Syntheses, Crystal Structures and an Overview of Alkali Metal Maleates

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The crystal structures of four alkali salts of maleic acid have been determined by single crystal X-ray diffraction: crystals of rubidium hydrogen maleate, $RbH(C_4H_2O_4)$, are very nearly centrosymmetrical, *i. e.*, only one hydrogen atom position in the crystal structure violates the centrosymmetry. Thus, the space group is $Pbc2_1$ rather than *Pbcm*. The compound is isotypic with potassium hydrogen maleate, $KH(C_4H_2O_4)$, which has previously been described in space group *Pbcm*. It has been reinvestigated to prove that the correct space group is also $Pbc2_1$. The isotypic pair of rubidium hydrogen maleate maleic acid, $RbH(C_4H_2O_4)\ H_2(C_4H_2O_4)$, and caesium hydrogen maleate maleic acid, $CsH(C_4H_2O_4)H_2(C_4H_2O_4)$, crystallise in the triclinic space group $P\bar{1}$. The geometry of the maleate units in these compounds corresponds well to data of other metal maleates. The only significant variation, concerning the intra-anionic hydrogen bond, is discussed. Furthermore, an overview of previously reported metal maleate structures is given, with special regard to the symmetry of the intramolecular hydrogen bond.

Key words: Maleate, Crystal Structure, Symmetry, Hydrogen Bond

Introduction

In the past, we have extensively studied various metal carboxylates, such as succinates [1], malates [2, 3] and adipates [4]. Recently, we extended these studies to the family of maleates. Although a search in the literature as well as in data bases (CSD [5], PC-PDF [6]) has shown that a rather large number of metal salts of maleic acid have been described in the past (Table 1), some possible combinations remain unreported. In this paper, several new alkali metal maleates are presented: rubidium hydrogen maleate, $RbH(C_4H_2O_4)$, rubidium hydrogen maleate maleic acid, $RbH(C_4H_2O_4)H_2(C_4H_2O_4)$ and caesium hydrogen maleate maleic acid, $CsH(C_4H_2O_4)H_2(C_4H_2O_4)$, referred to as RbHMal, RbH_3Mal_2 and CsH_3Mal_2. Additionally, we have reinvestigated the crystal structure of potassium hydrogen maleate, $KH(C_4H_2O_4)$, referred to as KHMal, which had previously been reported to crystallise in the centrosymmetric space group *Pbcm* by Darlow and Cochran [12]. Because the unit cell parameters are very similar to those of RbHMal, suspicion arose that its crystal structure might also be non-centrosymmetric, and a redetermination of the crystal structure was necessary to solve this problem. More generally, we have investigated the question of symmetry of the maleate units in other salts of maleic acid.

Results and Discussion

Structure of RbHMal and KHMal

The determination of the atomic arrangement of RbHMal initially yielded a centrosymmetric crystal structure (the apparent space group being *Pbcm*). In this space group, however, the maleate molecule would be symmetrical, with the hydrogen atom of the intra-anionic hydrogen bond being virtually in the middle between the two oxygen atoms (possible symmetries of the maleate molecule are shown in Fig. 1). Albeit such a symmetrical molecular structure is possible by a symmetric hydrogen bond or by disorder (disorder has been reported previously; see below), a refinement in the lower symmetric space group $Pbc2_1$ (without a centre of symmetry), resulted in a model that agreed better with the experimental data. Furthermore, the oxygen and carbon atoms could be shown to deviate slightly but significantly from their respective centrosymmetric positions of the space group *Pbcm*. Moreover, the difference between the C–O distances in the acid group and the mesomeric carboxylate obviously confirm the lower symmetry (Fig. 2).

Table 1. Metal maleate compounds: Overview of the stoichiometries, space groups (s. g.) and unit cell parameters (Å and deg). (Maleate = $C_4H_4O_4{}^{2-}$).

Sample	*a*	*b*	*c*	α	β	γ	s. g.	PDF no.	Ref.
Li_2Maleate	9.631	12.131	12.705	90	107.96	90	$C2/c$		[7]
Na_2Maleate·H_2O	20.979	10.004	6.369	90	100.15	90	$C2/c$		[8]
LiHMaleate·$2H_2O$	5.858	6.051	18.800	90	91.47	90	$P2_1/n$	36-1960	[9, 10]
NaHMaleate·$3H_2O$	5.927	6.288	11.222	104.0	91.47	100.26	$P\bar{1}$		[11]
KHMaleate	4.578	7.791	15.953	90	90	90	$Pbc2_1$		[12], this work
RbHMaleate	4.674	7.667	16.455	90	90	90	$Pbc2_1$		this work
RbH_3Maleate$_2$	5.762	9.556	10.546	79.903	88.324	73.811	$P\bar{1}$		this work
CsH_3Maleate$_2$	5.738	9.746	10.613	78.971	88.685	73.881	$P\bar{1}$		this work
Ag_2H_2Maleate$_2$	10.608	3.722	12.976	90	91.11	90	$P2_1/n$		[13]
Ag_2Maleate	5.298	9.253	11.261	90	101.85	90	$P2_1/n$		[14]
CaMaleate·$2H_2O$	8.54	10.83	6.84	90	90	90	$P2_12_12_1$		[15]
SrMaleate·$4H_2O$	11.476	7.027	12.344	90	115.74	90	$P2_1/n$		[16]
MnMaleate·$3H_2O$	8.260	13.341	7.731	90	115.35	90	Cc	54-1758	[17]
CoMaleate·$3H_2O$	8.118	13.175	7.497	90	115.17	90	Cc	54-1791	[18, 19]
NiMaleate·$6H_2O$	7.186	8.659	9.613	113.34	95.95	105.53	$P\bar{1}$	53-1585	[20]
CuMaleate·H_2O	8.78	7.88	5.35	90	90	125.1	$P112_1$		[21]
CuHMaleate·H_2O	8.433	6.695	4.951	90	90	90	$Pm2_1n$		[22]
MgH_2Maleate$_2$·$6H_2O$	10.207	11.829	6.745	90	104.2	90	$P2_1/c$	50-1925	[23, 24]
CaH_2Maleate$_2$·$5H_2O$	11.737	6.477	19.593	90	90	90	$Pnam$		[25]
BaH_2Maleate$_2$·$4H_2O$	6.528	19.009	11.493	90	92.345	90	$P2_1/c$		[26]
MnH_2Maleate$_2$·$4H_2O$	7.374	9.755	5.325	106.65	86.68	115.44	$P\bar{1}$	54-1793	[17]
FeH_2Maleate$_2$·$4H_2O$	5.279	7.399	9.302	109.25	104.73	93.37	$P\bar{1}$	55-1979	[27, 19]
CoH_2Maleate$_2$·$4H_2O$	5.222	7.340	9.239	109.17	104.52	93.31	$P\bar{1}$		[19]
NiH_2Maleate$_2$·$4H_2O$	7.309	9.134	5.170	104.65	92.88	108.40	$P\bar{1}$	51-2104	[28, 29]
ZnH_2Maleate$_2$·$4H_2O$	7.337	9.219	5.222	104.67	93.03	108.86	$P\bar{1}$	56-1535	[28]
CuH_2Maleate$_2$·$4H_2O$	3.594	18.79	9.69	90	90	93.25	$I112/m$		[21]
CdMaleate·$2H_2O$	6.087	16.310	7.000	90	93.8	90	Cc	55-1166	[30]
SnMaleate	7.35	16.84	5.32	90	90	90	$P2_1ab$		[31]
PbMaleate	9.920	6.979	8.293	90	111.09	90	$P2_1/c$		[32]
PrH_3Maleate$_3$·$8H_2O$	7.286	10.402	16.761	72.11	87.77	70.85	$P\bar{1}$		[33]
GdH_3Maleate$_3$·$8H_2O$	10.317	16.627	7.192	91.99	109.18	72	$P\bar{1}$		[34]

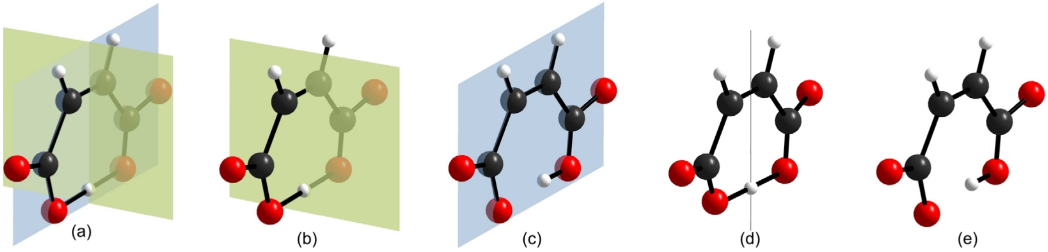

Fig. 1. The hydrogen maleate anion with its intramolecular hydrogen bond. When the hydrogen atom is considered to be located in the middle (or is not there at all, *i. e.*, in the maleate dianion), the molecule can assume point symmetry $mm2$ (C_{2v}, a), or just m (C_s), with the mirror plane perpendicular to the molecular plane (b). This conformation can be conceived as a result from slight rotations about the C1–C2 and C3–C4 bonds in opposite directions. With the hydrogen atom off-centre, the molecule can still assume symmetry m (C_s), with the molecule in the mirror plane (c). Another possibility is point symmetry 2 (C_2), if the C1–C2 and C3–C4 bonds are rotated in the same direction (d). In most cases, however, the symmetry is 1 (C_1) because of slight deviations from the ideal symmetry (e). Figs. 1 to 5 were drawn with the programme Diamond [48].

Since only minuscule deviations and one hydrogen atom violate the alleged centrosymmetry of the crystal structure, both statistical checks of the structure factors using the programme Collect [35], and the final symmetry check with the programme Platon [36] recommended the centrosymmetric space group. Nevertheless, the electron density calculated from the Fourier maps clearly showed that the hydrogen atom is located off-centre on one side of the molecule.

Table 2. Crystal structure data for the title compounds.

	KHMal	RbHMal	RbH_3Mal_2	CsH_3Mal_2
Formula	$KH(C_4H_2O_4)$	$RbH(C_4H_2O_4)$	$RbH_3(C_4H_2O_4)_2$	$CsH_3(C_4H_2O_4)_2$
M_r	154.16	200.53	316.61	364.05
Crystal size, mm^3	$0.05 \times 0.04 \times 0.03$	$0.08 \times 0.06 \times 0.06$	$0.10 \times 0.07 \times 0.05$	$0.30 \times 0.10 \times 0.10$
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic
Space group	$Pbc2_1$	$Pbc2_1$	$P\bar{1}$	$P\bar{1}$
a, Å	4.575(1)	4.674(1)	5.765(1)	5.740(1)
b, Å	7.804(2)	7.997(1)	9.556(1)	9.756(1)
c, Å	15.958(2)	16.455(1)	10.548(1)	10.624(1)
α, deg	90	90	79.84(1)	79.01(1)
β, deg	90	90	88.30(1)	88.67(1)
γ, deg	90	90	73.87(1)	73.86(1)
V, Å^3	569.8(1)	615.1(1)	549.3(1)	560.7(1)
Z	4	4	2	2
D_{calcd}, g cm^{-3}	1.80	2.17	1.91	2.16
$\mu(MoK_\alpha)$, cm^{-1}	0.9	8.0	4.5	3.3
$F(000)$	312	384	312	348
hkl range	$\pm 7, \pm 12, \pm 27$	$\pm 7, \pm 12, \pm 26$	$\pm 8, -13/14, -16/13$	$\pm 18, \pm 13, \pm 31$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.806	0.804	0.754	0.703
Reflections measured	2515	2691	12708	4526
Reflections unique	2311	2477	3872	3125
Data with $F_o \geq 4\sigma(F_o)$	1828	1481	2938	2866
R_{int}	0.030	0.028	0.034	0.023
Parameters refined	94	94	183	183
$R(F)^a$ [for $F_o \geq 4\sigma(F_o)$]	0.0293	0.0293	0.0285	0.0255
$wR(F^2)^a$ (all refls.)	0.0797	0.0716	0.0651	0.0631
Weighting parameters a/b	0.0360 / 0.0950	0.0296 / 0.1150	0.0240 / 0.1570	0.0275 / 0.2329
x(Flack)	−0.02(8)	0.14(6)	–	–
GoF $(F^2)^a$	1.03	1.00	1.04	1.03
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.30 / −0.26	0.38 / −0.31	0.69 / −0.98	0.60 / −1.07

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, $P = (F_o^2 + 2F_c^2)/3$. *Note*: Scattering factors for neutral atoms were employed in the refinement.

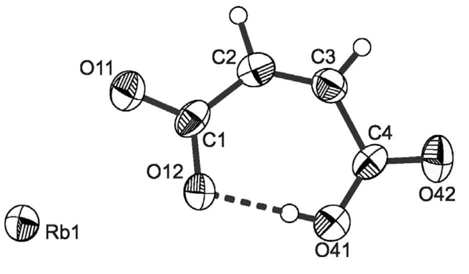

Fig. 2. Molecular structure and connectivity in RbHMal and KHMal as shown for the Rb compound (displacement ellipsoids at the 50 % probability level; H atoms with arbitrary radii).

When comparing the unit cell parameters of RbHMal with those of potassium hydrogen maleate [14], the relation of these two structures becomes easily apparent. However, Darlow and Cochran reported space group *Pbcm*. This is plausible since the photographic methods used in that investigation were then of limited accuracy, and the detection of one hydrogen atom in a crystal with potassium is not always possible even with high-resolution CCD detectors, and even less so with film data. In a second paper by Darlow [37], calculations on the geometry of the symmetric hydrogen maleate ion were made, but without any new experimental input, based on the data of the previous paper. Other attempts to generally clarify the question of the symmetry of hydrogen maleate were ambiguous: James and Matsushima [38] investigated hydrogen maleate ions in a "symmetric environment" in the crystal structure of imidazolium hydrogen maleate and concluded that the "intramolecular hydrogen bond may possibly be symmetric". However, we assumed that both the rubidium and the potassium salt might be isostructural. Therefore, we reinvestigated the crystal structure of KHMal. A refinement of the data, starting with the initial parameters from RbHMal gave good agreement. Again, the electron density between the carboxylate oxygen atoms showed an off-centre peak at the same spot where the hydrogen atom is located

Table 3. Fractional coordinates and isotropic or equivalent isotropic displacement parameters[a] for the title compounds.

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}	*x*	*y*	*z*	U_{eq}/U_{iso}
	KHMal:				*RbHMal:*			
K1/Rb1	−0.23763(5)	0.2498(1)	1.0002(2)	0.03393(9)	−0.23778(4)	0.24987(7)	1.0000(3)	0.04047(9)
O11	0.2631(6)	0.4179(3)	0.9286(2)	0.0416(6)	0.2643(9)	0.4142(5)	0.9240(4)	0.0488(8)
O12	0.0170(7)	0.2959(5)	0.8268(2)	0.0405(6)	0.0248(8)	0.3001(6)	0.8244(4)	0.053(1)
C1	0.2226(6)	0.3985(4)	0.8525(2)	0.0312(7)	0.2258(9)	0.3985(7)	0.8483(4)	0.038(1)
C2	0.4073(9)	0.4894(5)	0.7918(3)	0.0348(6)	0.4004(9)	0.4904(9)	0.7910(5)	0.045(1)
H2	0.572(8)	0.563(4)	0.824(2)	0.046(9)	0.527(9)	0.571(5)	0.821(3)	0.05(1)
C3	0.4097(8)	0.4870(5)	0.7082(2)	0.0309(6)	0.4112(9)	0.4854(8)	0.7103(5)	0.040(1)
H3	0.540(7)	0.545(4)	0.685(2)	0.035(9)	0.558(8)	0.534(4)	0.686(2)	0.03(1)
C4	0.2134(7)	0.3953(4)	0.6475(2)	0.0295(6)	0.2189(9)	0.3961(7)	0.6495(4)	0.039(1)
O41	0.0137(7)	0.2964(5)	0.6744(2)	0.0422(6)	0.0255(9)	0.2973(6)	0.6767(4)	0.055(1)
O42	0.2628(6)	0.4209(3)	0.5720(2)	0.0434(6)	0.2703(9)	0.4235(4)	0.5786(4)	0.052(1)
H41	0.011(4)	0.295(2)	0.727(2)	0.053(7)	0.023(6)	0.298(3)	0.724(2)	0.042(9)
	RbH_3Mal_2:				*CsH_3Mal_2:*			
Rb1/Cs1	0.79485(3)	0.36174(2)	0.12868(2)	0.04488(8)	0.79708(3)	0.36013(2)	0.12472(1)	0.03759(9)
O11a	0.8311(2)	0.0221(2)	0.1860(1)	0.0500(3)	0.8254(3)	0.0153(2)	0.2023(2)	0.0477(5)
O12a	0.5509(2)	0.1370(2)	0.3062(1)	0.0521(3)	0.5445(4)	0.1300(3)	0.3179(2)	0.0507(5)
C1a	0.6244(3)	0.0412(2)	0.2349(2)	0.0343(3)	0.6171(4)	0.0376(3)	0.2467(2)	0.0332(5)
C2a	0.4540(3)	−0.0436(2)	0.2065(2)	0.0339(3)	0.4428(5)	−0.0395(3)	0.2138(2)	0.0341(5)
H2a	0.300(4)	−0.014(2)	0.245(2)	0.039(5)	0.298(7)	−0.014(4)	0.246(3)	0.040(8)
C3a	0.4862(3)	−0.1475(2)	0.1329(2)	0.0355(3)	0.4716(4)	−0.1373(3)	0.1385(2)	0.0343(5)
H3a	0.350(4)	−0.185(2)	0.122(2)	0.043(5)	0.333(7)	−0.171(4)	0.118(3)	0.050(10)
C4a	0.6999(3)	−0.2177(2)	0.0592(2)	0.0354(3)	0.6838(5)	−0.2051(3)	0.0653(2)	0.0327(5)
O41a	0.8984(2)	−0.1749(1)	0.0569(1)	0.0436(3)	0.8846(3)	−0.1676(2)	0.0680(2)	0.0412(4)
H41a	0.876(5)	−0.101(3)	0.106(3)	0.086(9)	0.882(9)	−0.103(4)	0.119(4)	0.08(1)
O42a	0.6843(3)	−0.31509(16)	0.0009(1)	0.0519(3)	0.6640(4)	−0.2953(2)	0.0033(2)	0.0475(5)
O11b	1.1254(2)	0.1880(2)	0.3824(2)	0.0556(4)	1.1239(4)	0.1844(3)	0.3925(2)	0.0510(5)
H11b	1.286(4)	0.161(4)	0.363(3)	0.115(12)	1.283(4)	0.140(4)	0.370(3)	0.063(11)
O12b	1.2560(2)	0.2832(2)	0.5332(1)	0.0481(3)	1.2564(3)	0.2876(2)	0.5331(2)	0.0440(4)
C1b	1.0917(3)	0.2508(2)	0.4812(2)	0.0370(3)	1.0922(4)	0.2519(3)	0.4862(2)	0.0338(5)
C2b	0.8349(3)	0.2849(2)	0.5258(2)	0.0404(4)	0.8378(5)	0.2881(3)	0.5313(2)	0.0378(5)
H2b	0.732(4)	0.247(2)	0.483(2)	0.051(6)	0.726(6)	0.257(4)	0.489(3)	0.038(8)
C3b	0.7371(3)	0.3615(2)	0.6170(2)	0.0388(4)	0.7451(5)	0.3639(3)	0.6214(2)	0.0373(5)
H3b	0.564(4)	0.375(2)	0.635(2)	0.050(6)	0.583(7)	0.374(4)	0.642(3)	0.040(8)
C4b	0.8419(3)	0.4339(2)	0.7065(2)	0.0377(3)	0.8559(5)	0.4336(3)	0.7086(2)	0.0348(5)
O41b	1.0721(2)	0.4353(2)	0.6977(1)	0.0431(3)	1.0831(4)	0.4358(2)	0.6946(2)	0.0422(4)
H41b	1.139(4)	0.379(3)	0.640(2)	0.066(7)	1.144(7)	0.384(4)	0.636(3)	0.054(10)
O42b	0.7131(3)	0.4912(2)	0.7866(2)	0.0643(4)	0.7348(4)	0.4878(3)	0.7910(2)	0.0569(6)

[a] Definition of the equivalent isotropic displacement parameters according to ref. [41].

in RbHMal. As in RbHMal, a refinement in the centrosymmetric space group *Pbcm* yielded higher *R* values and larger displacement parameters. In addition, a Kurtz and Perry test [39] using a Nd:YAG laser in our laboratory resulted in a weak but significant generation of the second harmonic of the pumping laser light. We therefore have strong evidence for the assumption that $Pbc2_1$ is the correct space group also for KHMal. For both compounds, the Flack parameters [40] confirm that the non-centrosymmetric crystal structure is correct. The crystal data, details of the measurements and the refinements of all title compounds are given in Table 2. The atomic coordinates and the equivalent isotropic displacement parameters (according to [41]) are listed in Table 3, the anisotropic displacement parameters have been deposited. Selected interatomic distances and calculated bond valence sums are given in Tables 3 and 4, and the hydrogen bonding systems are listed in Table 5. Observed and calculated structure factors are available from the authors.

The packing of the components in the crystals resembles a herring bone-like arrangement (Fig. 3a). The cations are irregularly 8-coordinated, the K–O distances are ranging from 2.816(3) to 3.030(4) Å and the Rb–O distances from 2.919(4) to 3.180(7) Å, equivalent to bond valence sums of 1.016 and 1.065 (Table 4). Bond valence calculations were carried out using the parameters from [43]. The M–O polyhedra are packed

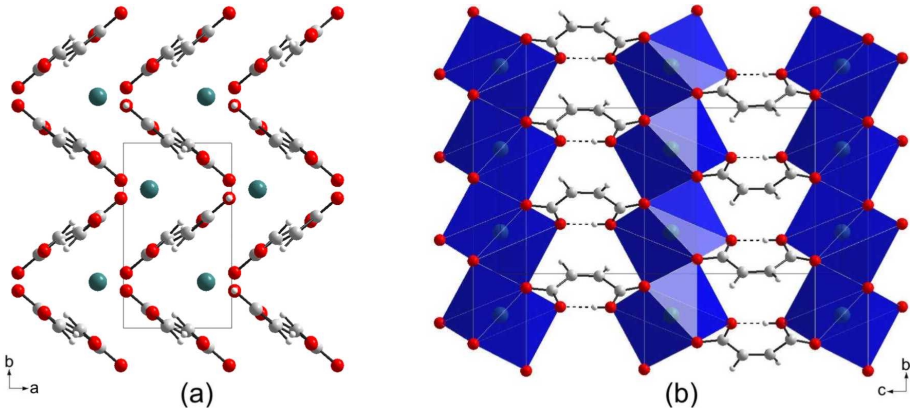

Fig. 3. Packing diagram of the structures of RbHMal and KHMal. The herring bone-like arrangement of the molecules is visible when viewed along [001] (a), the near mirror symmetry when viewed along [100] (b). Hydrogen bonds are indicated as dashed lines, Rb–O polyhedra are omitted in (a) for clarity.

Table 4. Me–O distances (Å), with estimated standard deviations in parentheses, and calculated bond valence sums[a] of the cations in the title compounds.

KHMal			RbHMal		
K–O42	2.816(3)	0.157	Rb–O42	2.919(4)	0.170
K–O11	2.833(3)	0.150	Rb–O11	2.951(5)	0.156
K–O11	2.871(3)	0.136	Rb–O11	2.964(5)	0.150
K–O11	2.876(3)	0.134	Rb–O11	2.966(5)	0.150
K–O42	2.883(3)	0.131	Rb–O42	2.980(5)	0.144
K–O42	2.886(3)	0.130	Rb–O42	3.039(5)	0.123
K–O12	3.024(4)	0.090	Rb–O12	3.164(7)	0.088
K–O41	3.030(4)	0.088	Rb–O41	3.180(7)	0.084
⟨K–O⟩	2.902	Σ 1.016	⟨Rb–O⟩	3.020	Σ 1.065
RbH$_3$Mal$_2$			CsH$_3$Mal$_2$		
Rb–O42a	3.041(2)	0.136	Cs–O42b	3.191(2)	0.123
Rb–O42b	3.058(2)	0.117	Cs–O41b	3.225(2)	0.113
Rb–O41a	3.069(1)	0.113	Cs–O41a	3.232(2)	0.111
Rb–O11a	3.142(1)	0.093	Cs–O42a	3.243(2)	0.107
Rb–O41b	3.144(2)	0.092	Cs–O11a	3.266(2)	0.101
Rb–O12a	3.193(2)	0.081	Cs–O42a	3.268(2)	0.100
Rb–O42a	3.211(2)	0.077	Cs–O42a	3.296(2)	0.093
Rb–O11b	3.245(2)	0.07	Cs–O11b	3.339(2)	0.083
Rb–O42a	3.289(2)	0.062	Cs–O12a	3.357(2)	0.079
⟨Rb–O⟩	3.155	Σ 0.841	⟨Cs–O⟩	3.269	Σ 0.910

[a] Bond valence parameters were calculated using the programme VALENCE [42].

Table 5. Hydrogen bonds in the title compounds.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
KHMal, intramolecular bond:				
O41–H41···O12	0.84(2)	1.60(2)	2.431(2)	178(2)
RbHMal, intramolecular bond:				
O41–H41···O12	0.78(3)	1.65(3)	2.431(2)	179(3)
RbH$_3$Mal$_2$, intramolecular bond:				
O41a–H41a···O11a	0.93(2)	1.53(2)	2.460(2)	179(3)
— intermolecular bonds:				
O11b–H11b···O12a	0.92(2)	1.60(2)	2.503(2)	170(4)
O42b–H12b···O12b	0.90(2)	1.60(2)	2.495(2)	178(3)
CsH$_3$Mal$_2$, intramolecular bond:				
O41a–H41a···O11a	0.91(2)	1.54(2)	2.437(3)	169(5)
— intermolecular bonds:				
O11b–H11b···O12a	0.94(2)	1.57(2)	2.469(3)	158(4)
O42b–H12b···O12b	0.89(2)	1.58(2)	2.467(3)	179(4)

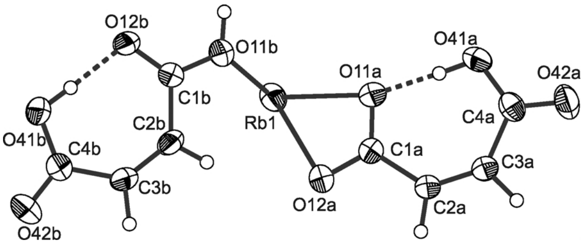

Fig. 4. Molecular structure and connectivity in RbH$_3$Mal$_2$ and CsH$_3$Mal$_2$ as shown for the Rb compound (displacement ellipsoids at the 50 % probability level; H atoms with arbitrary radii).

to form layers parallel (001), which are in turn connected by the anions to a three-dimensional framework (Fig. 3b).

Structure of RbH$_3$Mal$_2$ and CsH$_3$Mal$_2$

The packing in the isotypic structures of the acid salts RbH$_3$Mal$_2$ and CsH$_3$Mal$_2$ (Fig. 4) is different from that in RbHMal and KHMal: All anions and acid molecules are oriented more or less parallel to $[0\,1\,\bar{1}]$, resulting in a sheet-like arrangement (Fig. 5), with the alkali metal cations in the interstices. There are two crystallographically different moieties in the structure, one being a molecule of maleic acid, the other a mono-deprotonated unit, *i. e.*, a hydrogen maleate

Table 6. Selected bond lengths (in Å) and bond angles (in deg) of the title compounds in comparison with the corresponding mean values of other metal maleate compounds, with estimated standard deviations in parentheses. The mean values were calculated from all the structures listed in Table 1.

Compound	C1–C2	C2–C3	C3–C4	C1–C2–C3	C2–C3–C4	O–H[a]	C1–C2–C3–C4[b]
KH Mal	1.468	1.335	1.503	131.10	130.30	0.84	3.1
RbH Mal	1.448	1.331	1.522	131.00	130.40	0.78	8.2
RbH$_3$Mal$_2$ (a)	1.503	1.340	1.500	129.26	131.43	0.93	2.6
RbH$_3$Mal$_2$ (b)	1.505	1.335	1.501	128.35	132.28	0.90	2.0
CsH$_3$Mal$_2$ (a)	1.491	1.331	1.493	129.30	131.50	0.90	1.7
CsH$_3$Mal$_2$ (b)	1.493	1.332	1.493	128.50	132.20	0.89	1.9
Mean	1.49(2)	1.34(1)	1.49(2)	129(3)	129(3)	1.0(2)	2(3)

[a] The given O–H distance refers to the acid hydrogen atom that constitutes the intramolecular hydrogen bond; [b] torsion angles, absolute values are given and have been used for the calculation of the mean values.

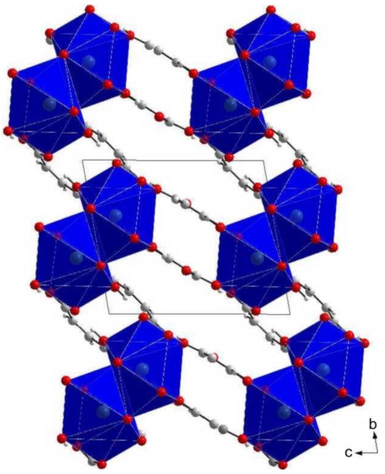

Fig. 5. Packing diagram of the structures of RbH$_3$Mal$_2$ and CsH$_3$Mal$_2$, viewed along [100].

anion (Fig. 4). The large alkali metal cations are irregularly 9-coordinated with Rb–O distances varying from 3.045(2) to 3.293(2) Å and Cs–O distances from 3.191(2) to 3.353(2) Å, which gives bond valence sums of 0.82 and 0.92, respectively, indicating slight undersaturation. These polyhedra form chains along [100] and are connected to a three-dimensional framework *via* the organic components.

Geometry of the molecules

In contrast to other four-carbon dicarboxylic acids (such as malic or succinic acid), the maleate molecule is a rather rigid unit: Because of the π bond, the carbon atoms of the backbone lie very nearly in one plane (torsion angles of the title compounds are given in Table 6). Through the intra-anionic hydrogen bond, the carboxylate groups of the acid salts are also situated in or close to this plane. The geometry of the maleate units in the title compounds corresponds quite well to literature data (Table 6), although the lengths of the C–C single bonds in KHMal and RbHMal deviate significantly. Nevertheless, the distance showing the highest variation among all the metal maleate structures concerns the intra-anionic hydrogen bond of the hydrogen maleate unit. In some compounds, this hydrogen bond is reported as nearly or even truly symmetrical, in others the hydrogen atom clearly lies on one side of the anion, making "donor" and "acceptor" distinguishable (Fig. 1). The highest possible point group symmetry of the molecule, *mm*2 (C_{2v}), has not been found yet in any of the reported compounds, the most frequently observed symmetry is 1 (C_1). Only in the copper hydrogen maleates CuHMal·H$_2$O [22] and CuH$_2$Mal$_2$·4H$_2$O [21] the anion has the symmetry *m* (C_s), with the mirror plane perpendicular to the molecular plane.

Conclusion

Through the description of the new hydrogen maleate RbHMal, the true crystal and molecular symmetry of the previously reported salt (KHMal) was discovered. When examining these crystal structures with less sensitive methods, one would easily assign space group *Pbcm*, as did the programmes commonly used for checking the correctness of structure determinations. Since most of the metal maleate structures have been investigated many years ago, when modern detectors were used only rarely or not at all, it is possible that some of the other compounds listed in Table 1 were published with the wrong space group. More precisely, those where the hydrogen maleate anion is reported to be symmetric could be concerned. Additionally, it is possible that static or dynamic disorder concerning the intramolecular hydrogen bond of the hydrogen maleate anion occurs as well as twinning of the two different states, thus pretending a higher symmetry of the crystal structure. We are currently conducting a systematic

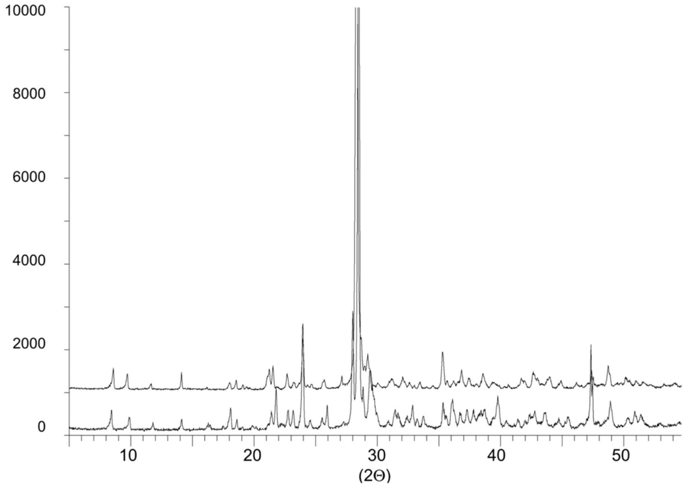

Fig. 6. Detail of the powder diagrams (angles in deg) of the isotypic structures of RbH_3Mal_2 and CsH_3Mal_2.

analysis of these hydrogen maleates in order to verify their structures.

Experimental Section

Syntheses

All crystals were obtained by slow evaporation of aqueous solutions of the compounds at approximately 295 K over a period of several weeks. All crystals were colourless and up to 0.5 mm in size. The solutions were prepared by dissolving the carbonates [K_2CO_3 (Fluka, 99.0 %), Rb_2CO_3 (Chemetall, 99.99 %), Cs_2CO_3 (Chemetall, 99.99 %)] in aqueous solutions of maleic acid (Merck, 99.0 %) in stoichiometric ratio of the constituents.

X-Ray structure determinations and refinement

The samples were studied under a microscope, and small crystals (average sizes 0.05 mm) were chosen for single-crystal analysis. The crystals were cut to approximately isometric dimensions and carefully washed with acetone to remove fragments from the surface.

Single-crystal X-ray intensity data were collected at 293 K on Bruker-Nonius diffractometers equipped with CCD area detectors using graphite-monochromatised MoK_α radiation (λ = 0.71073 Å). For all compounds, the whole Ewald spheres were measured, using multiple sets of φ and ω scans. The intensity data were processed with the Bruker-Nonius programme suites COLLECT [35] and SAINT-Plus [44] and corrected for Lorentz, polarisation, background and absorption effects [44, 45]. The crystal structures of the rubidium compounds were determined by automatic Patterson methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 [46]. Although the structures contained rather heavy atoms, all the hydrogen atoms could be located in the difference Fourier maps and refined freely without problems. For RbHMal, another refinement attempt was made in the higher-symmetric space group *Pbcm*, but the *R* values were slightly higher, and the acid hydrogen atom could not be refined without problems. Using anisotropic treatment of the non-hydrogen atoms and unrestrained isotropic treatment of the hydrogen atoms, the refinements converged at *R* values between 0.026 and 0.029.

For the refinement of the crystal structure of the caesium compound, the parameters from RbH_3Mal_2 were taken as initial values which proved to fit very well. Similarly, the crystal structure of KHMal was refined using initially the parameters of RbHMal. In the latter case, however, another refinement attempt was then made in the centrosymmetric space group *Pbcm*, which proved to be less successful.

In addition to the single crystal analyses, powder diffraction data were collected for the title compounds (Fig. 6). Although single-crystal data are superior as far as determination and refinement of the structural parameters (atomic positions and displacement parameters) are concerned, more accurate lattice parameters were obtained from the powder data by means of the Rietveld method [47]. Powder data were collected at r. t. on a Philips PW3020 X-ray powder diffractometer with Bragg-Brentano geometry. The powder patterns were submitted to the Powder Diffraction File [6].

CCDC 661288 (CsH_3Mal_2), 661289 (KHMal), 661291 (RbH_3Mal_2), 661292 (RbHMal) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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