cates, was supposed to be isomorphous with $NiSnCl_6.6H_2O$, with one formula unit per rhombohedral unit cell, and consequently, the water octahedron surrounding the Cu^{2+} ion was considered trigonally distorted. With such assumption, Bleany & Ingram (1950) used mixed crystals of $CuSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$ in their study of paramagnetic resonance, and Abragam & Pryce (1950) gave theoretical interpretation of the results thus obtained, assuming that the Cu^{2+} ion was subjected to a ligand field of trigonal symmetry. The Cu:Zn ratio in the mixed crystal used in the experiment has not been mentioned in the paper of Bleaney & Ingram. Assuming that the Cu^{2+} ion concentration was very low, it is quite probable that the structure of the mixed crystal resembled that of $ZnSiF_6.6H_2O$, and consequently the Cu^{2+} ions may indeed have been in a ligand field with trigonal symmetry. In that case, there should be no objection to the said studies, except that the results obtained do not relate to the actual ligand field in $CuSiF_6.6H_2O$. A careful study of paramagnetic resonance with the 'undiluted' salt would then be worthwhile. It would also be interesting to prepare mixed crystals with different Cu:Zn ratio, and find out for what maximum concentration of Cu^{2+} the structure resembles that of $ZnSiF_6.6H_2O$.

Fig. 1 shows a portion of the structure in orthogonal projection on the *xz* plane. One of each kind of hydrogen atom is identified. The bonds O(1)···F(1) and O(1)···F(2) follow the same pattern as in $CoSiF_6.6H_2O$. But while each of F(1), F(2) and F(3) takes part in two hydrogen bonds, F(4) seems to participate in only one; there appears an O(3)···O(4) bond instead. This makes the hydrogen bond configuration in this case rather different than that in $CoSiF_6.6H_2O$, where each F atom participates in two hydrogen bonds.

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A Neutron Diffraction Study of Potassium and Rubidium Hydrogen Oxydiacetate. The Dynamics of Their Hydrogen Bonds

BY J. ALBERTSSON AND I. GRENTHE

Inorganic Chemistry 1 *and Physical Chemistry* 1, *Chemical Center*, *University of Lund*, *P.O.B.* 740, *S*-220 07 *Lund*, *Sweden*

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The crystal structures of $KHO(CH_2COO)_2$ and $RbHO(CH_2COO)_2$ have been investigated by neutron diffraction to obtain information about the hydrogen-bond systems in these compounds. The structures were refined to $R=0{\cdot}036$ and $R=0{\cdot}030$, respectively. The positions of the heavy atoms are in agreement with earlier X-ray investigations. Both compounds consist of hydrogen oxydiacetate chains crosslinked by the alkali metal ion. The hydrogen bond (O–H···O) in the potassium compound is asymmetric and of length 2·476 (2) Å. The angle O–H···O is 174·2 (3)° and the covalent O–H bond length 1·152 (3) Å. In the rubidium compound the bond is symmetric. Its length is 2·449 (3) Å and the angle O···H···O is 175·0 (4)°. Analysis of the thermal motion parameters of the acid hydrogen atom indicates that, in $RbHO(CH_2COO)_2$, it vibrates anharmonically in a broad, single, and symmetric potential-energy well. The asymmetric O–H stretching frequency is less than 1000 cm^{-1} in both compounds.

Introduction

In a study of the hydrogen-bond system in the alkali hydrogen salts of oxydiacetic acid the crystal and molecular structures of $MHO(CH_2COO)_2$, M = Na, K, and Rb, have been determined from X-ray intensities (Albertsson, Grenthe & Herbertsson, 1973*a*, *b*). The compounds are hereafter denoted NaHOXY, KHOXY and RbHOXY, respectively. NaHOXY and KHOXY are isostructural and crystallize in the monoclinic space group $P2_1/c$ but RbHOXY is tetragonal with space group $I\bar{4}2d$. Both types of structures contain chains of oxydiacetate residues linked end-to-end by a short hydrogen bond of length 2·480 (2)* and 2·451 (2) Å in KHOXY and RbHOXY, respectively. The X-ray results indicate an asymmetric hydrogen bond in NaHOXY and KHOXY. The hydrogen–oxygen bond distances are 1·05 (3) and 1·44 (3) Å in KHOXY. The hydrogen atoms were located in the RbHOXY structure but could not be refined. Since there is a twofold axis between the hydrogen-bonded oxygen atoms in RbHOXY the bond must be symmetric with the hydrogen atom situated either on this axis or statistically distributed around it. The difficulty in making an experimental distinction between the two cases has been discussed extensively by Ibers (McGaw & Ibers, 1963; Ibers, 1964). A neutron diffraction study of KHOXY and RbHOXY has been made in order to get more accurate parameters for the hydrogen atoms to enable a better elucidation of the hydrogen bonds in the two types of structures. Crystal data for the compounds are given in Table 1.

Table 1. *Crystal data*

	KHOXY	RbHOXY
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$I\bar{4}2d$
a	7·102 (2) Å	8·4814 (2) Å
b	10·451 (1)	8·4814 (2)
c	8·558 (2)	18·0985 (9)
β	101·44 (2)°	–
V	622·5 Å^3	1301·9 Å^3
Z	4	8
D_x	1·837 g cm^{-3}	2·230 g cm^{-3}

Experimental

Suitable single crystals of KHOXY were grown by slow evaporation at room temperature of an aqueous solution of potassium hydrogen oxydiacetate. To prepare stout prismatic crystals of RbHOXY a water solution of rubidium hydrogen oxydiacetate had to be evaporated very slowly at a temperature above 50°C. At lower temperatures only thin plates were obtained.

The intensities of both compounds were recorded at room temperature with the computer controlled Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy reactor R2, Studsvik. The wavelength was 1·210 Å. A region of reciprocal space out to $\sin\theta/\lambda = 0{\cdot}64$ Å^{-1} for KHOXY and 0·69 Å^{-1} for RbHOXY was examined with the ω–2θ step scan technique. About 15 min were spent measuring each reflexion. The neutron flux at the specimens was about 10^6 cm^{-2} s^{-1}. The maximum number of counts obtained for a reflexion was 53000 for KHOXY and 246000 for RbHOXY. The crystals were arbitrarily mounted on the diffractometer to avoid errors caused by multiple diffraction. Two standard reflexions per structure were measured at regular intervals to provide a check on crystal and electronic stabilities. No significant variations were observed. The intensities were corrected for Lorentz and absorption effects. Corrections for secondary extinction were made in the refinement process.

1220 independent reflexions with intensities greater than $2\sigma_C(I)$ were measured for KHOXY from a crystal of volume 30·5 mm^3. 21 of these were badly centred in the scan interval and had their two background intensities differing by up to 50%. These reflexions were discarded. The standard deviations $\sigma_C(I)$ were estimated from counting statistics. The shape of the crystal could be described with 13 rational boundary planes. The linear absorption coefficient 1·40 cm^{-1} was calculated with a value of 34 barns for the incoherent scattering cross section for hydrogen. The resulting transmission factors varied from 0·53 to 0·76.

1013 reflexions were measured for RbHOXY. 100 of these had intensities less than $2\sigma_C(I)$. The crystal volume was 48·6 mm^3 and the shape of this crystal could be described with 15 boundary planes. Since two of these boundary planes were large and parallel [(010) and (0$\bar{1}$0)] an experimental linear absorption coefficient could be determined. The value obtained was 1·31 cm^{-1} corresponding to an incoherent scattering cross section for hydrogen of 42 barns. The transmission factors varied from 0·599 to 0·752. The space group extinctions hkl: $h+k+l \neq 2n$ and hhl: $2h+l \neq 4n$ of RbHOXY were checked by recording the intensities of all possible reflexions in the first octant with $\sin\theta/\lambda \leq 0{\cdot}35$ Å^{-1}. No violations were found.

Refinement

The structures were refined by minimizing the function $\sum w(|F_o|-|F_c|)^2$. Each reflexion was assigned a weight w with $w^{-1}=\sigma^2(|F_o|)=\sigma_C^2(|F_o|^2)/4|F_o|^2+C|F_o|^2$ where C is adjusted so that the average value of $\sum w(|F_o|-|F_c|)^2$ is fairly constant in different $|F_o|$ and $\sin\theta$ intervals. The convergence was followed by the conventional R and by the weighted $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. Preliminary values of the atomic parameters were taken from the X-ray structures. The 913 non-zero values of $|F_o|^2$ and $\sigma_C(|F_o|^2)$ measured for RbHOXY (reflexions with $0 \leq h$, $k \leq 11$ and $0 \leq l \leq 24$) were reduced to a set of 486 independent data ($h \leq k$) by mean-value calculations.

Corrections for extinction were made with the expression $|F_o|_{\text{corr}}=|F_o|\,[1+(\bar{T}2|F_c|^2g\lambda^3/V^2\sin 2\theta)]^{1/4}$ where g is the extinction parameter which is a constant in the isotropic case or derived from a tensor in the anisotropic case (Coppens & Hamilton, 1970). The units used for $\bar{T}$, λ, and V are cm, Å, and Å^3, respectively. The mean path lengths $\bar{T}=-\ln A/\mu$, where A is the transmission factor and μ the linear absorption coefficient, do not vary much between the equivalent reflexions hkl and khl ($h,k,l \geq 0$) for the actual RbHOXY crystal so mean values of $\bar{T}$ were also calculated and used for isotropic extinction correction of the derived set of independent data.

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

With anisotropic thermal parameters assigned to all atoms of KHOXY and with $C=0{\cdot}0009$ in the weight function, $R=0{\cdot}038$, $R_w=0{\cdot}046$ were obtained with an isotropic extinction correction. The value of the refined parameter g is 34800 (1200). This corresponds to a mosaic spread parameter of approximately 1·67″ or a domain size of 4·2 μm depending on whether a Zachariasen (1967) Type I or Type II description is used. Both a Type I and a Type II anisotropic extinction correction converged to $R=0{\cdot}036$, $R_w=0{\cdot}044$. Corresponding positional and thermal parameters in the two models agree within one standard deviation. In the Type I calculation mosaic spread parameters of 1·95, 1·70, and 1·04″ were obtained. The Type-II calculation gave domain-size parameters of 3·34, 4·13, and 5·25 μm. For this crystal extinction is probably affected both by mosaic spread and domain size and a proper description would lie between the Type-I and Type-II models. Arbitrarily the results of the Type-I calculations were chosen. The extinction correction factor as given above is for the majority of the reflexions in the range 1·00–1·30 but values as high as 2·88 (for the reflexion 020) are obtained.

Isotropic extinction correction, anisotropic thermal parameters, and $C=0{\cdot}0010$ in the weight function gave $R=0{\cdot}030$ and $R_w=0{\cdot}039$ for RbHOXY. The refined value of g is 1210(150) corresponding to a mosaic spread parameter of 50″ (Type I) or a domain size of 15 μm (Type II). The extinction correction factor is, for all reflexions except three, in the range 1·00–1·10. The maximum value is 1·23.

Table 2. *Atomic coordinates with standard deviations* ($\times 10^5$)

KHOXY

	x	y	z
K	26758 (29)	796 (20)	10164 (28)
O(1)	17593 (18)	26223 (13)	5303 (18)
O(2)	−7037 (20)	11398 (13)	16672 (19)
O(3)	−22686 (20)	28305 (14)	23781 (19)
O(4)	45238 (21)	15985 (13)	−7607 (19)
O(5)	53873 (19)	35020 (14)	−15629 (18)
C(1)	3121 (16)	32565 (11)	11386 (15)
C(2)	−9636 (15)	22979 (10)	17742 (14)
C(3)	30089 (16)	34820 (11)	−90 (15)
C(4)	43909 (15)	27631 (11)	−8221 (14)
H(1)	−34964 (37)	20689 (28)	29140 (34)
H(2)	−5976 (41)	38073 (31)	1998 (42)
H(3)	9244 (45)	39153 (31)	20932 (43)
H(4)	21940 (45)	41573 (32)	−8590 (45)
H(5)	38390 (45)	40286 (32)	9813 (43)

RbHOXY

	x	y	z
Rb	0	0	11583 (10)
O(1)	25045 (23)	$\frac{1}{4}$	$\frac{1}{8}$
O(2)	9914 (17)	25565 (25)	−362 (7)
O(3)	32482 (18)	26137 (22)	−6712 (7)
C(1)	34501 (14)	25681 (19)	6104 (5)
C(2)	24266 (16)	25743 (14)	−723 (6)
H(1)	$\frac{1}{4}$	26763 (50)	$-\frac{1}{8}$
H(2)	42406 (43)	15502 (55)	580 (17)
H(3)	41744 (47)	36313 (52)	609 (19)

The refinement of RbHOXY was performed assuming the hydrogen atoms H(1) linking the oxydiacetate residues into chains to be situated on the twofold axes between the residues. An attempt to refine a model

Table 3. *Thermal parameters with standard deviations* ($\times 10^5$)

The form of the temperature factor is exp $(-\beta_{11}h^2-2\beta_{12}hk\ldots)$. The root-mean-square components R_i with standard deviations ($\times 10^3$ Å) of thermal displacement along the ellipsoid axes are also listed.

KHOXY

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
K	1065 (41)	355 (18)	949 (31)	79 (20)	449 (29)	36 (18)	134 (4)	146 (3)	194 (3)
O(1)	935 (26)	355 (13)	1150 (23)	76 (14)	659 (20)	33 (13)	111 (3)	141 (3)	214 (2)
O(2)	1163 (28)	331 (13)	1197 (23)	−3 (14)	593 (20)	42 (13)	134 (3)	144 (2)	216 (2)
O(3)	998 (28)	440 (14)	1193 (24)	−65 (13)	724 (21)	−114 (12)	112 (3)	153 (3)	222 (2)
O(4)	1237 (29)	346 (14)	1244 (24)	131 (14)	815 (21)	66 (13)	118 (2)	141 (3)	231 (2)
O(5)	1021 (28)	421 (13)	1084 (23)	42 (13)	646 (20)	80 (12)	119 (3)	135 (2)	200 (2)
C(1)	889 (23)	324 (11)	1003 (19)	9 (12)	558 (17)	−46 (11)	113 (3)	135 (2)	200 (2)
C(2)	713 (21)	348 (12)	717 (16)	−9 (10)	371 (14)	−53 (9)	109 (2)	138 (2)	169 (2)
C(3)	926 (23)	333 (11)	922 (19)	13 (11)	532 (17)	−16 (10)	117 (3)	136 (2)	194 (2)
C(4)	706 (22)	349 (12)	733 (17)	43 (10)	331 (15)	24 (9)	115 (2)	139 (2)	168 (2)
H(1)	1406 (53)	714 (26)	1287 (41)	77 (27)	424 (38)	−185 (25)	166 (4)	198 (3)	227 (4)
H(2)	1683 (58)	859 (30)	1894 (57)	426 (33)	884 (48)	565 (33)	169 (4)	179 (4)	300 (4)
H(3)	2124 (66)	806 (31)	1938 (57)	−515 (36)	1075 (51)	−634 (34)	161 (4)	178 (4)	326 (4)
H(4)	2039 (65)	913 (33)	2047 (57)	663 (38)	1209 (51)	676 (37)	161 (4)	178 (4)	326 (4)
H(5)	2132 (66)	934 (34)	1824 (55)	−547 (37)	961 (52)	−654 (35)	168 (4)	192 (4)	312 (4)

RbHOXY

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Rb	759 (21)	891 (23)	217 (6)	29 (16)	0	0	166 (2)	181 (2)	190 (3)
O(1)	651 (17)	1103 (22)	102 (4)	0	0	−20 (9)	130 (3)	154 (2)	201 (2)
O(2)	758 (16)	1584 (26)	147 (3)	16 (20)	−38 (6)	7 (10)	150 (2)	171 (2)	240 (2)
O(3)	1041 (19)	1094 (20)	110 (3)	95 (22)	67 (6)	−2 (7)	130 (2)	190 (2)	207 (2)
C(1)	669 (13)	1121 (17)	109 (3)	−2 (17)	28 (4)	−29 (6)	131 (2)	158 (2)	203 (2)
C(2)	752 (13)	767 (13)	106 (3)	12 (15)	20 (5)	−13 (5)	131 (2)	166 (2)	168 (2)
H(1)	1618 (57)	1113 (48)	297 (13)	0	281 (25)	0	178 (5)	201 (4)	277 (5)
H(2)	1260 (48)	2263 (69)	222 (8)	767 (50)	16 (17)	−28 (19)	173 (4)	194 (4)	312 (5)
H(3)	1459 (54)	2121 (70)	249 (9)	−764 (54)	−13 (18)	−17 (20)	186 (4)	204 (4)	309 (5)

with H(1) statistically distributed around these twofold axes was not successful since the thermal parameter β_{33} of H(1) became negative. A refinement with fixed β_{33} resulted in a position of H(1) very near the twofold axis while the values of R and R_w increased a little. The model best describing the observed intensities of RbHOXY thus seems to have the hydrogen atoms H(1) symmetrically situated between the oxydiacetate residues.

The coherent scattering amplitudes used were $\bar{b}_{\mathrm{Rb}} = 0{\cdot}703\ (7)$, $\bar{b}_{\mathrm{K}} = 0{\cdot}370$, $\bar{b}_{\mathrm{O}} = 0{\cdot}580$, $\bar{b}_{\mathrm{C}} = 0{\cdot}665$, and $\bar{b}_{\mathrm{H}} = -0{\cdot}374 \times 10^{-12}$ cm (Bacon, The Neutron Diffraction Commission, 1972). As the scattering amplitude for Rb was changed from $\bar{b}_{\mathrm{Rb}} = 0{\cdot}81\ .\ 10^{-12}$ cm in the tabulation issued in 1969 (The Neutron Diffraction Commission, 1969) to $\bar{b}_{\mathrm{Rb}} = 0{\cdot}71\ .\ 10^{-12}$ cm in the tabulation of 1972 the value of this amplitude was included as a variable parameter in the refinement.

Table 4. *Observed and calculated structure factors for* KHOXY

In each group the running index l, $|F_o| \times 100$, and $|F_c| \times 100$ are given.

```
H= -8 K= -4
-1 182 203
 0 115 101

H= -8 K= -3
-1 110 113
 0 119 115

H= -8 K= -2
-2 399 417
-1 325 346
 0 297 312

H= -8 K= -1
 0 554 571

H= -8 K=  0
-2 547 550
 0 490 503

H= -7 K= -7
-2 172 204
-1 294 339
 0  91  97

H= -7 K= -6
-1 145 160
 0 190 188

H= -7 K= -5
-2 185 192
 0 146 144

H= -7 K= -4
-4 139 158
-3 142 151
-1  71  80
 0  83  76

H= -7 K= -3
-4  69  86
-3 139 141
-2 169 176
-1  87  81
 0 346 352

H= -7 K= -2
-4  66  57
-3 129 146
-2  60  60
-1 201 210
 0  58  41

H= -7 K= -1
-5 122 126
-4  58  51
-3 155 158
-2 158 161
 0 774 775

H= -7 K=  0
-4 172 171
-2 139 137
 0 376 391

H= -6 K= -8
-2 175 215
 0 119 115

H= -6 K= -7
-4 430 417
-3 302 299
-2  76  77
-1 116 109
 0  79  83

H= -6 K= -6
-4 111  98
-3 300 299
-2  97  90
 0 105 104

H= -6 K= -5
-4 350 348
-3 247 237
-2 157 166
-1  74  60
 0  68  62

H= -6 K= -4
-3 161 165
-2 103 103
-1 177 185
 0 338 338

H= -6 K= -3
-6 121 131
-5  88  96
-4 172 170
-3 102 108
-2 157 158
-1 272 274
 0 100 111

H= -6 K= -2
-5 167 165
-4 228 221
-3 229 220
-1 337 337
 0 176 183

H= -6 K= -1
-6 197 197
-4 195 187
-3 179 177
-2 114 117
-1 243 246
 0  92 115

H= -6 K=  0
-4 179 194
-2 150 152
 0 256 262
 2 746 700
 4 806 602

H= -6 K=  1
 0 119 115
 1 301 309
 2 302 306
 4 861 863

H= -6 K=  2
 0 176 183
 1 159 156
 2 758 763
 3 475 469
 4 258 244

H= -6 K=  3
 0 105 111
 2  91  92
 3  77  74
 4 535 541

H= -6 K=  4
 0 317 338
 2 267 283
 3 465 461

H= -5 K=-10
-1 305 310
 0  70  74

H= -5 K= -9
-3 260 261
-2 131 135
-1 484 525

H= -5 K= -8
-4 174 166
-3 219 225
-2 266 272
-1 459 450
 0 160 159

H= -5 K= -7
-5 268 268
-4 258 263
-3 127 129
-2 200 206
-1 472 471
 0 316 306

H= -5 K= -6
-6  77 101
-5 193 200
-4 160 169
-2 354 528
-1 124 124
 0 101  92

H= -5 K= -5
-6 163 156
-3  84  82
-2 304 306
-1 425 423
 0 190 181

H= -5 K= -4
-5 243 237
-4 238 252
-2 399 385
-1 199 200
 0 291 285

H= -5 K= -3
-7 122 117
-5 116 124
-4  97  96
-3 485 462
-2  57  51
-1 404 395

H= -5 K= -2
-7 119 105
-6 253 249
-5 134 132
-4 326 320
-2 382 371
-1 403 387
 0 189 183

H= -5 K= -1
-7 141 139
-6 268 250
-5  79  55
-3 307 298
-2 407 397
-1 253 245
 0  58  51

H= -5 K=  0
-6 182 187
-4 282 263
-2  54  62
 0 252 257
 0 257 257
 2  98  91
 4  88  84
 6 1015 1057

H= -5 K=  1
 0  53  51
 1 192 193
 2 543 544
 3  60  61
 4 614 625
 5 124 126
 6 489 480

H= -5 K=  2
 0 187 183
 1 340 342
 2 117 128
 3  86  77
 4 574 582
 5  64  66
 6 757 773

H= -5 K=  3
 1 351 353
 2  87  85
 4 628 640
 5 422 418

H= -5 K=  4
 0 277 285
 1 201 203
 2 153 157
 3  89  90
 4  50  51
 5 242 264

H= -5 K=  5
 0 180 181
 1 109 106
 2  68  46
 3 262 267
 4 386 389

H= -5 K=  6
 0  88  92
 1  78  66
 2 134 135

H= -4 K=-11
-2  99 119
 0  90  86

H= -4 K=-10
-3 492 469
-2 107 119
-1 165 171
 0 110 119

H= -4 K= -9
-5 189 190
-4  93 100
-3 184 193
-2 139 143
-1 342 345
 0 101  91

H= -4 K= -8
-5  70  80
-4  84  78
-3 345 340
-2 298 288
-1 221 216
 0 128 120

H= -4 K= -7
-6  94  85
-4 150 138
-3 292 281
-2  65  47
-1 266 255
 0 552 542

H= -4 K= -6
-5  95  92
-4 286 275
-3 210 200
-2 223 213
-1 398 395
 0 563 551

H= -4 K= -5
-7 118 129
-6 218 207
-5  97 102
-4  94  83
-3 130 127
-2 302 352
-1 109 108
 0 635 619

H= -4 K= -4
-8 121 138
-5 156 160
-4 226 218
-3 144 146
-2 183 176
-1 321 307
 0 236 235

H= -4 K= -3
-8 121 135
-7 147 144
-5  73  72
-4  88  97
-3 367 347
-2 752 726
-1 268 242
 0 418 410

H= -4 K= -2
-8 316 307
-7  89  98
-5 197 196
-4  56  60
-2 152 150
-1 927 913
 0  82  93

H= -4 K= -1
-8 264 251
-5 190 181
-4 440 403
-3  89  89
-2 160 168
-1  66  68
 0 136 130

H= -4 K=  0
-8 601 528
-4 678 609
 0 612 611
 0 620 611
 2 207 204
 4 725 751
 6 644 661

H= -4 K=  1
 0 130 130
 1  51  36
 3 261 259
 4  69  77
 5 103 102
 6 528 543
 7 166 168

H= -4 K=  2
 0  94  93
 1 483 477
 2  82  77
 3 332 328
 4 450 452
 5  60  46
 6 409 410
 7 569 561

H= -4 K=  3
 0 418 410
 1 474 475
 2 307 297
 3 321 322
 4 111 105
 6 236 228

H= -4 K=  4
 0 235 235
 1 124 126
 2  67  66
 3 161 153
 4 171 173
 5 189 189
 6 505 513

H= -4 K=  5
 0 628 619
 1 126 124
 2 345 342
 3 125 118
 4  99  97
 5 241 245

H= -4 K=  6
 0 549 551
 1 662 650
 2 559 554
 3  82  80
 4 110 117
 5 150 163

H= -4 K=  7
 0 531 542
 1 300 313
 2 194 214
 4 131 147

H= -3 K=-12
 0  74  81

H= -3 K=-11
-4 219 217
-3 368 356
-1 273 317
 0  78  72

H= -3 K=-10
-5 135 137
-4 355 337
-3 185 197
-2 148 152
-1 211 218
 0  84  87

H= -3 K= -9
-6 173 176
-5 243 239
-3 229 221
-2  93  95
-1 582 569
 0 346 337

H= -3 K= -8
-7  64  43
-5 187 185
-3 208 202
-2 213 219
-1 294 302
 0 176 173

H= -3 K= -7
-6  95 100
-3 360 345
-2 154 148
-1 168 189
 0 380 380

H= -3 K= -6
-7 190 179
-6  68  41
-5  98  96
-4 295 284
-3 101  98
-2 129 121
-1 379 369
 0 439 424

H= -3 K= -5
-7 320 311
-6  62  35
-5  77  70
-4  56  54
-2 466 457
-1 284 273
 0 121 115

H= -3 K= -4
-7 191 178
-5 190 191
-4 101  99
-3  68  70
-2  98  93
-1 259 256
 0 448 429

H= -3 K= -3
-9  76  79
-6 314 297
-3 233 221
-2 181 173
-1  53  58
 0 396 387

H= -3 K= -2
-8 239 234
-6 309 301
-5 238 228
-3 243 238
-2 164 153
-1 149 151
 0 511 499

H= -3 K= -1
-6 873 799
-5 132 127
-4  83  78

H= -3 K=  0
-8 156 163
 0 419 414
 2 622 646
 4 176 176
 6  54  61

H= -3 K=  1
 0  57  58
 1 303 293
 2  50  49
 3 317 325
 4 226 222
 5 227 223
 6 624 651
 7  91  95

H= -3 K=  2
 0 501 499
 1  80  90
 3  61  56
 4  96  89
 5 281 280

H= -3 K=  3
 0 399 387
 1 607 608
 2 213 217
 3 255 253
 4  89  91
 5 330 334
 6 121 119
 7 271 280

H= -3 K=  4
 0 434 429
 1 331 336
 2 326 319
 3 430 432
 4 397 397
 5 241 243
 6  86  87
 7  82  85

H= -3 K=  5
 0 111 115
 1 350 356
 2 434 433
 3  87  86
 4 289 289

H= -3 K=  6
 0 427 424
 1 221 224
 2 728 732
 3 297 309
 4 151 150

H= -3 K=  7
 0 371 380
 1 430 436
 2 735 721
 3 1006 1008
 4 501 506
 5  75  77

H= -3 K=  8
 0 170 173
 1 611 603
 2 519 530

H= -2 K=-12
-3 284 283
-2 198 199
-1 281 277
 0  98 121

H= -2 K=-11
-4  93  71
-2 303 317
-1 289 300
 0 107 199

H= -2 K=-10
-6 219 219
-5 157 166
-4 302 293
-3 277 279
-2 186 190
-1 395 390
 0 139 136

H= -2 K= -9
-6 100  93
-5 130 136
-4  59  50
-2 225 216
-2 233 216

H= -2 K= -8
-7 371 343
-6 148 151
-6 145 151
-5  40  43
-4 305 295

H= -2 K= -7
-8 143 148
-7 108 139
-7 139 139
-6  60  84
-6  91  84
-5  54  85
-5  82  85

H= -2 K= -6
-8  69  62
-7 133 151
-7 145 131
-6 108 107

H= -2 K= -5
-9 199 196
-8 187 187
-6  67  50

H= -2 K= -4
-9 115 112
-1  75  75

H= -2 K= -3
-8 121 126

H= -2 K= -2
-9 190 139
-8  69  80
-7 121 122

H= -2 K= -1
-9  72  71
-8 294 272

H= -2 K=  0
 0 356 343
 2  59  56
 6 705 746

H= -2 K=  1
 0 571 565
 1 158 158
 2 634 674
 4 228 230
 5 477 505
 6 227 227
 7  47  47
 8  45  54

H= -2 K=  2
 0 274 262
 1 606 623
 2 264 263
 3 480 493
 4 154 156
 5 337 347
 7 365 379

H= -2 K=  3
 0 197 190
 1 113 113
 2 135 135
 3 333 335
 4 174 174
 5 365 378
 6 200 200
 7 187 187

H= -2 K=  4
 0 371 364
 1  83  83
 2 317 315
 3 564 555
 4 369 377
 6 395 404
 7 137 139

H= -2 K=  5
 0  46  58
 1 440 447
 2 442 450
 3 265 247
 4 525 536
 5 135 130
 6  94  90

H= -2 K=  6
 0 155 155
 1  60  55
 2 121 115
 4 567 562
 5 552 561
 6 159 161

H= -2 K=  7
 0 143 144
 1 556 563
 2 524 516
 3 673 672
 4 504 498
 5  75  73

H= -2 K=  8
 0 313 316
 1 525 528
 2 495 526
 3 412 436
 4 358 382

H= -2 K=  9
 0  63  39
 1 405 413

H= -1 K=-13
 0 112 122

H= -1 K=-12
-3 168 151
-2  92 102
-1 367 379

H= -1 K=-11
-5 218 224
-4 309 307
-3  90  83
-2 309 306
-1 390 395
 0 278 294

H= -1 K=-10
-6 245 242
-5 330 318
-4 219 211
-3 154 153
 0 304 302

H= -1 K= -9
-7 145 153
-5 333 322
-3 260 251

H= -1 K= -8
-8 143 140
-7 422 411
-6  91  83
-5 367 348

H= -1 K= -7
-7 174 161

H= -1 K= -6
-9 154 150
-8 235 235
-7 204 203
-6  99  89

H= -1 K= -5
-9  91  63
-8 150 172
-7  93 101

H= -1 K= -4
-9 135 133
-8  81  76
-7 124 128

H= -1 K= -3
-10 112 106
-9 210 203
-8 238 246

H= -1 K= -2
-9 112 120
-8 209 200

H= -1 K= -1
-10 143 149
-9 102  90

H= -1 K=  0
-10  91  81
-8  73  80
 0  68  58
 2 487 536
 4 312 330
 6 130 132

H= -1 K=  1
 0 120 109
 1 157 160
 2 315 328
 3 213 210
 5 466 492
 6 169 170

H= -1 K=  2
 0 151 143
 1 206 203
 2 535 553
 3  45  37
 4 247 257
 5 541 565
 6 209 215
 7 567 592

H= -1 K=  3
 0 310 297
 2 113 112
 3 491 501
 4 432 448
 5 629 654
 6 416 439
 7 192 198

H= -1 K=  4
 0 392 386
 1 246 245
 2  97  90
 3 108 114
 4 583 601
 5 178 177
 6 263 260
 7  97 100

H= -1 K=  5
 0 239 233
 1  73  80
 2 180 184
 3  95  96
 4 336 334
 6 464 473
 7 274 281

H= -1 K=  6
 0 347 345
 1  73  62
 2 180 176
 3 482 482
 4 350 344
 5 370 380
 6 441 437

H= -1 K=  7
 0 338 343
 1 249 250
 2 167 166
 3 302 302
 4 285 269
 5 212 223

H= -1 K=  8
 0 102  98
 1 287 284
 2  57  66
 3 553 610
 4 174 199

H= -1 K=  9
 0 347 348
 1 684 688

H=  0 K=-13
-2 220 223
-1 267 270

H=  0 K=-12
-2 270 268
-1  61  52
 0 316 324

H=  0 K=-11
-5 187 175
-4 250 247
-3 207 208
-2 163 167
-1 352 333

H=  0 K=-10
-6 145 145
-5 254 255
-3 501 486
-2 284 285
-1 435 423
 0 620 608

H=  0 K= -9
-7 478 455
-6 105 109
-5 370 366
-4  69  82

H=  0 K= -8
-8 272 609
-7  62  57
-6 139 139
-5  93  87

H=  0 K= -7
-8 319 309
-7 394 382
-6 226 213

H=  0 K= -6
-9 284 282
-8 333 320

H=  0 K= -5
-9  92  63
-8 198 201
-7  59  68

H=  0 K= -4
-9  71  62
-8 189 196

H=  0 K= -3
-10  99 106
-9 250 264
-8 102 106

H=  0 K= -2
-10  73  66
-8 160 196

H=  0 K= -1
-10 112 113
-9  72  68
-8 107 108

H=  0 K=  0
-6  60  53
 2 182 193
 4 391 404
 6  57  58

H=  0 K=  1
 1 297 302
 2 179 184
 3 209 217
 4 451 465
 5 126 128
 6 162 160
 7 271 275

H=  0 K=  2
 0 1136 1202
 1 249 242
 2 202 199
 3 156 166
 5 368 379
 6 175 182
 7 388 394

H=  0 K=  3
 1 366 385
 2 234 234
 3  90  95
 4 248 251
 5 223 226
 6 340 354
 7 267 261

H=  0 K=  4
 0 460 455
 1 340 348
 4  59  57
 5 220 223
 6 505 511
 7 234 230

H=  0 K=  5
 1 526 529
 2 339 327
 3  57  48
 4  66  78
 5 177 178
 6 321 324

H=  0 K=  6
 0 573 565
 1 470 466
 3 309 316
 4 271 283
 6 111 104

H=  0 K=  7
 3 181 186
 4 132 151
 5 475 492

H=  0 K=  8
 0 417 403
 3 458 474

H=  0 K=  9
 1 280 270
 2  73  99
 3 548 529

H=  1 K=-13
-2 144 170
 0 121 122

H=  1 K=-12
-3  80  88
-2 347 339
-1 197 213

H=  1 K=-11
-3 394 383
-2 134 128
-1 365 357
 0 284 294

H=  1 K=-10
-6  65  74
-5 317 314
-3 200 193
-2  61  69
-1 491 468
 0 303 302

H=  1 K= -9
-7 550 541
-6 222 217
-4 291 277

H=  1 K= -8
-8 273 272
-7 121 126
-6 223 223
-5 664 640

H=  1 K= -7
-8 200 213
-7 425 427
-6 194 198

H=  1 K= -6
-8 124 120
-7  83  78

H=  1 K= -5
-9  79  77
-8 141 141

H=  1 K= -4
-8  78  67

H=  1 K= -3
-10  77  88
-9 144 145
-8 148 153

H=  1 K= -2
-9  68  64
-8 244 251

H=  1 K= -1
-10 456 447
-9 170 180

H=  1 K=  0
-10  77  77
 0  57  58
 2 412 394
 4 702 705
 6 399 399

H=  1 K=  1
 0 119 109
 1  38  32
 2 1580 1718
 3  77  70
 4 307 308
 5 297 303
 6 166 158
 7 310 307

H=  1 K=  2
 0 151 143
 1 117 116
 3 490 485
 4 125 126
 5 166 164
 6 217 230
 7  58  51

H=  1 K=  3
 0 291 297
 1  81  74
 2 403 397
 3 278 277
 4  85  90
 5 214 215
 7 220 234

H=  1 K=  4
 0 375 386
 1 574 599
 2 125 127
 3 251 247
 5 104 112
 6 267 266

H=  1 K=  5
 0 229 233
 1 447 464
 2 321 322
 3 177 177
 4 189 180
 5 245 247
 6  62  77

H=  1 K=  6
 0 334 345
 1 147 142
 2 164 166
 4 197 189
 5  98 104

H=  1 K=  7
 0 321 343
 1  55  65
 2 191 197
 3 223 217
 4  62  55
 5 400 388

H=  1 K=  8
 0  83  98
 1 269 276
 2 116 126
 3  99  86
 4 193 179

H=  1 K=  9
 0 334 348
 1 297 262
 2 542 555

H=  2 K=-12
-2  72  59
-1 216 206
 0 121 121

H=  2 K=-11
-2 149 148
-1 113 109
 0 203 199

H=  2 K=-10
-7 114 109
-6 103  90
-5 412 406
-4 105 105
-3  70  70
-2 179 183
-1 521 505
 0 139 136

H=  2 K= -9
-7 105  94
-6 139 134
-5 265 269
-4 159 160
-3 744 707

H=  2 K= -8
-8 104 120
-6 271 271
-5 701 677

H=  2 K= -7
-9 144 153
-8  87  82
-7  67  69
-6 264 263

H=  2 K= -6
-9 121 126

H=  2 K= -5
-10  81  73
-9  82  80
-8 175 174
-7 128 129

H=  2 K= -4
-10 205 197
-9  88 100
-6  68  57

H=  2 K= -3
-10 143 145
-9 134 138

H=  2 K= -2
-10 269 262
-9 160 164
-8 317 321

H=  2 K= -1
-10 317 307

H=  2 K=  0
-10  70  73
 0 351 343
 4 1710 1634
 6  91  75

H=  2 K=  1
 0 563 565
 1 140 133
 2  45  54
 3 447 426
 4 421 403
 5 311 309
 6 335 338

H=  2 K=  2
 0 260 262
 1  99  89
 2 108 103
 3  92  86
 4 919 881
 5  98 102
 6 137 134

H=  2 K=  3
 0 190 190
 1 406 402
 2 123 125
 3 438 425
 5 154 154
 6  75  64

H=  2 K=  4
 0 357 364
 1  81  75
 2 151 157
 3 177 176
 4 325 311
 5 116 106
 6  62  63

H=  2 K=  5
 0  70  58
 1  94  91
 2 218 220
 3 115 109
 5 199 201

H=  2 K=  6
 0 147 155
 1 184 188
 2 126 130
 3 177 179
 4 211 209
 5 222 226

H=  2 K=  7
 0 141 144
 1 140 143
 2 296 305
 3 165 168
 4  73  56

H=  2 K=  8
 0 300 310
 1 460 485
 2 108  93
 3 194 205

H=  2 K=  9
 1 333 344

H=  3 K=-12
-1 140 147
 0  63  81

H=  3 K=-11
-5  74  75
-4 268 295
-3 264 255
-2  72  94

H=  3 K=-10
-5 118 113
-4 118 127
-3 108 121
-2 215 223
-1 365 358
 0  84  87

H=  3 K= -9
-7 342 398
-4 107 106
-3 594 571
-1 384 372
 0 354 337

H=  3 K= -8
-8  85  66
-7 109 111
-6 173 161
-5  89  90
-4 312 300

H=  3 K= -7
-8 142 148
-7 310 313
-6 130 127

H=  3 K= -6
-9 282 278
-8 277 278
-7 232 237

H=  3 K= -5
-8 284 290
-7  56  55

H=  3 K= -4
-10  74  66
-9 183 181

H=  3 K= -3
-9 390 401
-8 376 382

H=  3 K= -2
-10 459 462
-9  95 117
-8 223 224

H=  3 K= -1
-10  81  72
-9 225 220
-8 319 326

H=  3 K=  0
-10 834 841
-8 709 743
 0 422 414
 2 890 839
 4  47  49
 6 281 289

H=  3 K=  1
 0  69  58
 1 154 158
 2 523 499

H=  4 K=-11
-4  66  65
-3 169 161
-1 189 191
 0  75  86

H=  4 K=-10
-6 109 150
-5 557 528
-4  65  54
-3 183 174
-2 107  94
-1 368 363
 0 112 119

H=  4 K= -9
-6 295 299
-5 231 226
-4 151 154
-3  74  60
-2 273 267
-1 258 266
 0  69  91

H=  4 K= -8
-8  66  77
-6 105 108
-5 319 314
-4 180 170
-3 129 138
-2 271 259
 0 105 120

H=  4 K= -7
-8 159 170
-7 352 348
-6 323 314

H=  4 K= -6
-8 112 123
-7 155 155
-6 173 170

H=  4 K= -5
-9  87  67
-8  77  91
-7 307 302
-6 368 365

H=  4 K= -4
-9 115 122
-8  79  81
-7 352 339

H=  4 K= -3
-10 190 193
-9 215 218
-8 129 143
-7  75  90

H=  4 K= -2
-9 137 143
-8 117 116

H=  4 K= -1
-10 151 159
-9 100 118
-8 1036 1069

H=  4 K=  0
-10 275 273
-8 197 199

H=  5 K=-11
-2 350 340

H=  5 K=-10
-4 612 589
-3 203 202
-1 132 129
 0  83  74

H=  5 K= -9
-6 215 221
-5 138 129
-3 584 567
 0  64  53

H=  5 K= -8
-7 255 252
-6 257 250
-5 290 283
-4 222 215
-3 142 144
-2 107  96
 0 164 159

H=  5 K= -7
-8  81  79
-7 101 109
-6  85  82
-5 253 245
-3 160 165
-2 228 220
 0 321 306

H=  5 K= -6
-7  59  36
-6 158 157
-5 452 428
-4 520 505

H=  5 K= -5
-7 120 123
-6 208 211
-5 495 466

H=  5 K= -4
-9  82  81
-8  87  80
-7  93 108
-6 147 132

H=  5 K= -3
-9 184 182
-8  87 101
-7 272 277
-6 124 130

H=  5 K= -2
-9  75  93
-8 333 330
-7  96  99

H=  5 K= -1
-9  57  44
-8 161 150

H=  5 K=  0
-10 138 140
-8 120 131

H=  6 K= -9
-4 352 334
-3 130 129
-2 139 132
-1  88  73

H=  6 K= -8
-6 204 198
-5 545 518
-4 287 280
-3 258 254
-2  73  51
-1 506 496
 0 119 115

H=  6 K= -7
-7 139 133
-6  69  76
-5  72  65
-3 353 347
-2 232 219
-1 222 227
 0  91  83

H=  6 K= -6
-7  77  67
-6 138 137
-5  63  58
-4 111 113
-2 195 182
-1 113 103
 0 113 104

H=  6 K= -5
-8 196 202
-7 127 122
-6  98 103
-5 260 253
-4 126 116
-3 504 473
-2 299 286
-1 159 155

H=  6 K= -4
-8 143 137
-7 134 130
-5 389 376
-4 260 258

H=  6 K= -3
-8 129 126
-7 113 106
-6 174 165
-5 133 137

H=  6 K= -2
-9 156 166
-7 157 155
-6 107 115

H=  6 K= -1
-8 192 184
-6 337 320

H=  6 K=  0
-6  72  62
-4  86  73

H=  7 K= -8
-3  82  97
-2 225 232
-1 194 204

H=  7 K= -7
-5 119 110
-3 419 401
-2 121 130
-1 150 151
 0 116  97

H=  7 K= -6
-6 137 132
-5  60  75
-4 101 102
-2  85  78
-1 394 392
 0 193 188

H=  7 K= -5
-7 304 299
-6 200 206
-3 213 202
-2 172 170
 0 141 144

H=  7 K= -4
-6 239 220
-4 310 294
-2 124 126
-1 211 217
 0  72  76

H=  7 K= -3
-7  73  80
-6 175 166
-5 152 144
-3 203 203
-1 580 588
 0 345 352

H=  7 K= -2
-7 178 180
-5 158 158
-4 182 177
-3 125 120
-2 584 581
-1 117 102
 0  70  41

H=  7 K= -1
-6 291 282
-4 148 151
-5 181 181
-3 192 192
-2 583 581
-1 451 458
 0 764 775

H=  7 K=  0
-8 353 353
-6 256 245
-4 395 381
-2 1001 994
 0 379 391

H=  8 K= -6
-2  81  67
-1 104 105

H=  8 K= -5
-4 251 243
-3 125 123

H=  8 K= -4
-5 196 196
-4 145 156
-2  77  74
-1 120 136
 0 109 101

H=  8 K= -3
-6  65  73
-4 187 181
-3 135 135
-2 265 252
 0 105 115

H=  8 K= -2
-6 420 409
-3  75  77
-1 165 165
 0 300 312

H=  8 K= -1
-6 248 238
-5 167 162
-4 150 145
-3 247 248
-2 286 287
-1 140 142
 0 549 571

H=  8 K=  0
-6 256 254
-4  94  84
-2 135 136
 0 480 505

H=  9 K=  0
-2 262 260
```

Table 5. *Observed and calculated structure factors for* RbHOXY

In each group the running index l, $|F_o| \times 100$, and $|F_c| \times 100$ are given. An asterisk denotes a reflection with zero weight.

H= 0 K= 0		
4	1069	1075
6	1547	1569
12	1343	1349
16	2421	2420
20	185	199
24	165	178
H= 0 K= 1		
1	621	649
3	189	192
5	143	145
7	362	359
9	445	456
11	338	349
13	425	430
15	230	210
17	264	250
19	239	236
23	220	220
H= 0 K= 2		
0	2615	2508
2	229	241
4	1551	1568
6	261	272
8	511	504
12	1217	1203
16	1859	1871
18	208	202
20	297	289
22	157	139
24	139	147
H= 0 K= 3		
1	900	941
5	479	494
7	738	767
9	354	363
11	340	341
15	497	499
17	661	655
21	153	141
23	644	640
H= 0 K= 4		
0	2591	2518
2	233	234
4	282	289
6	325	321
8	633	631
10	311	311
12	227	228
14	573	564
16	1464	1434
18	136	155
20	112	95
22	209	205
H= 0 K= 5		
1	652	658
3	733	740
5	462	461
7	502	508
9	526	540
11	127	115
13	674	673
15	672	675
17	305	294
19	218	225
21	193	208
H= 0 K= 6		
0	841	854
2	389	402
4	1488	1484
6	605	604
8	1220	1231
10	214	210
12	1108	1098
14	553	552
16	696	703
20	445	458
H= 0 K= 7		
1	364	306
5	430	442
7	301	373
9	543	535
11	245	236
13	232	222
15	484	488
19	109	89
H= 0 K= 8		
0	1743	1713
2	376	356
4	362	361
6	165	156
8	879	835
10	237	243
12	240	238
14	141	122
16	997	1027
18	264	283
H= 0 K= 9		
1	431	428
3	116	87
5	262	262
7	149	126
9	125	135
13	207	206
15	381	402
H= 0 K= 10		
0	737	732
2	269	273
4	425	400
6	190	196
8	253	259
10	136	104
12	219	222
H= 0 K= 11		
1	404	407
5	194	211
H= 1 K= 1		
2	314	333
6	1179	1189
10	480	476
14	1288	1291
18	572	578
22	789	787
H= 1 K= 2		
1	295	306
3	377	393
5	890	913
7	737	747
9	378	368
11	688	681
13	260	249
17	255	257
19	250	242
21	334	330
23	696	695
H= 1 K= 3		
0	1086	1126
2	794	811
4	579	591
6	523	523
8	108	93
10	405	412
12	585	591
14	1324	1311
16	832	836
18	229	229
20	234	233
22	519	508
H= 1 K= 4		
1	683	700
5	192	186
7	1079	1087
9	932	926
11	214	215
13	117	98
15	797	798
17	153	168
19	239	238
21	136	142
23	478	523
H= 1 K= 5		
0	1828	1821
2	353	363
4	191	187
6	964	972
8	1396	1384
10	284	261
12	142	151
14	784	759
16	1239	1226
18	337	333
22	770	827
H= 1 K= 6		
1	530	525
3	326	325
5	365	370
7	530	532
9	343	339
11	258	245
13	353	314
15	159	137
17	455	453
21	120	121
H= 1 K= 7		
0	745	762
2	380	379
4	168	181
6	635	623
8	1069	1066
10	283	283
14	808	787
16	530	542
18	191	197
20	162	180
H= 1 K= 8		
1	951	938
3	437	415
5	466	443
7	403	404
9	391	406
11	426	422
13	264	257
15	704	686
17	517	555
H= 1 K= 9		
0	200	202
2	560	539
4	201	205
6	206	202
8	153	152
10	196	175
12	320	313
14	777	725
16	179	151
H= 1 K= 10		
1	284	274
3	383	377
5	243	236
7	115	102
11	120	129
13	273	292
H= 1 K= 11		
2	246	243
4	157	154
6	168	174
8	131	124
H= 2 K= 2		
0	2407	2483
8	291	282
12	199	121*
16	1518	1484
20	163	140
24	115	125
H= 2 K= 3		
1	462	477
3	361	381
5	331	348
7	1383	1380
9	1131	1124
11	449	464
13	441	444
15	624	618
17	280	275
19	203	201
21	130	113
23	796	783
H= 2 K= 4		
0	112	65*
2	92	58*
4	683	695
6	131	135
8	444	446
10	186	176
12	513	492
14	182	164
16	184	124
18	149	129
22	126	108
H= 2 K= 5		
1	810	811
3	362	364
5	264	243
7	959	956
9	765	762
11	311	311
13	234	235
15	587	564
17	419	421
19	276	266
H= 2 K= 6		
0	935	964
2	113	99
4	329	345
6	264	251
8	1875	1832
10	247	223
12	355	340
14	116	89
16	512	506
20	157	143
H= 2 K= 7		
1	689	669
3	235	218
5	296	296
7	564	555
9	429	419
11	308	296
13	410	395
15	478	464
17	324	340
19	209	210
H= 2 K= 8		
0	590	587
2	278	276
4	768	747
6	218	215
8	335	327
10	268	283
12	441	437
14	188	188
16	486	475
H= 2 K= 9		
1	169	165
3	336	330
5	223	205
7	256	252
9	268	268
11	207	212
13	135	115
15	412	438
H= 2 K= 10		
0	1014	951
2	218	231
4	185	169
6	141	161
8	137	147
10	139	138
12	171	156
H= 2 K= 11		
3	119	119
5	361	385
7	154	167
H= 3 K= 3		
2	217	205
6	1190	1208
10	689	696
14	448	440
18	329	325
22	770	795
H= 3 K= 4		
1	697	720
3	345	359
5	470	500
7	592	600
9	212	210
11	334	330
13	277	275
15	611	590
17	403	387
19	204	195
21	155	154
H= 3 K= 5		
2	121	109
4	303	307
6	1085	1080
8	552	543
10	555	558
12	127	128
14	506	494
18	211	209
20	244	240
H= 3 K= 6		
1	119	93
3	325	325
5	315	313
7	495	510
9	452	464
11	226	248
13	376	373
15	224	227
17	165	156
19	114	111
H= 3 K= 7		
0	172	195
2	402	398
4	457	455
6	606	602
8	689	673
12	250	242
14	618	594
16	117	99
18	169	177
H= 3 K= 8		
1	593	578
3	405	401
5	361	351
7	223	232
11	312	320
13	212	202
15	423	430
17	334	358
H= 3 K= 9		
2	383	374
6	237	244
10	221	221
14	474	502
H= 3 K= 10		
1	244	249
3	299	301
7	343	335
9	299	316
11	138	106
H= 3 K= 11		
0	249	244
2	250	266
6	171	218
H= 4 K= 4		
0	193	172
4	362	367
8	1755	1758
12	233	226
16	294	268
20	221	232
H= 4 K= 5		
1	310	318
3	581	589
5	381	386
7	177	182
9	128	115
11	172	165
13	619	619
15	359	350
17	255	231
19	146	128
21	171	190
H= 4 K= 6		
0	122	96
2	240	244
4	917	903
6	159	162
8	1154	1113
10	258	277
12	551	531
14	225	239
H= 4 K= 7		
1	284	277
3	228	230
5	258	254
7	292	272
9	403	386
11	176	176
13	160	161
15	424	422
17	146	134
H= 4 K= 8		
0	577	572
2	274	263
6	140	116
8	1167	1113
10	193	187
14	194	219
16	252	265
H= 4 K= 9		
1	632	615
3	110	87
5	216	192
7	204	206
9	185	174
13	132	114
H= 4 K= 10		
0	129	104
2	255	257
4	235	234
6	192	187
10	142	157
H= 4 K= 11		
1	109	89
H= 5 K= 5		
2	413	415
6	616	612
10	221	217
14	552	534
18	172	180
H= 5 K= 6		
1	277	271
3	239	238
5	253	252
7	209	206
9	429	424
11	130	122
13	174	163
15	134	152
17	154	142
H= 5 K= 7		
0	215	211
2	329	320
4	197	197
6	482	483
8	176	173
10	190	178
12	149	173
14	519	515
16	164	161
H= 5 K= 8		
1	277	285
3	417	418
5	381	365
7	165	168
9	181	169
11	283	287
13	316	325
H= 5 K= 9		
0	133	125
2	181	189
4	130	120
6	404	394
8	290	292
12	122	113
H= 5 K= 10		
1	289	307
3	127	160
5	189	202
7	127	88
H= 6 K= 6		
0	735	742
4	465	458
8	1880	1778
12	257	272
16	290	294
H= 6 K= 7		
1	387	390
3	122	107
5	285	283
7	115	89
9	142	144
11	118	119
13	194	198
15	216	223
H= 6 K= 8		
0	115	103
2	140	163
4	707	674
8	1040	985
10	106	88
12	400	432
H= 6 K= 9		
1	316	329
3	200	213
5	110	105
7	275	268
9	417	438
H= 6 K= 10		
0	484	517
2	224	244
H= 7 K= 7		
2	198	227
6	529	507
10	170	163
H= 7 K= 8		
1	381	369
3	212	210
5	320	326
7	158	174
9	305	339
H= 7 K= 9		
0	111	123
2	365	353
4	163	157
6	212	230
H= 8 K= 8		
0	549	530

The parameters obtained in the last cycles of refinement are given in Tables 2 and 3. Observed and calculated structure factors are listed in Tables 4 and 5. The program system used has been briefly described by Oskarsson (1973).

The heavy-atom structures

Both neutron diffraction studies have confirmed the structures previously found by X-ray diffraction. The structures are shown in Figs. 1 and 2. In KHOXY the hydrogen oxydiacetate chains run parallel to [201] and in RbHOXY parallel to **c**. The oxydiacetate residue is planar in both compounds. All the residues are parallel in KHOXY but in RbHOXY there are two perpendicular sets of parallel planes. Selected interatomic distances and angles are given in Tables 6 and 7 and some dihedral angles within the oxydiacetate residues in Table 8.

Table 6. *The nearest neighbour oxygen atoms around the alkali metal ion*

The superscripts indicate the transformations applied to the x, y, z values given in Table 2. KHOXY: (i) $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $\bar{x}, \bar{y}, \bar{z}$; (iii) $\bar{x}, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, \bar{y}, \bar{z}$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$. RBHOXY: (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) $y, -\frac{1}{2}+x, \frac{1}{4}+z$.

KHOXY		RbHOXY	
K–O(1)	2·748 (3) Å	Rb–O(1)	3·006 (1) Å
K–O(2)	2·798 (2)	Rb–O(2)	3·175 (2)
K–O(2^{ii})	2·754 (3)	Rb–O(2^{iii})	3·087 (2)
K–O(3^{iii})	2·767 (3)	Rb–O(3^{iv})	2·932 (2)
K–O(4)	2·711 (3)		
K–O(4^{iv})	2·693 (2)		
K–O(5^{v})	2·935 (3)		

The alkali metal ion has seven oxygen neighbours in KHOXY forming a pentagonal bipyramid (Fig. 1 and Table 6). The oxygen atom O(5^{v}) cannot be regarded as coordinated since the distance K–O(5^{v}), 2·935 (3) Å, is longer than the distance K–H(4^{v}), 2·875 (4) Å. In RbHOXY the rubidium ion is surrounded by six oxygen atoms forming a distorted octahedron and by two oxygen atoms O(2) outside two adjacent triangular

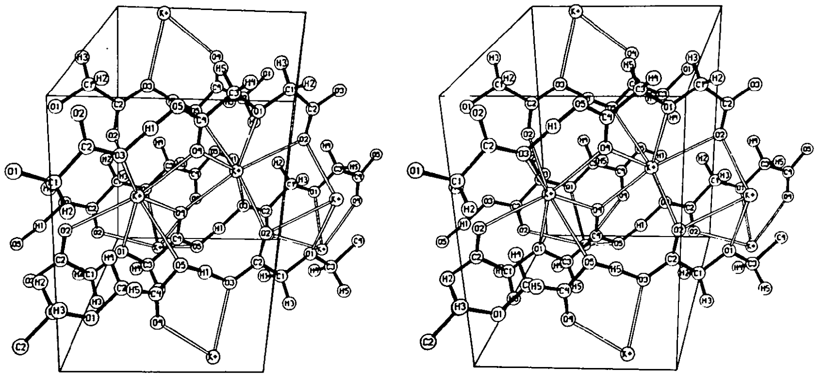


Fig. 1. A stereoscopic pair of drawings showing the content of a unit-cell of KHOXY. The *c* axis points towards the reader, *a* to the right, and *b* upwards.

Table 7. *Selected interatomic distances and angles in the oxydiacetate residue*

For superscripts, see legend to Table 6.

(*a*) Distances	KHOXY	RbHOXY
O(1)–C(1)	1·407 (2) Å	1·410 (2) Å
O(1)–C(3)	1·404 (2)	
C(1)–C(2)	1·522 (2)	1·510 (2)
C(3)–C(4)	1·511 (2)	
C(2)–O(2)	1·230 (2)	1·219 (2)
C(4)–O(4)	1·221 (2)	
C(2)–O(3)	1·275 (2)	1·289 (2)
C(4)–O(5)	1·294 (2)	
O(1)–O(2)	2·661 (2)	2·659 (2)
O(1)–O(4)	2·661 (2)	
C(1)–H(2)	1·090 (3)	1·095 (4)
C(1)–H(3)	1·091 (3)	1·091 (4)
C(3)–H(4)	1·093 (3)	
C(3)–H(5)	1·093 (3)	
(*b*) Angles		
C(1)–O(1)—C(3), $C(1^{i})$	112·08 (12)°	110·64 (16)°
O(1)–C(1)—C(2)	110·64 (10)	110·18 (12)
O(1)–C(3)—C(4)	110·11 (11)	
C(1)–C(2)—O(2)	120·81 (10)	122·02 (11)
C(3)–C(4)—O(4)	121·84 (11)	
C(1)–C(2)—O(3)	112·93 (11)	112·17 (12)
C(3)–C(4)—O(5)	113·37 (11)	
O(2)–C(2)—O(3)	126·25 (12)	125·80 (13)
O(4)–C(4)—O(5)	124·79 (12)	
C(2)–O(3)···H(1)	117·27 (16)	116·09 (13)
C(4)–O(5)—$H(1^{i})$	111·51 (18)	
H(2)–C(1)—H(3)	107·98 (31)	107·87 (32)
H(4)–C(3)—H(5)	108·15 (32)	

Table 8. *Some dihedral angles in the oxydiacetate residues*

	KHOXY	RbHOXY
O(3)–C(2)–C(1)–O(1)	178·23 (13)°	179·09 (14)°
O(5)–C(4)–C(3)–O(1)	169·99 (12)	
O(3)–C(2)–C(1)–H(2)	61·26 (24)	57·56 (29)
O(5)–C(4)–C(3)–H(5)	68·32 (25)	
O(3)–C(2)–C(1)–H(3)	55·61 (25)	59·31 (28)
O(5)–C(4)–C(3)–H(4)	49·09 (26)	

faces of this polyhedron (Fig. 2). The latter atoms are not coordinated since the distance Rb–H(1), 3·111 (3) Å, is shorter than Rb–O(2), 3·175 (2) Å.

The two oxydiacetate residues and the hydrogen bonds are shown in Fig. 3. The agreement within each pair of independent determinations (X-ray and neutron) of the oxydiacetate geometry is very satisfactory, as has been shown in half-normal probability plots in a separate communication (Albertsson, Grenthe & Herbertsson, 1973*b*). There are two independent ligand halves in KHOXY. The agreement between their corresponding bond lengths and bond angles is also very good (Table 7) which further corroborates the correctness of the structure determination. A probability plot shows, however, that the two halves are not completely equal. There is a minor change in conformation between them. The nonhydrogen atoms are coplanar in the ligand half containing the carboxyl group O(2)C(2)O(3) but in the other ligand half the ether oxygen atom is not located in the carboxyl plane. The carboxyl group is twisted about 7° around the C–C bond [Table 8 and Fig. 4(*a*)]. All the non-hydrogen atoms in the oxydiacetate residue in RbHOXY are coplanar.

In both structures the anisotropic thermal parameters β_{ij} determined for the heavy atoms are in general smaller than those determined in the X-ray diffraction studies. The probability plots indicate that the X-ray and neutron analyses are fairly accurate and that only

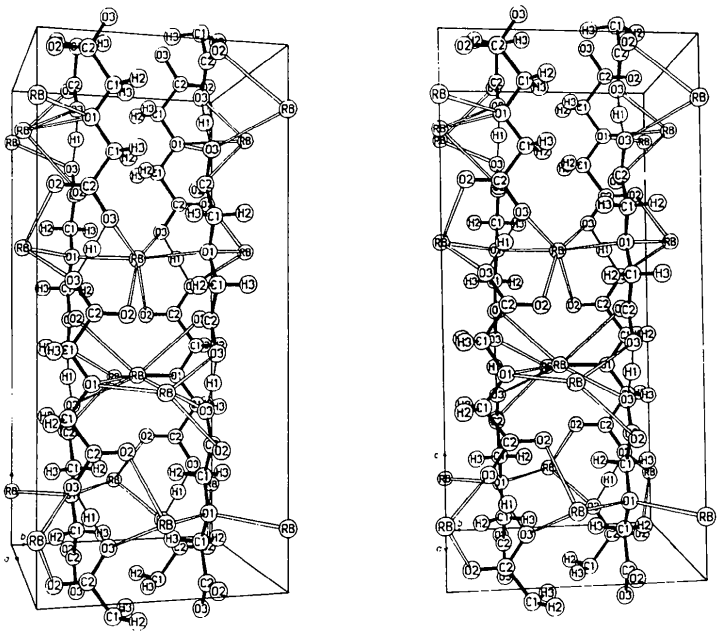


Fig. 2. A stereoscopic pair of drawings showing the content of a unit-cell of RbHOXY.

small systematic errors could have been introduced in the scaling of the data sets and in the corrections for absorption and extinction. Hence, we may ascribe the difference in the thermal parameters to a systematic error in the X-ray studies resulting from bonding effects (Coppens, 1968).

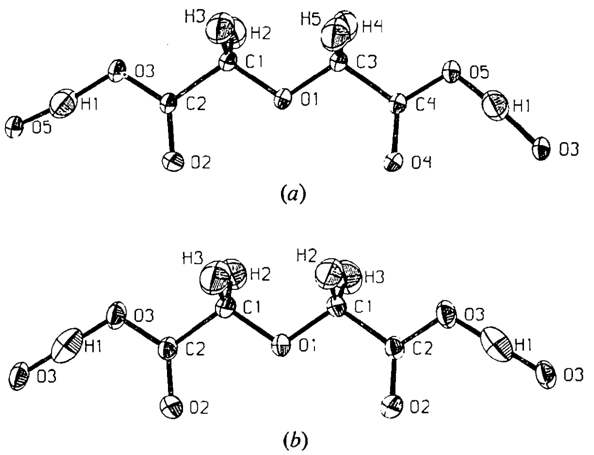
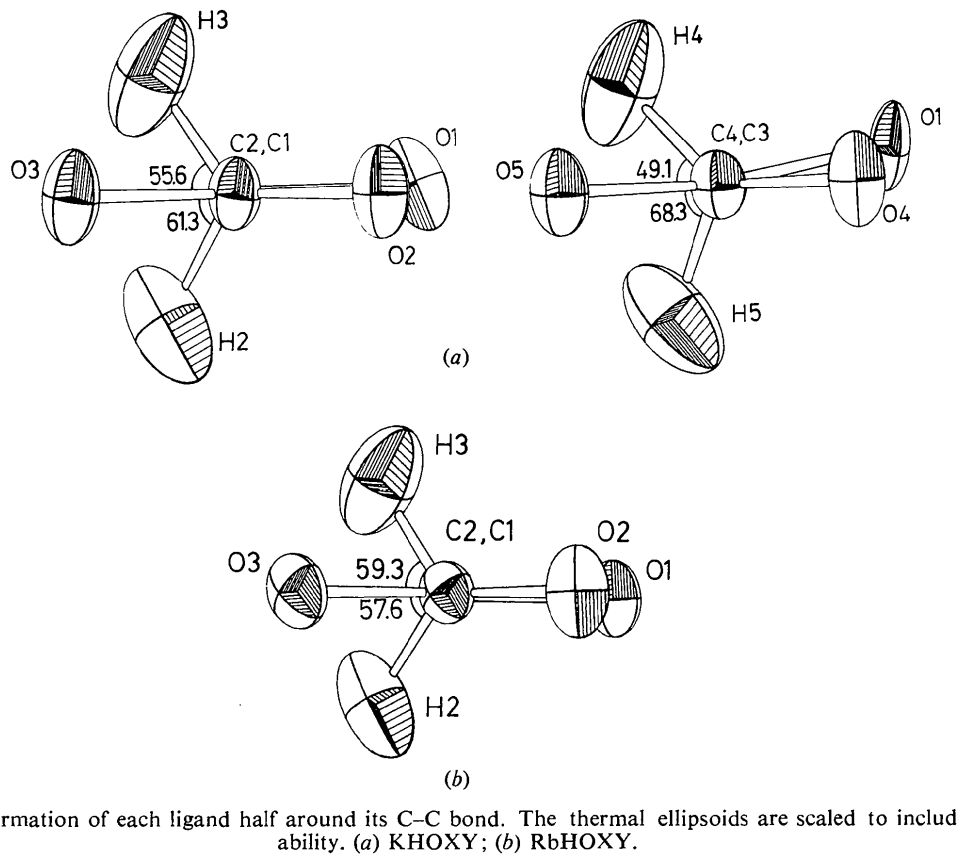


Fig. 3. The oxydiacetate residues and the hydrogen bonds. The thermal ellipsoids are scaled to include 50% probability. (*a*) KHOXY; (*b*) RbHOXY.

The methylene groups

The C–H bond lengths are the same in the two compounds (Table 7). The mean value is 1·092 (1) Å in KHOXY and 1·093 (3) Å in RbHOXY. The corresponding principal axes of the thermal ellipsoids for the hydrogen atoms are all of about the same length. The long axes are perpendicular to the line C(2)–C(4) in KHOXY and C(2)–C(2^{i}) in RbHOXY but their angles with the C–H bond directions are in all cases about 70°. No simple depiction of the thermal vibrations has been found but one component might be a libration of the oxydiacetate residues around axes parallel to the lines through the carboxyl carbon atoms since the thermal ellipsoids of all the oxydiacetate atoms in both compounds have their long principal axes perpendicular to this direction.

We have estimated the amplitude of the motion of each hydrogen atom relative to the carbon atom by calculating the r.m.s. quantities $[R^2_{C-H}(H)-R^2_{C-H}(C)]^{1/2}$. R_{C-H} is the r.m.s. component of the total thermal displacement in the direction of the C–H bond. The results are given in Table 9. The mean value in KHOXY is 0·101 Å and in RbHOXY 0·087 Å. If we assume simple harmonic motion of the hydrogen atoms the amplitudes correspond to the C–H stretching frequencies 1600 and 2200 cm^{-1}, respectively. These



(*a*)

(*b*)

Fig. 4. The conformation of each ligand half around its C–C bond. The thermal ellipsoids are scaled to include 50% probability. (*a*) KHOXY; (*b*) RbHOXY.

values are somewhat low compared to the value 2900 cm^{-1} found in the infrared spectra of the compounds but they are of the right order of magnitude. The amplitude should have been 0·076 Å to give the frequency 2900 cm^{-1}. In view of the approximations involved in our calculations we conclude that the thermal parameters of the methylene hydrogen atoms are physically reasonable. As a consequence we can assume that this will be true also for the thermal parameters of the acid hydrogen atoms.

Table 9. *The root-mean-square components of thermal displacement along the* C–H *bonds in the methylene groups*

KHOXY	$R_{C-H}(H)$	$R_{C-H}(C)$	$[R^2_{C-H}(H)-R^2_{C-H}(C)]^{1/2}$
C(1)–H(2)	0·177 (4) Å	0·148 (2) Å	0·098 (8) Å
C(1)–H(3)	0·170 (4)	0·135 (2)	0·104 (8)
C(3)–H(4)	0·162 (4)	0·126 (2)	0·102 (8)
C(3)–H(5)	0·175 (4)	0·143 (2)	0·101 (8)
RbHOXY			
	$R_{C-H}(H)$	$R_{C-H}(C)$	$[R^2_{C-H}(H)-R^2_{C-H}(C)]^{1/2}$
C(1)–H(2)	0·203 (4) Å	0·185 (2) Å	0·084 (8) Å
C(1)–H(3)	0·209 (4)	0·189 (2)	0·090 (8)

The hydrogen bonds

Geometric data for the hydrogen bonds are given in Table 10. In KHOXY the oxygen–oxygen distance is 2·476 (2) Å. The bond is asymmetric but with a long covalent O–H bond distance, 1·152 (3) Å. There is no indication of a disordered hydrogen arrangement. Some other short asymmetric hydrogen bonds with long O–H distances have been found in neutron diffraction studies of sulphonic and nitranilic acid hydrates containing the aquo-oxonium ($H_5O_2^+$) and diaquo-oxonium ($H_7O_3^+$) ions. Data for these bonds are also included in Table 10. There is no obvious correlation between the distances O–H and O···O. The asymmetric hydrogen bond in KHOXY causes a small difference between the two single bonded C–O distances: C(2)–O(3) is 0·019 (3) Å shorter than C(4)–O(5) (Table 7).

The hydrogen bond in RbHOXY is symmetric and 0·027 (4) Å shorter than the bond in KHOXY. The oxygen–oxygen distance is 2·449 (3) Å. The angle O···H···O is about the same as in KHOXY, *i.e.*, the hydrogen bond is almost linear in both compounds. The acceptor and donor angles C–O···H differ by 5·8 (3)° in KHOXY but, owing to the symmetry, are equal in RbHOXY (Table 7).

Fig. 3 shows that the thermal ellipsoid describing the total motion of H(1) in RbHOXY is strongly prolate, approximately in the direction of the bond. This is not the case for H(1) in KHOXY. The intensities from RbHOXY are best accounted for by a model with H(1) located on twofold axes between the oxydiacetate residues but this fact does not exclude a disordered arrangement with half-hydrogen atoms on each side of the axes resulting in a prolate 'thermal' ellipsoid.

To choose between these two possibilities we may estimate the motion of the hydrogen atom relative to the motion of the oxydiacetate residue approximated by the motion of the hydrogen bonded oxygen atoms and compare the amplitudes thus obtained with spectroscopic evidence. The amplitudes of the relative motion can of course be calculated from the differences in mean square displacements as was done above for the C–H stretching vibrations but we have in this case calculated the ellipsoids defined by $\beta_{ij}(H)-\beta_{ij}(O)$, where O is O(5) in KHOXY and O(3) in RbHOXY (Sequeira, Berkebile & Hamilton, 1967). The advantage of this method is that both the amplitudes and the directions of the difference motion are obtained.

The ellipsoids describing the total motion and those describing the difference motion of the hydrogen atoms H(1) are compared in Table 11. To have all the three roots of the secular equation for the difference ellipsoid in KHOXY positive we had to change the values of $\Delta\beta_{13}$ and $\Delta\beta_{23}$ by about 2σ. This indicates that the approximations are rather crude but we accept the result since the mean square amplitudes along the principal axes obtained are almost equal to the difference in mean square displacements of H(1) and O(5) in the same directions.

The two hydrogen bonds with the difference ellipsoids representing the hydrogen atoms are shown in Fig. 5. Both ellipsoids are prolate in the direction of the bond and it is reasonable to relate the amplitude in this direction with the asymmetric stretching frequency of the O–H···O bond. For the short symmetric and almost symmetric hydrogen bonds in RbHOXY and KHOXY, respectively, values around 1000 cm^{-1} would be expected (Speakman, 1972). At −175°C the frequencies found in the infrared spectra are 800(50) cm^{-1} in KHOXY and 600(50) cm^{-1} in RbHOXY (Lindgren, 1973).

Table 10. *The hydrogen bond in* RbHOXY *and* KHOXY *and short, asymmetric hydrogen bonds in sulphonic and nitranilic acid hydrates*

	O···O	O–H	O···H	O–H···O
RbHOXY	2·449 (3) Å	1·226 (2) Å	1·226 (2) Å	175·04 (44)°
KHOXY	2·476 (2)	1·152 (3)	1·328 (3)	174·24 (27)
$C_6H_2(NO_2)_3SO_3H.4H_2O^a$	2·436 (2)	1·128 (3)	1·310 (3)	175·0
$C_6H_3COOH(OH)SO_3H3.H_2O^b$	2·44 (1)	1·10 (1)	1·34 (1)	180
$C_6(NO_2)_2(OH)_2O_2.6H_2O^c$	2·45	1·18	1·27	180

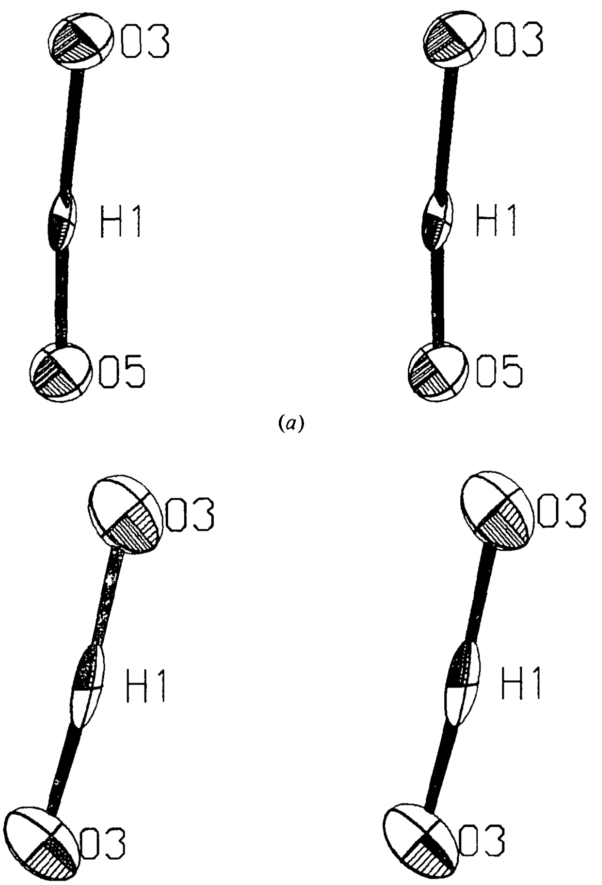
(*a*) Lundgren & Tellgren (1973); (*b*) Williams, Peterson & Levy (1972); (*c*) Williams & Peterson (1969).

Table 11. *The thermal ellipsoids for the acid hydrogen atoms*

The root-mean-square amplitudes along the principal axes and the angles these make with the hydrogen bond.

	Total motion		Difference motion	
Compound	Amplitude	Direction	Amplitude	Direction
KHOXY	0·166 (4) Å	67 (4)°	0·040 (17) Å	82 (4)°
	0·198 (3)	45 (5)	0·100 (06)	114 (5)
	0·227 (4)	128 (5)	0·153 (05)	154 (5)
RbHOXY	0·178 (5)	110 (2)	0·026 (33)	90
	0·201 (4)	90	0·093 (09)	85 (3)
	0·277 (5)	160 (2)	0·208 (07)	175 (3)

In order to estimate the energy difference between the ground and first excited state in KHOXY from the diffraction data we assume the the hydrogen atom H(1) has a simple harmonic motion in a single potential-energy well. The mean square displacement along the longest principal axis of the difference ellipsoid then gives 700 cm^{-1}. Compared to the frequency found at −175°C this is a very satisfactory value. If we also assume simple harmonic motion of frequency 600 cm^{-1} for the hydrogen atom H(1) in RbHOXY we must ascribe the difference between the calculated and observed mean square amplitudes along the bond (0·015 Å^2) to a static disorder of the hydrogen atom in RbHOXY. This results in a model with half-hydrogen atoms located 0·12 Å from the twofold axis, each undergoing harmonic vibration with an r.m.s. amplitude of 0·17 Å. Hence, this model turns out to be unrealistic as the first excited level is above the barrier between the two potential-energy wells. The frequency must be 1200 cm^{-1} before the barrier reaches the energy of the first vibrational state and much higher to give a true disordered arrangement. Such a frequency is not in agreement with the spectroscopic evidence. We conclude that in the short symmetric hydrogen bond in RbHOXY the hydrogen atoms vibrates anharmonically in a broad, single, and symmetric potential-energy well.



(*a*)

(*b*)

Fig. 5. Thermal motion in the hydrogen bonds. The motion of the oxygen atoms has been subtracted from that of the hydrogen atoms. The drawings are stereoscopic. The ellipsoids enclose 50% probability. (*a*) KHOXY; (*b*) RbHOXY.

One should notice the close agreement between this result and the result obtained for the symmetric hydrogen bond in potassium hydrogen bis(acetylsalicylate) in the neutron diffraction study by Sequeira, Berkebile & Hamilton (1967). The two difference ellipsoids have the same orientation with respect to the bond and the lengths of the principal axes are mutually equal.

The two short principal axes of the difference ellipsoids may be related to the OH bending vibrations. The shortest axes correspond to the bending out of the carboxyl plane. The r.m.s. amplitudes are very small, about 0·04 Å, but the errors involved are so large that the amplitudes are still within 3σ of the amplitudes calculated from the infrared frequencies (1200 cm^{-1} in KHOXY, 1230 cm^{-1} in RbHOXY). For the bending in the carboxyl plane the amplitudes correspond to frequencies of about 1800 cm^{-1}.

To obtain additional information of the hydrogen bond systems in KHOXY and RbHOXY, infrared spectra of these two compounds and of their deuterated counterparts are now being investigated at various temperatures. A neutron diffraction study of the deuterated rubidium compound has also been started.

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The Structure of Strychnine Sulfonic Acid Tetrahydrate

BY DODDAHALLI S. SAKEGOWDA, L. CARTZ AND S. NATARAJAN

Materials Science Division, Department of Mechanical Engineering, Marquette University,
1515 *West Wisconsin Avenue, Milwaukee, Wisconsin* 53233, *U.S.A.*

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Strychnine sulphonic acid tetrahydrate, $C_{21}H_{22}N_2O_2.SO_3.4H_2O$, crystallizes in space group $P2_12_12_1$ with $a=14{\cdot}007$ (4), $b=20{\cdot}379$ (5), $c=7{\cdot}441$ (3) Å, $Z=4$. The crystal data were collected on a General Electric single-crystal diffractometer. The structure* was solved by direct methods with the cosine values of the structure invariants. Refinement by a block-diagonal least-squares procedure resulted in a final R of 7·9% for 1388 observed reflections. Hydrogen atoms were located in a difference synthesis. The molecules are held together by hydrogen bonds between water molecules and sulfur-oxygens. The strychnine molecule is compared in three of its derivatives.

Introduction

Several isomeric sulfonic acids of strychnine and of various strychnine derivatives have been reported by Leuchs and his collaborators (Leuchs & Weber, 1909; Leuchs & Rauch, 1914; Leuchs & Schwaebel, 1914). Strychnine sulfonic acids are produced by bubbling sulfur dioxide into a suspension of strychnine and manganese dioxide in water (Edward, 1972). The position of the sulfonic acid group in these compounds is not known so far.

The structure of the strychnine molecule was established on chemical grounds by the independent work of Robinson & Stephen (1948) and Woodward & Brehm (1948). The molecular configuration favored by Robinson and Woodward was confirmed by X-ray methods by Bokhoven, Schoone & Bijvoet (1951), and Robertson & Beevers (1950). The first group used the isomorphous replacement method with strychnine sulfate and selenate pentahydrates and the second used strychnine hydrobromide dihydrate but the hydrogen atoms were not located. The structure of strychnine sulfonic acid tetrahydrate was solved by direct methods with structure invariants. The molecular configuration given in Fig. 1 shows the numbering of atoms and ring designations. The hydrogen atoms are omitted from the diagrams but are given the same numbers as the atoms to which they are bonded. Wherever two hydrogen atoms are bonded to the same atom, they are indicated by the atom number followed by *A* or *B*. Oxygen of a water molecule is indicated by O(*W*) and oxygen bonded to sulfur by O(S).

The structure is particularly interesting in that the position of attachment of the sulfonic acid group is at a tertiary rather than the expected secondary carbon atom adjacent to nitrogen. The method of formation of the compound, based on its structure, would seem to be *via* a ring opening followed by a ring closure reaction of the ether ring as is known to occur in the formation of a number of other derivatives of strychnine (Manske, 1965).

Experimental

Crystals of strychnine sulfonic acid tetrahydrate were grown from a methanol/water solution, and are needle-shaped and colorless. A crystal with dimensions of about 0·10 × 0·10 × 0·15 mm was used for data collection. X-ray measurements were carried out on a General Electric single-crystal diffractometer. The crystal was

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* The structure was solved at 'The Workshop on the Use of Structure Invariants in Phase Determination'. Medical Foundation of Buffalo and SUNY/Buffalo, July 10-30, 1972.