

The Solid State Structures of Potassium and Rubidium Salicylate by High Resolution X-Ray Powder Diffraction

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Abstract. We report the *ab initio* structure solution of rubidium-salicylate $C_7H_5O_3Rb$ and the crystal packing of potassium-salicylate $C_7H_5O_3K$ by high resolution X-ray powder diffraction. The compounds are of interest for the understanding of the mechanism of Kolbe-Schmitt type reactions. $C_7H_5O_3Rb$ (**I**) crystallizes in space group $P2_1/n$, $Z = 4$, with unit cell parameters $a = 7.2110(1) \text{ \AA}$, $b = 26.5258(3) \text{ \AA}$, $c = 4.23110(6) \text{ \AA}$, $\beta = 106.843(1)^\circ$, and $V = 774.60(2) \text{ \AA}^3$. $C_7H_5O_3K$ (**II**) crystallizes in space group $P\bar{1}$, $Z = 2$, with unit cell parameters $a = 7.3575(2)$, $b = 13.6399(3)$, $c = 3.8622(1) \text{ \AA}$, $\alpha = 95.955(4)^\circ$, $\beta = 103.326(2)^\circ$, $\gamma = 92.994(4)^\circ$, and $V = 373.95(2) \text{ \AA}^3$. Both compounds exhibit similar crystal packing

schemes and consist of layers of distorted RbO_8 resp. KO_7 polyhedra perpendicular to the b -axis and phenol rings almost perpendicular to the layers pointing up and down. The molecular structure is held together by van der Waals forces between the phenyl groups of different layers. The sample of $C_7H_5O_3K$ shows extremely anisotropic peak broadening and stacking faults which could not be satisfactorily modeled by the available models.

Keywords: Rubidium-salicylate; Potassium-salicylate; Crystal structure; Kolbe-Schmitt-Synthesis

Die Kristallstruktur von Kaliumsalicylat und Rubidiumsalicylat mittels hochauflösender Pulverdiffraktometrie

Inhaltsübersicht. Wir berichten über die *ab initio* Strukturklärung von Rubidiumsalicylat $C_7H_5O_3Rb$ und die Kristallpackung von Kaliumsalicylat $C_7H_5O_3K$ mittels hochauflösender Röntgenpulverdiffraktometrie. Die Strukturen der Verbindungen sind von Interesse für die Interpretation der Kolbe-Schmitt-Synthese. $C_7H_5O_3Rb$ (**I**) kristallisiert in der Raumgruppe $P2_1/n$, $Z = 4$, mit den Gitterparametern $a = 7,2110(1) \text{ \AA}$, $b = 26,5258(3) \text{ \AA}$, $c = 4,23110(6) \text{ \AA}$, $\beta = 106,843(1)^\circ$ und $V = 774,60(2) \text{ \AA}^3$. $C_7H_5O_3K$ (**II**) kristallisiert in der Raumgruppe $P\bar{1}$, $Z = 2$, mit den Gitterparametern $a = 7,3575(2) \text{ \AA}$, $b = 13,6399(3) \text{ \AA}$, $c = 3,8622(1) \text{ \AA}$, $\alpha = 95,955(4)^\circ$,

$\beta = 103.326(2)^\circ$, $\gamma = 92.994(4)^\circ$, und $V = 373.95(2) \text{ \AA}^3$. Beide Verbindungen zeigen ähnliche Packungsmuster, die aus Schichten von verzerrten RbO_8 - bzw. KO_7 -Polyedern senkrecht zur b -Achse bestehen. Die Phenylringe sind senkrecht zu diesen Schichten angeordnet und liegen alternierend oberhalb bzw. unterhalb dieser Polyeder. Die van der Waals-Wechselwirkungen zwischen den Phenylringen stabilisieren die Kristallpackung wesentlich. Die Probe von $C_7H_5O_3K$ zeigt eine extrem anisotrope Peakverbreiterung sowie Stapelfehlernungen, die mit den vorhandenen Modellen nicht befriedigend erklärt werden konnten.

Introduction

The carboxylation of alkali phenolates, known as Kolbe-Schmitt synthesis [1] leads to two main reaction products: alkali-ortho-hydroxybenzoate, also known as alkali-salicylate and alkali-para-hydroxybenzoate. The reaction is an important industrial solid state reaction with many applications in the synthesis of pigments, fertilizers and pharmaceuticals such as aspirin [2, 3]. More recent applications of alkaline-salicylates include e.g. their use as additives to improve the oxidation resistance of silicone oil lubricants [4] or as catalysts on chemiluminescence reactions [5]. Despite

its importance, and although the reaction is known since the middle of the last century [6], its mechanism and the crystal structures of its products are still unknown. Many models for the reaction mechanism have been published so far [7]. The type and the amount of the reaction products are strongly influenced by the reaction conditions like temperature, pressure, time, type of the alkaline cation and solvent [8]. Under typical reaction conditions (120°C , 5 atm), the carboxylation of dry sodium-phenolate leads to an almost quantitative yield of sodium-salicylate, whereas carboxylation of higher homologues leads to a strong increase of the para product with increasing size of the alkali metal [9].

We have started a program to solve the crystal structures of the substances related to Kolbe-Schmitt type reactions in order to get more insight into its mechanism. Whereas the crystal structure of salicylic acid is known for a long time [10 - 12], until recently, none of the crystal structures of any

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solvent free unsubstituted alkali- or earthalkali-salicylate or *para*-hydroxy-benzoate has been published. This can be understood by the fact that all attempts to grow single crystals failed so far. Nevertheless, it was possible to solve the crystal structure of sodium-*para*-hydroxy-benzoate [13] from high resolution X-ray powder diffraction. The sample suffered from severe strain broadening with the full width of half maximum of reflections having similar directions in reciprocal space differing by a factor of up to four. The successful structure determination and refinement was made possible by the application of a phenomenological microstrain model[14]. Furthermore, the structures of most of the reactants (solvent free alkali-phenolates) have recently been solved using single crystal and high resolution powder diffraction [15, 16]. Here we report the refined crystal structure of rubidium-salicylate (**I**) and the crystal packing of potassium-salicylate (**II**) by high resolution X-ray powder diffraction. Since the compounds are the end products of the Kolbe-Schmitt synthesis, their structures are of particular interest for *in situ* investigations with temperature and time resolved powder diffraction.

Experimental Section

Materials

All manipulations of solvents and substances were carried out in dry argon using standard Schlenk and vacuum techniques. Tetrahydrofuran (thf) was purified and dried according to the standard procedures. 9.7g of potassium or 21.4g rubidium (0.25 mol) was covered with thf and heated until melting under rapid stirring. A solution of 34.5g of *o*-hydroxybenzoic acid (0.25 mol) in 100ml of thf was added dropwise over 1h to the stirring finely dispersed alkali. After completion of the reaction, half of the solvent was evaporated. A white powder precipitated which was filtered off and dried at 353K in a Schlenk vessel, from which it was transferred to glass capillaries in a glove box under argon atmosphere.

Powder X-Ray Diffraction Experiments

For the X-ray powder diffraction experiments, the samples were sealed in glass capillaries of 0.7 mm diameter. High resolution powder diffraction data were collected at the SUNY X3B1 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. X-rays of wavelength 1.14937(2) Å for **I** and 1.15013(2) Å for **II** were selected by a double Si(111) monochromator. Wavelengths and the zero point have been determined from 7 well defined reflections of the NBS1976 flat plate alumina standard. The diffracted beam was analyzed with a Ge(111) crystal and detected with a Na(Tl)I scintillation counter with a pulse height discriminator in the counting chain. The incoming beam was monitored by an ion-chamber for normalization for the decay of the primary beam. In this parallel beam configuration, the resolution is determined by the analyzer

Tabelle 1 Lattice parameters and selected details of refinements of C₇H₅O₃Rb and C₇H₅O₃K. R-p, R-wp, and R-F refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, respectively, defined in [45].

	C ₇ H ₅ O ₃ Rb	C ₇ H ₅ O ₃ K
<i>a</i> /Å	7.2110(1)	7.3576(2)
<i>b</i> /Å	26.5258(3)	13.6399(3)
<i>c</i> /Å	4.2311(1)	3.8622(1)
<i>a</i> /°	90	95.955(4)
<i>β</i> /°	196.843(1)	103.326(2)
<i>γ</i> /°	90	92.994(4)
<i>V</i> /Å ³	774.60(2)	373.95(2)
<i>V</i> / <i>Z</i> /Å ³	193.65	186.98
<i>Z</i>	4	2
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
ρ -calc/(g/cm ³)	1.908	1.564
Formula weight	221.58	175.21
μ /cm ⁻¹	34.8	24.6
Temperature/K	295	295
R-p/%	3.8	9.2
R-wp/%	5.2	15.1
R-F/%	7.2	15.9
No. of reflections	285	325
No. of variables	24	14
No. of refined atoms (including H)	15	15
Wavelength/Å	1.14937(2)	1.15013(2)
2 Θ range/°	2.00–26.99, 6.2 sec/step	2.00–34.99, 6.2 sec/step
counting time	27.00–48.45, 12.2 sec/step	35.00–51.01, 18.2 sec/step
Step size 2 Θ /°	0.01	0.01

crystal instead of by slits [17]. Data of **I** were taken at room temperature in steps of 0.01° 2 Θ for 6.2 seconds at each step from 2° to 26.99° and for 12.2 seconds at each step from 27° to 48.45°. Data of **II** were taken at room temperature in steps of 0.01° 2 Θ for 6.2 seconds at each step from 2° to 34.99° and for 18.3 seconds at each step from 35° to 51.01°.

Although Θ -scans did not show serious crystallite size effects, the samples were spun around Θ during measurement for better statistics. Low angle diffraction peaks showed a strong asymmetry due to axial divergence and had an intrinsic full width at half maximum of 0.021°2 Θ for (**I**) and 0.022 °2 Θ for (**II**).

Data reduction was performed using the GUF1 program [18]. The diffraction patterns could be indexed on basis of a monoclinic lattice for **I** and a triclinic lattice for **II** with lattice parameters given in Tab. 1 [19]. The space group of **I** could be unambiguously determined as *P*2₁/*n*, whereas for **II** either *P*1 or *P* $\bar{1}$ remained. The number of formula units per unit cell (*Z*) directly followed from geometrical considerations. A Le-Bail fit [20] using the program FULLP-ROF [21] worked well to extract 195 integrated intensities up to 41.6° 2 Θ for **I** and 310 integrated intensities up to 50.0° 2 Θ for **II**. The obtained integrated intensities were used as input for the direct methods program SIRPOW92 [22]. Despite the relatively low quality of the powder diffraction data of **II**, it was possible in both cases to detect the alkali cation and part of the salicylate molecule without hydrogen atoms.

Tabelle 2 Positional parameters and $U_i/\text{\AA}^2 \times 10^2$ of rubidium- and potassium-salicylate at $T = 295$ K; the Rietveld statistical estimates are given in parenthesis. The values of the temperature factors are constrained to be equal within the rigid bodies.

	x/a	y/b	z/c	U_i
Rb(1)	.2231(4)	.5456(1)	.9891(8)	5.3(2)
C(1)	.7110(12)	.7146(2)	.7102(15)	1.2(3)
C(2)	.8716(11)	.7029(2)	.5983(17)	1.2(3)
C(3)	.5780(11)	.6767(2)	.7277(16)	1.2(3)
C(4)	.8991(10)	.6533(2)	.5038(18)	1.2(3)
C(5)	.6056(8)	.6270(2)	.6332(12)	1.2(3)
C(6)	.7661(7)	.6154(2)	.5213(13)	1.2(3)
H(1)	.6904(15)	.7517(3)	.7808(21)	1.2(3)
H(2)	.9708(13)	.7312(3)	.5853(24)	1.2(3)
H(3)	.4582(13)	.6854(3)	.8113(24)	1.2(3)
H(4)	.0190(11)	.6446(3)	.4203(27)	1.2(3)
O(1)	.4761(12)	.5901(3)	.6502(20)	1.2(3)
C(7)	.7911(9)	.5662(2)	.4201(12)	.7(3)
O(2)	.6685(11)	.5303(3)	.4435(23)	.7(3)
O(3)	.9322(13)	.5560(3)	.3108(27)	.7(3)
K(1)	.7990(11)	.4185(5)	.4889(22)	7.47(30)
C(1)	.6692(17)	.9142(4)	.2202(28)	2.79(34)
C(2)	.8457(15)	.8946(4)	.1533(26)	2.79(34)
C(3)	.5367(13)	.8351(6)	.2185(26)	2.79(34)
C(4)	.8896(11)	.7958(5)	.0846(27)	2.79(34)
C(5)	.5807(9)	.7363(5)	.1498(16)	2.79(34)
C(6)	.7571(10)	.7167(4)	.0829(21)	2.79(34)
H(1)	.6366(23)	.9875(5)	.2712(40)	2.79(34)
H(2)	.9440(19)	.9533(6)	.1546(34)	2.79(34)
H(3)	.4058(15)	.8497(9)	.2682(39)	2.79(34)
H(4)	1.0206(12)	.7812(8)	.0349(41)	2.79(34)
O(1)	.4541(11)	.6607(7)	.1481(24)	2.79(34)
C(7)	.7834(13)	.6211(4)	-.0496(19)	2.79(34)
O(2)	.6687(16)	.5460(4)	-.0091(27)	2.79(55)
O(3)	.9267(18)	.6038(7)	-.1694(37)	2.79(34)

Rietveld Refinements

The Rietveld refinements were performed using the program package GSAS [23, 24] (Fig. 1). In case of **I**, the background was highly structured which indicates short order and deviations from the average structure due to correlated displacement of atoms. This was not investigated further and the background for **I** and **II** was modeled manually using GUF1 [18]. A very small amount of an unidentified additional phase, presumably a solvate, with broader peak shapes was observed in the powder pattern of **I**. The peak-profile was described by a pseudo-Voigt function, in combination with a special function that accounts for the asymmetry due to axial divergence [25, 26]. The powder pattern of **II** shows severe anisotropic peak broadening and ill shaped peak shapes which can be attributed to stacking faults. The microstrain model used for sodium-*para*-hydroxy-benzoate [14] was not able to fit the peak shape satisfactory. From the distortions of peak shapes and centroids, we suspect that the broadening is due to stacking faults; at present we are not aware of a satisfactory method to deal with such disorder in a Rietveld refinement.

In order to stabilize the refinements, two rigid bodies, one for the phenyl ring and one for the carboxyl group were used. It is unnecessary to determine either of these molecular moieties, which have well established structure. A comparison of similar *para*- or *ortho*-substituted benzene ring compounds in the literature shows that the deviations from planarity as well as the deviations from hexagonal sym-

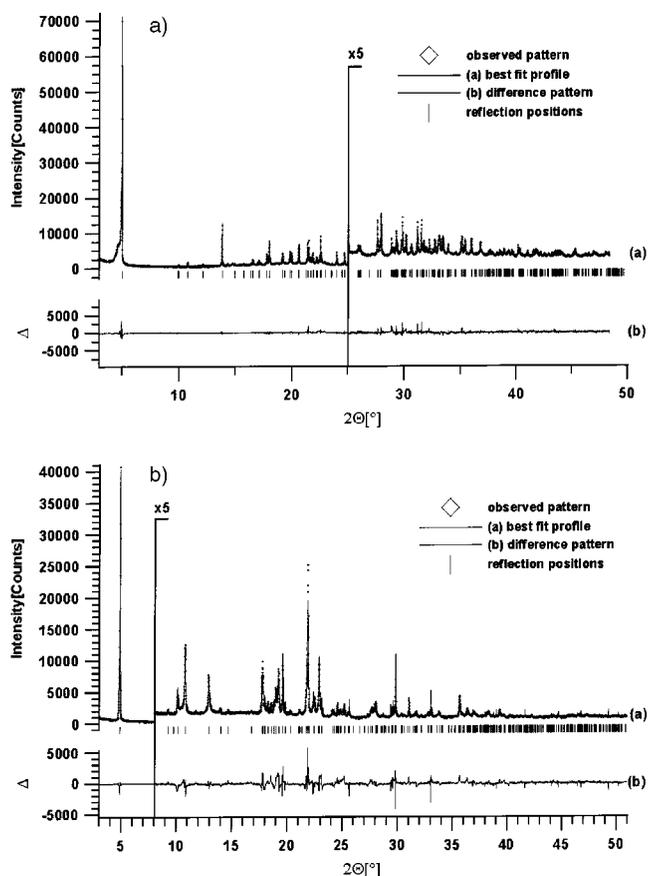


Fig. 1a, b Scattered X-ray intensity for rubidium-salicylate (a, above) and potassium-salicylate (b, below) at $T = 295$ K as a function of diffraction angle 2θ . Shown are the observed pattern (diamonds), the best Rietveld-fit profile in $P2_1/n$ (a) resp. $P\bar{1}$ (b) (line a), the difference curve between observed and calculated profile (line b), and the reflection markers (vertical bars). The wavelengths were $\lambda = 1.14937(2)$ Å (a) and $\lambda = 1.15013(2)$ Å (b). The higher angle part starting at $25^\circ 2\theta$ (a) resp. $8^\circ 2\theta$ (b) is enlarged by a factor of 5.

metry for both molecules are negligably small compared to the accuracy of the present results. (see, e.g., single crystal structures of *p*-hydroxybenzoic acid monohydrate [27], *p*-nitrobenzoic-acid [28], *p*-methoxybenzoic-acid [29], *p*-fluorobenzoic-acid [30], *p*-hydroxybenzoic-acid and *p*-hydroxybenzoic-acid-acetone complex [31], potassium hydrogen di-*p*-hydroxybenzoate-hydrate [32], monorubidium-orthosulfobenzoate [33], alkali-metal-biphtalates and orthosulfobenzoates [34], salicylic-acid [12], calcium- and strontium-salicylate-dihydrate [35], zink-salicylate-dihydrate [36], diaquobis(salicylato)copper(II) [37], copper salicylate tetrahydrate [38], rubidium hydrogen bisacetylsalicylate [39], potassium hydrogen bisacetylsalicylate [40], rubidium acid phthalate [41]).

The rigid bodies were set up in a way that several intramolecular bond distances remained as refinable parameters and only the 6-fold symmetry of the C6-ring and the 120° angles of the CO_2 group were held fixed. In addition, the

two rigid bodies were constrained in a way that only the dihedral angle between the phenyl and the carboxyl group remained as a free parameter. This important step reduced the number of independent positional parameters from 42 down to 13 (3 rotational, 3 translational, 6 bond lengths, 1 dihedral angle).

In a final cycle of refinement of **I**, all non-hydrogen atoms were turned loose. They remained close to their original positions, but the weighted profile R-factor increased by several percent, indicating that the refinement is not entirely stable. A Rietveld refinement with a salicylate molecule turned by 180° around its molecular axis led to a similar crystal packing, with slightly worse profile R-factors and small but distinct differences between observed and calculated powder pattern showing up in the high angle region, ruling out this possible solution.

The agreement factors of the Rietveld refinement (R-values) are listed in Table 1. The coordinates of **I** using rigid bodies are given in Tab.2. A selection of intra- and intermolecular distances is given in Table 3.

Due to the relatively low quality of the powder data of **II**, no intramolecular bond lengths could be refined. Therefore, the same flexible body as obtained from the refinement of **I** was used (identical bond lengths, refined three translations, three rotations, and one torsion). The final positional coordinates of **II** are listed in Table 2, (lower part).

Description of the Structure

Despite their different crystal system and space groups, the crystal structures of **I** and **II** show the same type of packing. The crystal structures are based on layers of RbO_8 (respectively KO_7) polyhedra, perpendicular to the *b*-axis and phenyl rings perpendicular to those layers pointing along the *b*-axis alternately in both directions (Fig. 2). Every alkali cation is coordinated to oxygen atoms from 6 different salicylate molecules in form of an irregular polyhedron (Fig. 3). The polyhedra can be described as trigonal prisms with additional oxygen atoms above two **II** respectively one **I** of the rectangular faces, therefore forming distorted pyramids with long bonds between the peaks of the pyramid and the central cations. The alkali cations are shifted towards the rectangular faces of the trigonal prisms which are not covered by pyramids. Pairs of these polyhedra are linked into Rb_2O_{14} , respectively K_2O_{12} dimers via a common pyramidal edge leading to a short cation-cation distance. These binuclear groups are quite unfavorably connected via their triangular faces of the prisms thus forming infinite stacks along *c*-axis. In the case of **I**, these stacks are further connected via 4 edges (2 on each side) to form 2-dimensional infinite sheets (Fig. 4). The bond distances between the rubidium atom and the oxygen atoms are in the range 3.821 Å to 3.258 Å, comparable to that of other compounds containing rubidium atoms coordinated by oxygen atoms [33,

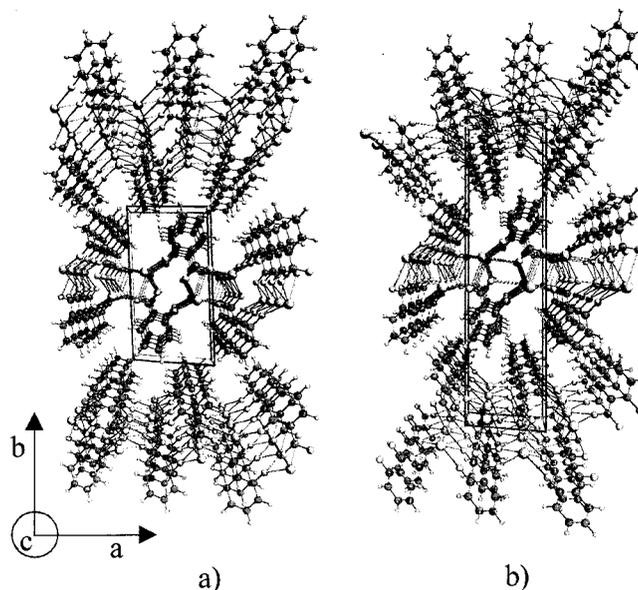


Fig. 2a, b Packing diagram of the layered structures of rubidium-salicylate in $P2_1/n$ (a) and potassium-salicylate in $P\bar{1}$ (b) at $T = 295$ K using the program SCHAKAL [43]. The RbO_8 resp. KO_7 layers are perpendicular to the *c*-axes.

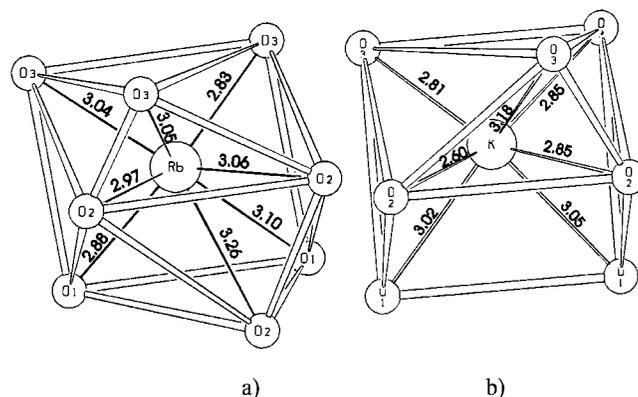


Fig. 3a, b Coordination polyhedra of rubidium-salicylate (a) and potassium-salicylate (b) at $T = 295$ K using the program SCHAKAL [43]. Bond lengths between the cation and the oxygen atoms in Å.

41]. There is no interchange between the rubidium atom and the π -system of the phenyl ring.

The phenol rings point out almost perpendicular on both sides from of the layer formed by the RbO_8 polyhedra in an alternating way (Fig. 2). There they are rotated in different directions by $18.2(4)^\circ$ relative to the *ab*-plane and $\pm 13.6(2)^\circ$ relative to the *bc*-plane, allowing the phenol- and carboxyl oxygen atoms to be coordinated to the rubidium atom at the same time. Although severe twisting of the carboxyl group relative to the phenol ring is common for alkali-*para*-hydroxybenzoates and -salicylates [13, 40], refinement of this parameter resulted in a small value of $1.7(4)^\circ$ for **I**

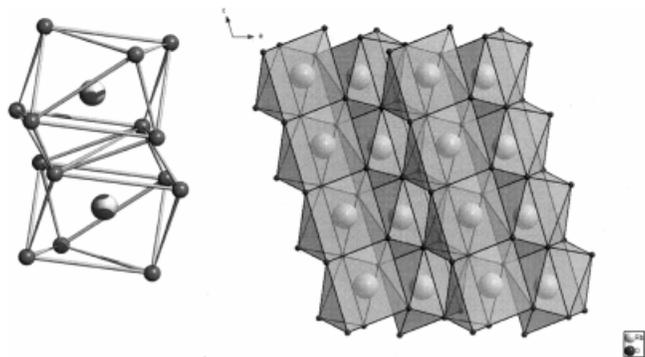


Fig. 4 Stacking of coordination polyhedra of rubidium-salicylate at $T = 295$ K draw by the program SCHAKAL [43]; Right: sheets of semitransparent coordination polyhedra of rubidium-salicylate at 295 K draw by the program DIAMOND [44].

Tabelle 3 Selected bond-distance ranges and intramolecular distances of rubidium-salicylate in Å. The given esd's are Rietveld statistical estimates and should be multiplied by a factor of six as discussed in [42].

	Rubidium-salicylate	Literature values of related compounds
Rb-Rb (within ladder)	4.048(6), 4.231(6)	3.97
Rb-Rb (between ladders)	4.647(6)	–
Rb-O	2.83(1)..3.10(1), 3.26(1)	2.80..3.14, (3.28)
Rb-C (carboxylic) (shortest)	3.384(6)	–
C-O (phenolic)	1.37(1)	1.36..1.39
C-O (carboxyl)	1.26(1), 1.32(1)	1.19..1.25; 1.26..1.32
C-C (phenyl)	1.407(3)	1.33..1.42
C(phenyl)-C(carboxyl)	1.40(1)	1.47..1.52
C-H (phenyl)	1.05	1.04..1.08
H-H (shortest interchain)	2.36(1)	–
O-O (carboxyl)	2.24(1)	2.14
O-O (carboxylic-phenolate)	2.431(6)	2.51..2.61

which was considered as non-significant and therefore fixed to 0° .

The molecular structure is held together by van der Waals forces between the phenyl groups of different layers. The intramolecular bond lengths of the salicylate molecule in **I** are within the typical range found for that class of molecules, except for the bond lengths between the phenyl and the carboxyl group, which turned out to be too short (Tab. 3). This may be attributed to a correlation to the size of the phenyl ring or the limited accuracy of powder diffraction data, suggesting that the given esd's of the Rietveld refinement should be multiplied by a factor of 6 as discussed in [42].

Results and Discussion

The first crystal structures of base free alkaline-salicylates could be determined from high resolution X-ray powder diffraction data. More generally speaking, it is now possible on a fairly routine basis to solve small molecule structures

by high resolution powder diffraction, within the accuracy of single crystal diffraction in the early sixties. Even with low quality powder data exhibiting severe disorder due to stacking faults and lattice strain, as in case of potassium-salicylate, packing schemes can be derived, although a discussion of individual bond lengths is not possible.

Due to the fact that different orientations of the salicylate molecule lead to similar packing schemes with little differences in the powder patterns, it is quite likely that the occurrence of both orientations in the crystal structure would lead to stacking faults and internal strain which are observed in particular in the powder pattern of **II**.

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