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The Crystal Structures of Rubidium and Sodium Acid Salts of α-Methoxy-α-phenylacetic Acid

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Abstract

The crystal structures of the rubidium, $RbH(C_9H_9O_3)_2$, and sodium, $NaH(C_9H_9O_3)_2$, acid salts of the racemate of α-methoxy-α-phenylacetic acid (Hmopa) have been determined. $RbH(mopa)_2$ is monoclinic, space group $C2/c$, with unit-cell parameters $a = 26.770 (15)$, $b = 6.979 (3)$, $c = 9.496 (4)$ Å, $\beta = 89.42 (2)°$, $Z = 4$. $NaH(mopa)_2$ is orthorhombic, space group $Pbcn$, with $a = 27.589 (14)$, $b = 8.811 (5)$, $c = 7.155 (5)$ Å, $Z = 4$. The hydroxyl H is on an inversion center in $RbH(mopa)_2$ and on the twofold axis in $NaH(mopa)_2$ and thus binds two identical mopa enantiomers in $NaH(mopa)_2$ and one mopa and its chiral mate in $RbH(mopa)_2$. The symmetrical hydrogen bonds have strong covalent character with O–H distances of 1·230 (4) Å in $RbH(mopa)_2$ and 1·226 (2) Å in $NaH(mopa)_2$. Both structures involve Rb–O and Na–O polyhedral chains along the c axis. In $NaH(mopa)_2$, carbonyl and methoxy O atoms are coordinated to the alkali-metal cations; in

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$RbH(mopa)_2$, hydroxyl, carbonyl and methoxy O atoms are coordinated to the cations.

Introduction

The alkali acid salts of α-methoxy-α-phenylacetic acid (Hmopa) exhibit properties which are distinctly different from those of most other acid salts. Relatively high solvolytic and thermal stabilities of both small-sized (Na^+) and large-sized (K^+, Rb^+, Cs^+) alkali-metal acid salts with respect to the neutral salts and the apparent instabilities of the NH_4^+ and Li^+ acid salts with respect to salts of other acids are two such features. Compere (1970), in a detailed infrared study on these compounds, outlined several striking features: participation of the methoxy O in ionic bonding with the alkalis, two carboxyl O atoms in $NaH(mopa)_2$ and $KH(mopa)_2$ salts symmetrically bonded to H, and four equivalent carboxyl O atoms in the $RbH(mopa)_2$ and $CsH(mopa)_2$ salts bonded to the H. Interpretation of the infrared data proved to be incorrect both in the structural details (although some 'partial' structural resemblance to that of the X-ray analysis exists), and in the conclusion that there were four equivalent carboxyl O atoms in the

large-alkali-metal salts (even though the infrared data do suggest electronic similarity for the C—O carboxyl bonds).

Experimental section

Single crystals of both salts were prepared by E. L. Compere Jr. The crystals are prisms elongated parallel to [100], with nearly equal cross section. They were broken into nearly cubic fragments, approximately 0·15 mm in mean dimension. Weissenberg photographs revealed crystals of high quality with small mosaic spread, suitable for data collection with Mo $K\alpha$ radiation. Intensity data were collected for RbH(mopa)$_2$ on a Pailred semi-automated diffractometer. The cell parameters were refined by least squares for fifteen high-angle Friedel pairs on a Picker FACS-1 diffractometer. Cell parameters for NaH(mopa)$_2$ were refined in the same manner and the entire data set was collected on the Picker diffractometer.

The structure of RbH(mopa)$_2$ was solved by heavy-atom methods from a three-dimensional Patterson synthesis. Attempts to solve NaH(mopa)$_2$ in the same way failed. It was solved by direct methods using a modified version of MULTAN (Germain, Main & Woolfson, 1971). Refinement of the non-hydrogen atoms used the neutral-atom scattering curves of Cromer & Mann (1968). Toward the conclusion of refinement, a difference-Fourier synthesis revealed the hydroxyl H atoms in special positions: on an inversion center for RbH(mopa)$_2$ and along the twofold rotor for NaH(mopa)$_2$. These atoms, labelled H(1), were refined isotropically (the y parameter for the NaH salt was also refined). Location of the remaining H atoms in the difference maps revealed the orientation of the methoxy H atoms. The H atoms, H(2)–H(10), were included as fixed atoms with $d_{C-H} = 0.95$ Å and normal geometries. Their isotropic temperature factors were assigned the values of the refined attached C atoms. Neutral scattering curves were used for the H atoms. The final cycles minimized $\sum w||F_o| - |F_c||^2$ where $w = \sigma^{-2}(F)$. The reliability factors and experimental details are summarized in Table 1, atomic coordinates in Tables 2 and 3.*

Important bond distances are presented as a cartoon of the Hmopa molecule in Fig. 1.

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34776 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details on* RbH(mopa)$_2$ *and* NaH(mopa)$_2$

	RbH(mopa)$_2$	NaH(mopa)$_2$
(A) Crystal cell data		
a (Å)	26·770 (15)	27·589 (14)
b (Å)	6·979 (3)	8·811 (5)
c (Å)	9·496 (4)	7·155 (5)
β (°)	89·42 (2)	
Space group	C2/c	Pbcn
Z	4	4
Formula	RbH(C$_9$H$_9$O$_3$)$_2$	NaH(C$_9$H$_9$O$_3$)$_2$
ρ(calc.) (Mg m^{-3})	1·560	1·353
Specific gravity (Compere, 1970)	1·587	1·354
(B) Intensity measurements		
Diffractometer	Pailred semi-automated	Picker FACS-1
Crystal orientation	ω axis = [010]	φ axis = [001]
Maximum (sin θ)/λ (Å^{-1})	0·60	0·60
Scan speed (deg min^{-1})	1·0	2·0
Base scan width	2·5	2·0
Background counts	Stationary, 20 s at beginning and end of scan	
Independent F_o	1058	1617
Variable parameters	115	117
Radiation	Mo $K\alpha$ ($\lambda = 0.7107$ Å), graphite monochromator	
(C) Refinement of the structures		
R*	0·060	0·054
R_w	0·049	0·051

* $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. RbH(mopa)$_2$: *atomic-coordinate parameters* ($\times 10^4$, *for* H $\times 10^3$) *with their estimated standard deviations*

The H atoms H(2) through H(10) are fixed-atom contributions and are at calculated positions. This also applies to Table 3.

	x	y	z
Rb	0	1210 (1)	$\frac{1}{4}$
O(1)	4691 (2)	−73 (6)	4051 (4)
O(2)	4626 (2)	3066 (6)	4391 (4)
O(3)	4091 (1)	3512 (5)	2080 (4)
C(1)	4521 (2)	1593 (9)	3742 (6)
C(2)	4181 (2)	1598 (8)	2491 (6)
C(3)	3863 (2)	3589 (10)	707 (6)
C(4)	3708 (2)	490 (8)	2803 (6)
C(5)	3631 (2)	−1322 (10)	2313 (7)
C(6)	3207 (3)	−2337 (10)	2621 (8)
C(7)	2839 (3)	−1538 (12)	3421 (8)
C(8)	2901 (3)	283 (12)	3947 (8)
C(9)	3335 (2)	1287 (10)	3634 (7)
H(1)	500	0	500
H(2)	435	97	174
H(3)	399	466	21
H(4)	394	245	21
H(5)	351	373	82
H(6)	388	−190	173
H(7)	317	−360	227
H(8)	254	−223	360
H(9)	265	84	453
H(10)	337	255	399

Table 3. NaH(mopa)$_2$: *atomic-coordinate parameters with their estimated standard deviations*

The x coordinates are $\times 10^5$ for the non-hydrogen atoms; the rest are as in Table 2.

	x	y	z
Na	0	9665 (1)	$\frac{1}{4}$
O(1)	3459 (6)	6138 (2)	6426 (2)
O(2)	1855 (6)	8456 (2)	5357 (2)
O(3)	7383 (6)	8138 (2)	2436 (2)
C(1)	4041 (8)	7248 (3)	5301 (3)
C(2)	7896 (8)	6972 (2)	3817 (3)
C(3)	9703 (10)	7747 (3)	712 (3)
C(4)	12952 (8)	6985 (3)	4662 (3)
C(5)	14366 (9)	8131 (3)	5859 (4)
C(6)	18953 (11)	8175 (3)	6595 (4)
C(7)	22220 (9)	7048 (4)	6166 (4)
C(8)	20874 (9)	5896 (3)	4996 (4)
C(9)	16251 (8)	5858 (3)	4244 (3)
H(1)	0	620 (5)	$\frac{1}{4}$
H(2)	73	601	325
H(3)	101	668	65
H(4)	128	823	65
H(5)	77	808	-30
H(6)	121	890	618
H(7)	199	898	740
H(8)	254	707	668
H(9)	231	512	470
H(10)	153	505	343

Fig. 1. Cartoon of the Hmopa molecule. The labelling of the atoms corresponds to Tables 2 and 3. The top values are for the RbH salt, followed by the NaH salt. Underlined values are for averages from *International Tables for X-ray Crystallography* (1968).
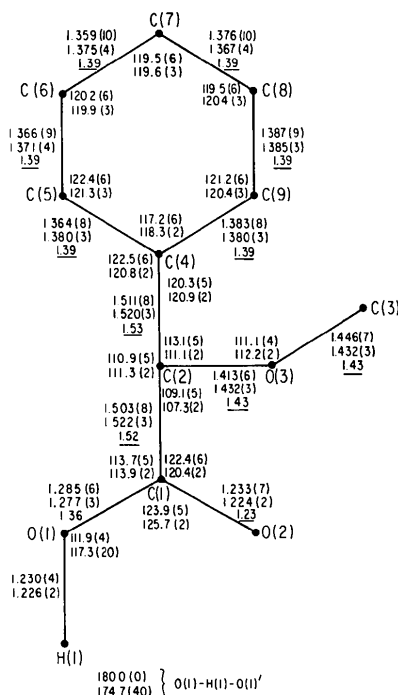
Discussion

Chirality in the crystals

In both NaH(mopa)$_2$ and RbH(mopa)$_2$, the hydroxyl H atoms occur on symmetry elements, and are therefore symmetrical or symmetrically disordered with d(O—H) = 1·226 (2) and 1·230 (4) Å respectively. In NaH(mopa)$_2$ the H binds two identical mopa fractions, and in RbH(mopa)$_2$ one mopa and its chiral mate. This suggests a simple description of the two structures based on group–subgroup relations among their space groups.

In general, for any space group G_3 there can be found, as a subgroup, at least one sheet group $G_{3,2}$, the latter having as its domain the plane of finite thickness. The *difference* $G_3 - G_{3,2}$ contains those elements in G_3 not found in $G_{3,2}$. Call these elements collectively $\{S_j\}$. We now ask what *composition* of one element found in $\{S_j\}$, call it $\{s_j\}$, with the collection of elements $\{G_{3,2}\}$ will give us the collection $\{G_3\}$, that is $\{G_{3,2}\}.\{s_j\} = \{G_3\}$.

For further convenience of description, we append ($n+$, $m-$), where $n+$ are the number of equivalent molecules of one hand (say left) and $m-$ the number of molecules of the other hand (say right) implicit in the group. For *Pbcn*, we can write $\{P2_122_1\}(4+, 0-).\{\bar{1}\}$ = $\{Pbcn\}(4+, 4-)$ and for *C2/c* $\{P2/c\}(2+, 2-).\{\bar{1}_{(2)}\}$ = $\{C2/c\}(4+, 4-)$ where $\bar{1}_{(2)}$ is equivalent to the center at $(\frac{1}{4},\frac{1}{4},0)$ in *C2/c*. For the former, the axis normal to the sheet group is b and for the latter it is c. In other words, NaH(mopa)$_2$ can be considered as a subdomain of two pairs of left-handed molecules from which, by inversion at the origin, the right-handed complementary domain is generated; while, for RbH(mopa)$_2$, one subdomain possesses both right and left pairs, which are replicated by inversion at $(\frac{1}{4},\frac{1}{4},0)$ in the complementary domain.

Bonding to the alkali metals

Figs. 2 and 3 feature the O coordinations about the alkali-metal atoms. There are three unique O atoms in NaH(mopa)$_2$ and RbH(mopa)$_2$: the hydroxyl O [$\cdots$C—O—H, = O(1)], carbonyl O [($\cdots$C=O), = O(2)], and methoxy O [$\cdots$C—O—CH$_3$, = O(3)]. The first two are carboxyl O atoms but we wish to distinguish that which is protonated. In NaH(mopa)$_2$, O(1) is not coordinated by the cation, but O(2) is coordinated by two Na$^+$ and O(3) by one Na$^+$. The NaO$_6$ polyhedron is a distorted square plane [2 O(2) + 2 O(3)] with an opposing bifurcated apex [2 O(2)]. The Na—O average distance of 2·37 Å is close to the 2·41 Å for six coordination listed in MacGillavry & Rieck (1968). This is one of the two admissible C_{2v} polyhedra (Britton & Dunitz, 1973). They link to symmetry-equivalent polyhedra by inversion across shared edges [O(2)—

O(2)[1] to form a linear chain which runs parallel to [001]. In the RbH(mopa)$_2$ salt, an O(1) is also coordinated by the alkali-metal atom forming the RbO$_8$ polyhedron. The average Rb—O = 2·99 Å is within the range of 2·90–3·20 Å distances (MacGillavry & Rieck, 1968). The polyhedron corresponds to polyhedron number 14 of Britton & Dunitz (1973), and can be obtained from the NaO$_6$ polyhedron by extending outward the bifurcated apices and inserting two O(1) atoms. These polyhedra are linked by sharing edges across inversion centers [O(2), O(2)[1]] to form a zigzag chain which runs parallel to [001].

The occurrence of the protonated carboxyl O in a symmetrical bond, the participation of O(2) and O(3) in bonding to the alkalis, and the appearance of polyhedral chains confer low solubility on these salts with respect to the neutral salts in aqueous media. Such symmetrical bonds exhibit strong covalent character, as demonstrated recently by Stevens, Lehmann & Coppens (1977) in sodium hydrogen diacetate. However, the large isotropic thermal-vibration parameters for these H atoms in our structures do not preclude the possibility that some disorder may exist and that the bonds are not strictly symmetrical.
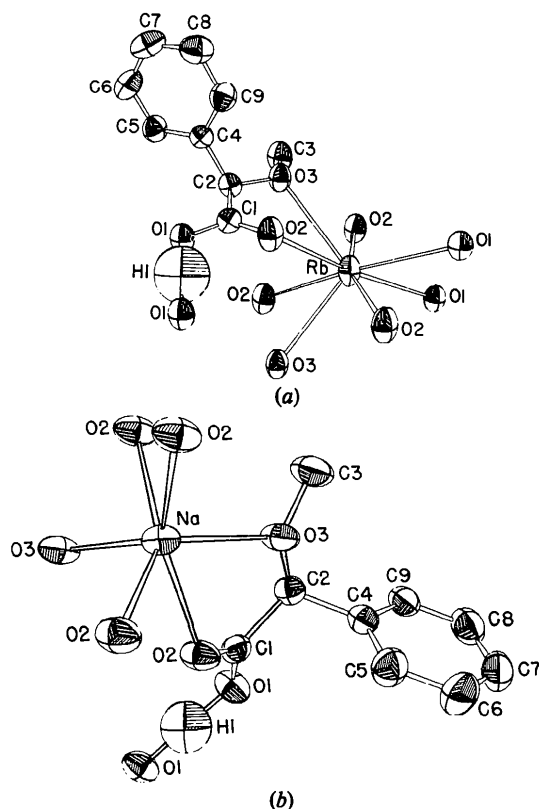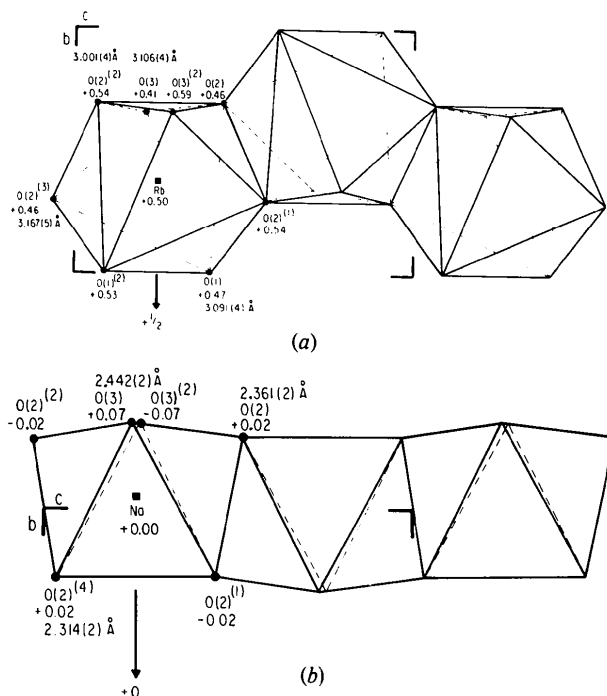

Fig. 3. (a) Polyhedral diagram of the edge-sharing kinked chain based on eight-coordinate O polyhedra about Rb. Heights are given in fractional coordinates. Non-equivalent Rb—O distances are given. The cell outline and the twofold rotor are shown. Symmetry-equivalent atoms are written with superscripts. (b) Polyhedral diagram of the edge-sharing linear chain based on six-coordinate O polyhedra about Na.

Fig. 2. ORTEP plots (Johnson, 1965) of thermal-vibration ellipsoids for (a) RbH(mopa)$_2$ and (b) NaH(mopa)$_2$ (both at the 50% probability level).

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