

Rubidium Hydrogen Thiodiacetate and Potassium Hydrogen Thiodiacetate

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Abstract. Monoclinic, space group $P2_1/c$, $Z=2$. $\text{RbC}_4\text{H}_5\text{O}_4\text{S}$: $a=7.209$ (1), $b=4.857$ (1), $c=12.437$ (1) Å, $\beta=119.15$ (1)°, $V=380.33$ Å³ at 22°C; $D_x=2.048$, $D_m=2.06$ g cm⁻³. $\text{KC}_4\text{H}_5\text{O}_4\text{S}$: $a=7.227$ (1), $b=4.707$ (1), $c=11.912$ (2) Å, $\beta=117.27$ (1)°, $V=360.15$ Å³ at 22°C; $D_x=1.736$, $D_m=1.75$ g cm⁻³. The compounds are isostructural and the main feature is infinite zigzag chains of thiodiacetate ions held together by short hydrogen bonds. The O—O distance in the hydrogen bonds is 2.463 (23) in the Rb and 2.465 (13) Å in the K compound. The chains are cross-linked by the cations and the coordination about the cation is sixfold.

Introduction. Colourless crystals of Rb hydrogen thiodiacetate, RbHTDA, and K hydrogen thiodiacetate, KHTDA, were grown from aqueous solutions of H₂TDA and the alkali hydroxide (molar ratio 1:1) at room temperature. The crystals are monoclinic with systematic absences $h0l$ with $l=2n+1$ indicating space group $P2_1/c$ or Pc . The lattice constants were determined by least-squares refinement from powder data measured on a Guinier-Hägg XDC-700 powder camera with Al as internal standard at 22°C. Crystals of RbHTDA and KHTDA were mounted along **b** and integrated equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation (Ni-filtered). The layers with $0 \leq k \leq 4$ were recorded for RbHTDA and KHTDA, giving 626 and 554 independent reflexions corresponding to 72 and 68% of the unique quarter of the Cu $K\alpha$ spheres. The intensities were corrected for polarization and Lorentz effects, but not for absorption.

The E statistics were in favour of the centrosymmetric space group $P2_1/c$. The Rb parameters in RbHTDA were deduced from Harker sections. The cation is located in the special position $2(f)$ and the

S atom in $2(e)$. The weighting function used in the least-squares refinements was chosen according to Cruickshank as $w=1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$, where $a=8.0$, $c=0.02$, $d=0.002$ for RbHTDA and $a=2.0$, $c=0.02$, $d=0.004$ for KHTDA. The final values of $R=\sum||F_o|-|F_c||/\sum|F_o|=0.120$ and 0.121 , and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.146$ and 0.142 for RbHTDA and KHTDA respectively. The H atoms were included in the refinement with $B=3.0$ Å². In the last cycles the shifts in the parameters were less than 5% of the estimated standard deviations. The scattering factors for Rb⁺, K⁺, S, O, C and H were taken from *International Tables for X-ray Crystallography* (1974). Final positional and thermal parameters are given in Table 1.*

* A list of structure factors has been deposited with the British Lending Division as Supplementary Publication No. SUP 31871 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Rb ⁺	5000	1702 (4)	2500	1.92 (6)
S	0	2671 (11)	2500	1.81 (9)
O(1)	3453 (17)	8611 (25)	4834 (10)	3.05 (20)
O(2)	3739 (19)	6650 (25)	3298 (11)	3.40 (22)
C(1)	1104 (20)	5063 (30)	3796 (11)	2.00 (22)
C(2)	2911 (20)	6890 (30)	3939 (12)	1.91 (21)
K ⁺	5000	1710 (6)	2500	2.10 (7)
S	0	2592 (6)	2500	2.05 (7)
O(1)	3501 (10)	8547 (14)	4879 (6)	3.02 (13)
O(2)	3679 (10)	6624 (14)	3231 (7)	3.03 (13)
C(1)	1061 (12)	4972 (18)	3804 (7)	2.38 (14)
C(2)	2903 (12)	6828 (18)	3960 (7)	2.06 (14)
H(1)	7 (24)	655 (30)	418 (16)	
H(2)	135 (22)	387 (31)	438 (15)	

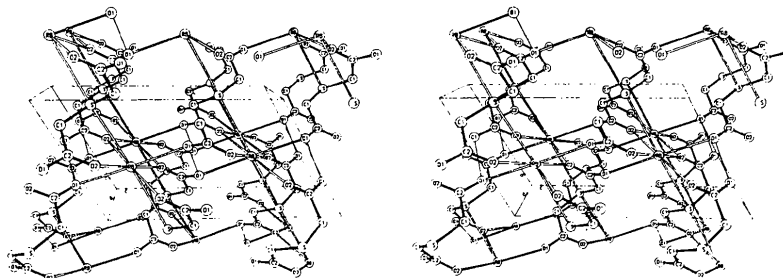


Fig. 1. A stereoscopic view of the structure of RbHTDA. Figs. 1–4 were drawn by the program ORTEP.

Discussion. The alkali hydrogen oxydiacetates have been studied (Albertsson, Grenthe & Herbertsson, 1973*a, b*; Herbertsson, 1976). A natural extension of this investigation was to determine the structures of the alkali hydrogen thiodiacetates. In the hydrogen oxydiacetates, chelates involving the ether O are formed and the question is whether or not corresponding chelates are found in the hydrogen thiodiacetates where the interaction between S and the alkali metal should be weaker.

The structures of RbHTDA (Fig. 1) and KHTDA are composed of infinite chains formed by hydrogen-bonded thiodiacetate ions. Fig. 2(*a*) shows the chains in projection on the *ac* plane and the zigzag form can be seen in Fig. 2(*b*), which is a projection on (10 $\bar{2}$). The chains are held together in three dimensions by the alkali metal ions. As seen from Fig. 2(*a*), channels parallel to **b** are formed throughout the structure.

The coordination about the alkali metal ion is six-fold and the polyhedron can be described as a distorted octahedron. Each octahedron is linked to two others by edge sharing, and in this way infinite chains are formed parallel to **b** as shown in Fig. 3.

The coordination distances are listed in Table 2 and the bond lengths Rb⁺-O and K⁺-O are in good agreement with those found in Rb and K hydrogen oxydiacetate (Albertsson, Grenthe & Herbertsson, 1973*a, b*). The difference between the average Rb⁺-O and K⁺-O distances (0.12 Å) is close to the difference be-

tween the ionic radii. The Rb⁺-S and K⁺-S distances, on the other hand, are almost identical and considerably longer than might be expected from the relative sizes of S and O, suggesting that there is very little interaction between S and the alkali metals. These values can be compared with the Cs⁺-S and the average Cs⁺-O distances, *viz.* 3.668 (2) and 3.22 (3) Å respectively, found in an unpublished investigation of Cs hydrogen thiodiacetate monohydrate made by the present author. The basic features of this structure are very similar to those described in the present investigation. A comparison of the M⁺-S and the M⁺-O distances in the three structures shows that the M⁺-S distances are approximately constant while the M⁺-O distances vary with the size of the alkali metal. This leads to the conclusion that the structure is determined by the hydrogen-bonded thiodiacetate ions and that the position of the alkali metal ions in the cell depends mainly on their interaction with the O atoms.

Table 2. *Interatomic distances (Å) and angles (°)*

(a) The ligands

	RbHTDA	KHTDA
S—C(1)	1.825 (14)	1.779 (8)
C(1)—C(2)	1.513 (19)	1.530 (11)
C(2)—O(1)	1.290 (18)	1.267 (10)
C(2)—O(2)	1.212 (18)	1.234 (10)
O(1)···O(2)	2.231 (17)	2.218 (10)
S·····O(2)	3.062 (13)	3.051 (7)
S·····O(1)	3.988 (12)	3.964 (7)
O(1)···O(1)	2.463 (23)	2.465 (13)
C(1)—H(1)		1.25 (15)
C(1)—H(2)		0.81 (15)

	RbHTDA	KHTDA
C(1)—S—C(1)	100.9 (9)	101.9 (6)
S—C(1)—C(2)	117.2 (9)	117.9 (6)
C(1)—C(2)—O(1)	111.3 (11)	113.8 (7)
C(1)—C(2)—O(2)	122.5 (13)	121.4 (7)
O(1)—C(2)—O(2)	126.2 (13)	124.9 (8)
O(1)···O(1)—C(2)	111.6 (10)	112.9 (6)
H(1)—C(1)—H(2)		93

(b) Dihedral angles

	RbHTDA	KHTDA
S—C(1)—C(2)—O(1)	175.6	-177.0
S—C(1)—C(2)—O(2)	-6.3	2.3

(c) The coordination

	RbHTDA	KHTDA
M ⁺ -2O(1)	2.943 (11)	2.800 (7)
M ⁺ -2O(2)	2.910 (12)	2.790 (7)
M ⁺ -2O(2)	2.952 (12)	2.857 (7)
M ⁺ -2S	3.635 (1)	3.637 (1)

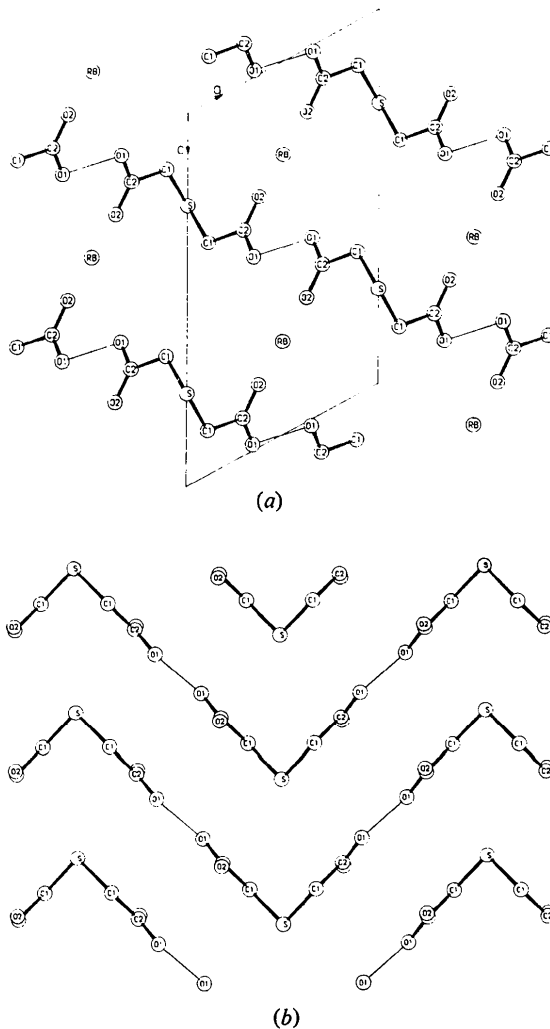


Fig. 2. (*a*) A projection on the *ac* plane. (*b*) A projection on (10 $\bar{2}$).

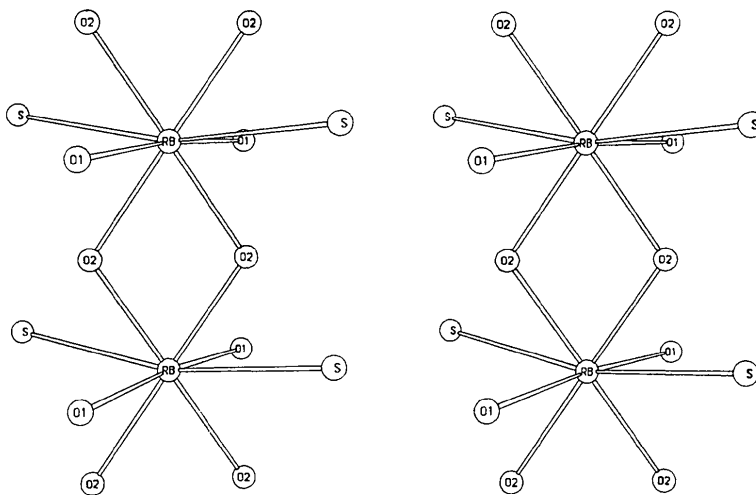
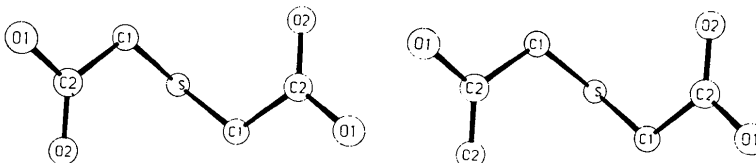
Fig. 3. The coordination around Rb^+ .

Fig. 4. The thiodiacetate ion.

The thiodiacetate ion is shown in Fig. 4 and its interatomic distances, angles, and dihedral angles are given in Table 2. While the non-hydrogen atoms are almost coplanar in thiodiacetic acid (Paul, 1967), the thiodiacetate ion is twisted in the present structures and the conformation is similar to that of monoclinic oxydiacetic acid (Herbertsson & Boman, 1973). The S atom is situated on a twofold axis and thus only one-half of the TDA ion is independent. The non-hydrogen atoms in the independent half are nearly coplanar (Table 3) and the angle between the halves is 87° in RbHTDA and 89° in KHTDA.

Table 3. Deviations (\AA) from the least-squares planes through the independent halves in the thiodiacetate ions

	RbHTDA	KHTDA
S	-0.033	-0.019
O(1)	-0.030	-0.020
O(2)	0.017	0.006
C(1)	0.049	0.025
C(2)	-0.003	0.007

The positions of the H atoms in the methylene group were refined only for KHTDA. In the difference map of RbHTDA, maxima could be found at the corresponding positions but no refinement was attempted. The O-O distance in the hydrogen bond is 2.463 (23) in RbHTDA and 2.465 (13) \AA in KHTDA with a centre of symmetry between the O atoms. The H atom involved in the hydrogen bonding could not be located; however, it must be positioned on, or close to, the centre of symmetry.

References

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