52, −0·10; (*b*) 64, 53, 1·69, 0·31; (*c*) 15, 14, 1·64, −0·40; (*d*) 21, 20, 1·30, −0·13; (*e*) 21, 13, 2·58, −0·36; (*f*) 63, 32, 3·35, −0·14; (*g*) 15, 14, 1·20, 0·22; (*h*) 15, 14, 1·42, −0·29; (*i*) 14, 10, 1·88, −0·14.

with the size of the cation. When the somewhat larger rubidium or caesium ion is used instead of the sodium or potassium ion, the changed packing of the infinite hydrogen oxydiacetate chains building up the structure enhances the symmetry of the compound. The short hydrogen bond connecting the oxydiacetate residues in both cases is changed from an asymmetric bond in NaHOXY and KHOXY to a symmetric bond in RbHOXY.

Table 7. *The nearest neighbour oxygen atoms around the rubidium ion*

Symmetry-related sites are denoted by (i) $x,\frac{1}{2}-y,\frac{1}{4}-z$; (ii) $\frac{1}{2}-x,y,-\frac{1}{4}-z$; (iii) $\bar{y},x,\bar{z}$; (iv) $y,-\frac{1}{2}+x,\frac{1}{4}+z$.

Rb–O(1)	2·998 (6) Å
Rb–O(2)	3·190 (6)
Rb–O(2^{iii})	3·093 (6)
Rb–O(3^{iv})	2·927 (7)

The oxydiacetate ion

The molecular structure of the oxydiacetate ion has been investigated in a number of compounds. X-rays have been used for the alkali hydrogen oxydiacetates NaHOXY, KHOXY, and RbHOXY and neutrons for KHOXY and RbHOXY (Albertsson, Grenthe & Herbertsson, 1973; Albertsson & Grenthe, 1973). One of the present authors has also investigated the tris(oxydiacetato)lanthanoidate complexes $Na_3[M(C_4H_4O_5)_3].2NaClO_4.6H_2O$, M = Nd (NDG), Gd (GDG), and Yb (YDG) (Albertsson, 1968, 1970). DG is an abbreviation for diglycollate which is the trivial name of oxydiacetate. In the lanthanoid compounds the hydrogen atoms were not located.

To compare the crystallographically independent oxydiacetate ions in the various structures we have used the method of half-normal probability plots (De Camp, 1973). Interatomic distances less than 4·65 Å are used as coordinates of the ion. Observed ranked values of $\delta m_i = |d(1)_i - d(2)_i|/[\sigma^2 d(1)_i + \sigma^2 d(2)_i]^{1/2}$ are plotted *versus* the expected values δx_i calculated according to Hamilton & Abrahams (1972). The quantities $d(1)_i$ and $d(2)_i$ are the corresponding intramolecular distances in the compared structures with estimated standard deviations $\sigma d(1)_i$ and $\sigma d(2)_i$. Representative results are given in Fig. 4.

There is no obvious difference between the oxydiacetate residues in the X-ray structures of NaHOXY and KHOXY [Fig. 4(*a*)]. The same result is arrived at when the X-ray and neutron structures of the residue in KHOXY and RbHOXY, respectively, are compared [Fig. 4(*b*) and (*c*)] despite the systematic error introduced in KHOXY by comparing C–H distances determined by X-ray and neutron diffractometry. The plots are linear with slopes of 1·52, 1·69, and 1·64 for the least-squares lines through points with δm_i less than 2·50. The intercepts lie near the origin indicating that no great systematic differences are present (Abrahams & Keve, 1971). If this is true the slopes can be taken as measures of the reliability of the estimated standard deviations. From Fig. 4(*a*)–(*c*) and a number of other probability plot comparisons we conclude that in general the standard deviations for interatomic distances and angles are underestimated by a factor of about 1·7 in our investigation of the alkali hydrogen oxydiacetates.

The two halves of the oxydiacetate residue in NaHOXY and KHOXY are crystallographically independent. The halves in the X-ray and neutron structures of KHOXY, respectively, are compared in Fig. 4(*d*) and (*e*). The standard deviations are multiplied by the factor 1·7. The estimated errors for the hydrogen atoms in the neutron structure are about ten times smaller than in the X-ray structure. This results in a detectable difference between the two halves in the neutron structure but not in the X-ray structure. The CH_2 groups are not identically located relative to the carboxylic groups and there is a difference in the single-bonded carboxylic C–O distances caused by the hydrogen-bond system. This difference between the ligand halves in the neutron structure of KHOXY is also a reason for the non-linear plot seen in Fig. 4(*f*), where a comparison with the ligand in the neutron structure of RbHOXY is made. Only one of the ligand halves in KHOXY is compatible with the ligand half in RbHOXY. Another difference between KHOXY and RbHOXY is that the acetic acid residues are slightly twisted in the former complex but nearly coplanar in the latter.

There are no great differences in the oxydiacetate ligand in lanthanoid tris-complexes [Fig. 4(*g*) and (*h*)]. The slopes 1·20 and 1·42 of the least-squares lines through points with δm_i less than 2·50 again indicate that the standard deviations have been underestimated. However, the errors involved are so large that the ligand in GDG is compatible with the oxydiacetate residue in, *e.g.*, the neutron structure of RbHOXY [Fig. 4(*i*)] in spite of the different bonding situation in the –COO groups.

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