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Mechanochemical Synthesis of Alkaline Earth Mg – Ba Saccharinates. Connectivity in the Crystal Structures of $Mg(sac)_2 \cdot 7H_2O$, $Ca(sac)_2 \cdot 7H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$ (sac = saccharinate)

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THIS PAPER IS DEDICATED TO PROF. BRANKO KAITNER ON THE OCCASION OF HIS 80TH BIRTHDAY

Abstract: Alkaline earth saccharinates Mg – Ba were synthesized by the known solution-based methods and also by mechanochemical synthesis. The compounds were characterized by TG/DSC, X-ray powder diffraction, and Mg, Ca and Ba saccharinates by single-crystal X-ray analysis. The structure of $Mg(sac)_2 \cdot 7H_2O$ (sac = saccharinate), is known but the diffraction data were collected at 170 K in this study for comparison with other structures. Crystals of hydrates of Ca – Ba saccharinates are very thin needle-like. A 4 μm crystal of $Ca(sac)_2 \cdot 7H_2O$ gave a low intensity diffraction pattern of sufficient quality to locate non-hydrogen atoms (triclinic crystal system, space group P-1, Z = 4). Crystals of strontium saccharinate were too thin for data collection, however the formula $Sr(sac)_2 \cdot 4H_2O$, proposed in a previous publication was confirmed by thermogravimetric analysis. Diffraction from a 12 μm thick crystal of $Ba(sac)_2 \cdot 4.5H_2O$ resulted in a complete data set (monoclinic crystal system, space group $P2/c$, Z = 8). In the corresponding structures, the Mg ion is six-coordinated forming an octahedron, both Ca ions are irregularly eight-coordinated with the polyhedra bridged by saccharinate ions into chains, whereas both Ba ions are irregularly nine-coordinated with the polyhedra sharing edges and corners through bridging water molecules and bridging saccharinate ions into double chains. All water molecules are included into hydrogen bonding into layers with only van der Waals and weak C–H···O bonds between the chains.

Keywords: mechanochemical synthesis, alkaline earth metals, saccharinate, crystal structure.

INTRODUCTION

THE structural properties of saccharin (systematic name: 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide)[1,2] and especially of its compounds with various metals have been rather intensively studied during the last five decades.[3–14] Various ligation properties of saccharin in compounds with different metals were studied, such as influence of the nature of the metal ion on the type of the metal-to-ligand bonding,[15] the bond valence model,[16] NMR studies,[17] influence of metal bonding on the saccharinate geometry.[13] Suspected carcinogenic nature of its sodium salt (known as Natreen) commonly used as an artificial sweetener in the formulation of foods and beverages was also investigated in terms of saccharin-induced mutagenicity in human clonal RSa cells.[18] It has been shown that saccharin can serve as a versatile polyfunctional ligand being included in the metal saccharinates as *i*) an ion; *ii*) a ligand coordinated through the nitrogen atom, the carbonyl oxygen atom, the sulfonyl oxygen atom/s or the nitrogen atom; *iii*) several of the above modes in the same compound; *iv*) a neutral molecule.[15]

Different types of bonding depend on the nature of the metal in the saccharinate compound. Many of these compounds were characterized by the Jovanovski group. Mostly ionic character of bonding was found for the alkaline and alkaline earth metals.[19] There are several structures of saccharinates with some alkaline metals, such as lithium, Li(sac)·11/6H_2O,[20] several different hydrates with sodium (Na(sac)·2/3H_2O,[3] Na(sac)·15/8H_2O,[12,21] and with potassium, $K_3(sac)_3$·2H_2O,[22] $K_3(sac)_3$·7/3 H_2O.[21] There are also mixed alkaline metal saccharinates such as $NaK(sac)_2$·H_2O[23] and $NaRb(sac)_2$·4H_2O.[24]

The first row transition metal ions form isomorphous coordination type complexes of the type $[M(sac)_2(H_2O)_4]$·2H_2O, with M = V,[11] Cr,[10] Mn,[4,25] Fe, Co and Ni,[4,8] Cu[6,25] and Zn.[4,9] There are also structures with bonding of more covalent character as in Cd,[4,9] Hg,[7] and Pb.[12] Structures of saccharin with all lanthanides have also been published.[26]

Of the alkaline earth metals only the structure of $Mg(sac)_2$·7H_2O[3] has been determined. Due to the lack of the suitable single crystals to solve the crystal structures of the saccharinates of alkaline earth metals, calcium, strontium and barium, and in order to get preliminary information on some of their structural characteristics, we have previously studied their X-ray powder diffractograms as well as their infrared spectra in the region of the OH, OD, CO and SO_2 stretching modes. The study of their infrared spectra in the region of the CO stretching vibrations indicated that the metal-to-saccharin bonds have mainly ionic character.[19]

Previously, the saccharinates of the mentioned alkaline earth metals were prepared by solution-based methods. Now we were interested to prepare them by mechanochemical synthesis. Mechanochemical synthesis is an efficient technique for synthesis or transformation in the solid state.[27–29] The reactants have to be chosen carefully not to get mixtures of products. We have published mechanochemical synthesis of several compounds.[30–33] Some reactions were very fast even by mixing with only a mortar and pestle.[33] We have also characterized a solid-state-to-solid-state transformation of five different compounds into one stable solvate only by neat grinding.[30]

Here we report both mechanochemical and solution-based synthesis[3,19] of the hydrates of magnesium, calcium, strontium and barium saccharinates, $Mg(sac)_2$·7H_2O, $Ca(sac)_2$·7H_2O, $Sr(sac)_2$·4H_2O and $Ba(sac)_2$·4.5H_2O. The compounds were characterized by X-ray powder diffraction (XRPD), and thermogravimetric/differential scanning calorimetry analysis (TG/DSC). The crystals of the hydrates of calcium, strontium and barium saccharinates are needle-like and very thin. After our continuous attempts in years, we have now managed to collect single-crystal X-ray diffraction data sets of calcium and barium saccharinates which were good enough to finally determine their crystal structures. Unfortunately, this was not the case with the Sr compound. The structure of $Ba(sac)_2$·4.5H_2O was of much better quality than that of $Ca(sac)_2$·7H_2O and is discussed in detail. The coordination polyhedra of the metal ions, the coordination mode of the saccharinate ligand, and the connectivity achieved through the saccharinates and hydrogen bonding in the hydrates of alkaline earth metals Mg, Ca and Ba is presented.

EXPERIMENTAL

Materials and Methods

All chemicals were purchased from commercial sources (Kemika, Alkaloid) and were used without purification. Infrared spectra were measured on a Thermo Scientific Nicolet iS50 FTIR Spectrometer equipped with an ATR module. A Retsch MM200 mill operating at 25 Hz, a 14 mL Teflon milling jar and one 8 mm steel ball were used for all mechanochemical syntheses.

Powder X-ray diffraction (PXRD) was performed on a Malvern Panalytical Aeris diffractometer in the Bragg-Brentano geometry with CuK_α radiation (λ = 1.54184 Å) at room temperature. The samples were placed on a silicon holder and the diffraction patterns were measured in the 2θ range 5 – 40° with a step size of 0.022° and 15.0 s per step. X-ray powder diffraction data were collected and visualized using the HighScore Plus program.[34]

Thermogravimetric analysis was performed on Mettler-Toledo TGA/DSC3+. 2 – 8 mg of samples were placed into alumina crucibles (70 µL) and heated in a temperature range 25 – 800 °C (Ca – Sr saccharinates) and 25 – 1200 °C (Mg saccharinate) and a constant heat rate of 10 K min^{-1} and under an oxygen flow of 50 mL min^{-1}.

Solution-based Synthesis

Hydrates of Mg, Ca, Sr and Ba saccharinates were prepared by gradually mixing of the corresponding carbonates and a warm aqueous solution of saccharin in a molar ratio 1:2 as previously published.[19] Colorless, very thin needle-shaped crystals were obtained after cooling of reaction mixture to the room temperature. Several attempts to get better quality crystals of Ca – Ba saccharinates by recrystallization failed (Figure 1).

Mechanochemical Synthesis

Synthesis of $Mg(sac)_2$·7H_2O

Magnesium carbonate (42.2 mg, 0.5 mmol) and saccharin (183.2 mg, 1.0 mmol) were placed into a Teflon milling jar and 45 µL of water was added (η = 0.2 mg µL^{-1}). Experiment was performed for 30 minutes and the resulting powder diffraction pattern was consistent with the crystal structure of $Mg(sac)_2$·7H_2O (Figure 2; CSD refcode: MGSACA10).[3]

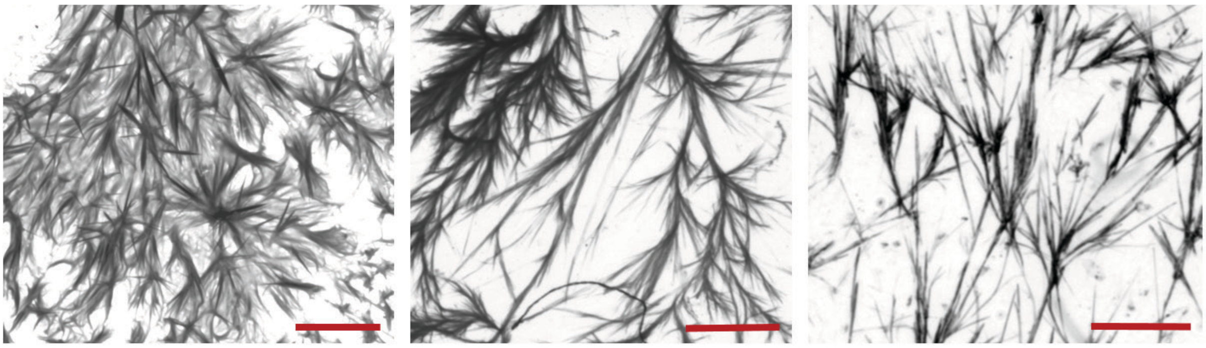

Figure 1. Crystals of $Ca(sac)_2 \cdot 7H_2O$ (left), $Sr(sac)_2 \cdot 4H_2O$ (middle) and $Ba(sac)_2 \cdot 4.5H_2O$ (right). The red line shows the scale of 1 mm.

Synthesis of $Ca(sac)_2 \cdot 7H_2O$

Calcium hydroxide (37.0 mg, 0.5 mmol) and saccharin (183.2 mg, 1.0 mmol) were placed into a Teflon milling jar and 44 µL of water was added (η = 0.2 mg µL^{-1}). Experiment was performed for 30 minutes and the resulting powder diffraction pattern was consistent with the crystal structure of $Ca(sac)_2 \cdot 7H_2O$ (Figure 2).

Synthesis of $Sr(sac)_2 \cdot 4H_2O$

Strontium carbonate (73.8 mg, 0.5 mmol) and saccharin (183.2 mg, 1.0 mmol) were placed into a Teflon milling jar and 51 µL of water was added (η = 0.2 mg µL^{-1}). Experiment was performed for 30 minutes and the resulting powder diffraction pattern was consistent with the one previously published for this compound obtained by the solution-based method[19] (Figure 2).

Synthesis of $Ba(sac)_2 \cdot 4.5H_2O$

Barium hydroxide octahydrate (157.7 mg, 0.5 mmol) and saccharin (183.2 mg, 1.0 mmol) were placed into a Teflon milling jar and 34 µL of water was added (η = 0.1 mg µL^{-1}). Experiment was performed for 30 minutes and the resulting powder was consistent with the crystal structure of $Ba(sac)_2 \cdot 4.5H_2O$ (Figure 2).

Single Crystal X-ray Diffraction

A prismatic crystal of $Mg(sac)_2 \cdot 7H_2O$ suitable for obtaining good single-crystal X-ray diffraction data was easy to find. However, over 100 thin needle-like crystals of calcium, strontium and barium saccharinates were tested before finding a 12 µm thick crystal that gave a relatively good data set for barium saccharinate, $Ba(sac)_2 \cdot 4.5H_2O$. The best diffraction data for calcium saccharinate, $Ca(sac)_2 \cdot 7H_2O$, was from a very thin crystal of only 4 µm giving very weak diffraction. Crystals of strontium saccharinate were very thin so not even the unit cell could be obtained. The best method for searching for a good crystal was under polarized light, since the transparent crystals gave some diffraction pattern whereas those that were opaque did not. The opaque needles were agglomerate of several thinner crystals. Crystals were mounted on cryo-loops with some Paratone N oil and transferred into a cold air stream at 170 K. All data were collected on a XtaLAB Synergy-S Dualflex HyPix diffractometer. All data were measured using CuKα radiation but the data for $Ba(sac)_2 \cdot 4.5H_2O$ were re-measured using MoKα radiation, and were better and will be given here. Data collection and reduction were performed by the CrysAlis software package.[35] The X-ray diffraction data were corrected for the Lorentz-polarization factor, and absorption effects by the multi-scan method empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2,[36] the structures were solved by the ShelXT[37] structure solution program using intrinsic phasing and refined by the full-matrix least-squares method based on F^2 against all reflections with ShelXL.[38] The riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ and with C–H = 0.95 Å was used for aromatic H atoms. All hydrogen atoms for magnesium saccharinate were found in the difference Fourier map and were refined isotropically. The data of calcium saccharinate were sufficient for finding non-hydrogen atoms. Only the Ca, S and O atoms were refined anisotropically. Water hydrogen atoms could not be located and could not be modelled. For barium saccharinate the H-atom parameters on water oxygen atoms were fixed or restrained with $U_{iso}(H) = 1.5U_{eq}(O)$. Water oxygen atoms O2W, O8W, O10W and O11W are located at special positions with an occupancy of 0.5. Geometrical parameters were calculated using Olex2[36] and PLATON.[39] Drawings of the structures were prepared by ORTEP[40] and MERCURY.[41]

The crystallographic data and details of data collection, structure solution and refinement are presented in Table 1.

CCDC 2252049 – 2252051 contain the supplementary crystallographic data for $Mg(sac)_2 \cdot 7H_2O$, $Ca(sac)_2 \cdot 7H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

Table 1. Crystal data and details of the structure determination

	$Mg(sac)_2 \cdot 7H_2O$	$Ca(sac)_2 \cdot 7H_2O$	$Ba(sac)_2 \cdot 4.5H_2O$
Empirical formula	$MgC_{14}H_{22}N_2O_{13}S_2$	$CaC_{14}H_{22}N_2O_{13}S_2$	$BaC_{14}H_{17}N_2O_{10.5}S_2$
Formula weight M_r	514.76	530.53	582.76
Chemical formula, moieties	$(Mg(sac)(H_2O)_5)$, (sac), $2(H_2O)$	$(Ca(sac)(H_2O)_6)$, (sac), (H_2O)	$(Ba_2(sac)_3(H_2O)_7)$, (sac), $2(H_2O)$
Crystal data			
Crystal system, space group	Triclinic, $P\,{-1}$	Triclinic, $P\,{-1}$	Monoclinic. $P\,2/c$
Crystal size / mm	$0.058 \times 0.042 \times 0.038$	$0.189 \times 0.004 \times 0.004$	$0.281 \times 0.012 \times 0.011$
Crystal habit, colour	Prism, colorless	Needle-like, colorless	Needle-like, colorless
Temperature / K	170	170	170
a / Å; b / Å; c / Å	6.98190(6); 11.20507(8); 14.31685(9)	6.936(2); 9.644(2); 33.623(4)	18.8637(6); 7.1588(3); 30.2235(11)
α / °; β / °; γ / °	79.9042(6); 78.1318(6); 82.7309(6)	90.910(14); 90.48(2); 107.63(3)	90; 97.626(3); 90
V / Å^3	1074.362(14)	2143.0(9)	4045.3(2)
Z	2	4	8
D_{calc} / mg m^{-3}	1.591	1.644	1.914
μ / mm^{-1}	3.187	5.005	2.228
$F(000)$	536	1104	2296
Data collection			
Radiation type, wavelength / Å	Cu$K\alpha$, λ = 1.5418	Cu$K\alpha$, λ = 1.54184	Mo$K\alpha$, λ = 0.71073
T_{min}; T_{max} for absorption correction	0.798; 1.000	0.457; 1.000	0.754; 1.000
2θ range for data collection / °	8.0 – 156.0	7.9 – 130.0	4.4 – 56.0
hkl range	$-8 \le h \le 8$, $-14 \le k \le 14$, $-17 \le l \le 18$	$-7 \le h \le 8$, $-10 \le k \le 11$, $-30 \le l \le 39$	$-24 \le h \le 24$, $-9 \le k \le 9$, $-39 \le l \le 39$
Scan type	ω	ω	ω
No. measured, independent, and observed reflections $I \ge 2\sigma(I)$	35095, 4429, 4429	12010, 6068, 1608	46602, 9516, 9516
R_{int}	0.032	0.348	0.102
Refinement on F^2			
No. data/restraints/parameters	4429/0/365	6068/0/412	9516/0/539
$R^{(a)}$ [$I \ge 2\sigma(I)$]; R [all data]	0.0226; 0.0238	0.1843; 0.3858	0.0811; 0.1277
$wR^{(b)(c)}$ [$I \ge 2\sigma(I)$]; wR [all data]	0.0614; 0.0606	0.3897; 0.4976	0.1625; 0.1781
Goodness of fit on F^2, $S^{(d)}$	1.053	1.015	1.092
Max. / min. electron density, $\Delta\rho_{max}$; $\Delta\rho_{min}$ / eÅ^{-3}	0.24/–0.33	1.61/–0.94	4.61/–1.99

(a) $R = \Sigma[||F_o|-|F_c||]/\Sigma|F_o|$

(b) $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

(c) $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$

(d) $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$

RESULTS AND DISCCUSION

Synthesis

In the solution-based reaction of carbonates of alkaline earth metals with aqueous solutions of saccharine, in a molar ratio 1 : 2, alkaline earth saccharinate hydrates were obtained as previously published.[3,19] Here, we have shown that these saccharinates can also be obtained by mechanochemical synthesis. The products were analyzed by powder X-ray diffraction (Figure 2).

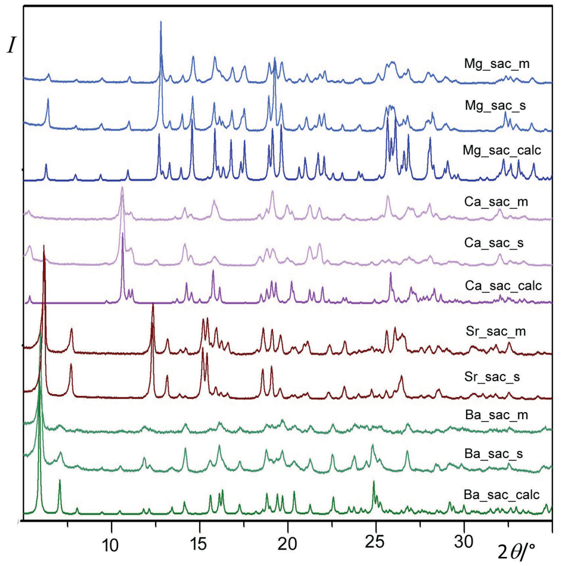

Figure 2. PXRD patterns in the 2θ range 5 – 35°. For each alkaline earth saccharinate, $Mg(sac)_2\cdot7H_2O$ (Mg_sac), $Ca(sac)_2\cdot7H_2O$ (Ca_sac), $Sr(sac)_2\cdot xH_2O$ (Sr_sac), $Ba(sac)_2\cdot4.5H_2O$ (Ba_sac), the corresponding pattern is denoted by _calc (calculated from the crystal structure), _s (crystals obtained by the solution-based method), _m (crystals obtained by mechanochemical synthesis). Since the structure of $Sr(sac)_2\cdot xH_2O$ could not be obtained there is no calculated powder pattern.

Crystal Structure of $Mg(sac)_2\cdot7H_2O$

The crystal structure was reported previously,[3] and will not be discussed in detail here. Drawing of the structure with the coordination polyhedron shown in green color is given in Figure 3. The atom-numbering scheme of cations, anions and water molecules of crystallization in the asymmetric unit, and an overlay of the published room temperature and the present low temperature $[Mg(sac)(H_2O)_5]^+$ cation, is given in the Supplementary Figures S1 and S2, respectively.

Characteristic of this structure is octahedrally coordinated Mg ion by one saccharinate through the carbonyl oxygen and five water molecules. One saccharinate and two water molecules do not coordinate the Mg ion but participate in hydrogen-bonding of the O–H···O and O–H···N type forming layers parallel to (001), with only weak C–H···O and van der Waals interactions between layers, (Figure 3 and Supplementary Figure S3). More details on the bond lengths, angles, hydrogen bonds and analysis of short ring-ring interactions is given in the Supplementary Tables S1, S2, S3 and S4, respectively.

Crystal Structure of $Ca(sac)_2\cdot7H_2O$

The quality of this crystal structure, with data obtained from a very thin crystal (Supplementary Figure 4) does not allow detailed analysis of the bond lengths and angles (bond lengths, angles, short ring-ring interactions, and interatomic distances between possible donors and acceptors of hydrogen bonds are given in the Supplementary Tables S5 – S8, respectively). The asymmetric unit consists of two Ca ions, two saccharinate ligands and twelve water molecules involved in coordination, and two saccharinates and two water molecules that do not coordinate Ca ions, Figure 4. Although it seems that there is a center of symmetry between the two Ca ions the structure could not be solved in half on this unit cell, and analysis in PLATON showed that there is no need to change the space group. The observed and calculated PXRD patterns are also in agreement, Figure 2. Both Ca ions are eight-coordinated with two sulfonyl oxygen bonded saccharinate ligands and six water molecules. The Ca–O bond lengths are in the range 2.35(2) to 2.67(2) Å, Table 2. Both coordinating saccharinates are bridging with the connectivity …Ca1-O11-S1-O12-Ca1… and …Ca2-O22-S2-O21-Ca2… and form infinite chains along the *a*-axis.

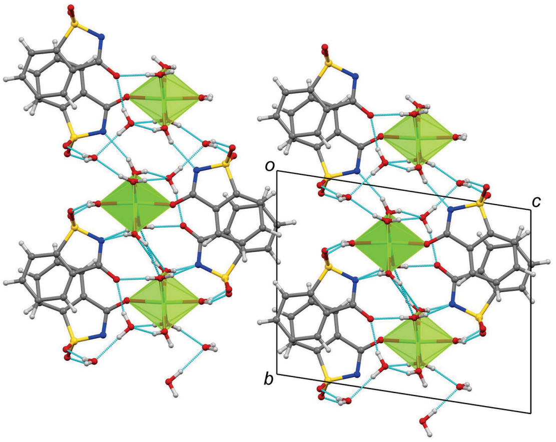

Figure 3. Projection of the crystal structure of $Mg(sac)_2\cdot7H_2O$ down the *a*-axis (in the *b*-*c* plane). The coordination polyhedra around Mg are shown in light green color and the hydrogen bonds in light blue color.

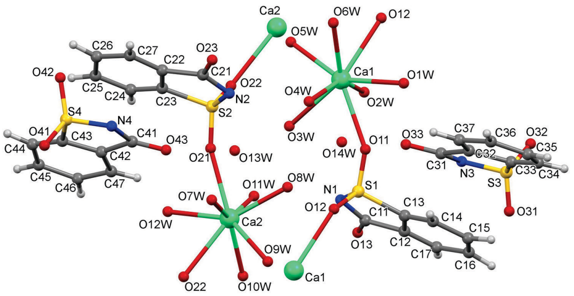

Figure 4. Drawing of the crystal structure of $Ca(sac)_2\cdot7H_2O$ with the atom numbering scheme.

The coordination polyhedra of the Ca ions (Figure 4) and packing in the unit cell is shown in Figures 5 and 6. From the interatomic distances involving the water molecules of the type O···O and O···N, since the hydrogen atoms were not located, it can be supposed that all water molecules are involved in hydrogen bonding. The chains are connected by hydrogen bonds, also involving the two saccharinates and two water molecules that are not involved in coordination of Ca ions, into double-layers parallel to (001), Figure 6. There are only van der Waals contacts between the layers.

Table 2. Bond lengths in the coordination spheres of the Ca cations (*d* / Å)

Ca1	O1W	2.445(15)	Ca2	O7W	2.36(2)
Ca1	O2W	2.390(19)	Ca2	O8W	2.33(3)
Ca1	O3W	2.565(17)	Ca2	O9W	2.507(18)
Ca1	O4W	2.35(2)	Ca2	O10W	2.384(16)
Ca1	O5W	2.424(19)	Ca2	O11W	2.37(2)
Ca1	O6W	2.395(16)	Ca2	O12W	2.481(18)
Ca1	O11	2.586(16)	Ca2	O21	2.460(17)
Ca1	O12[a]	2.567(18)	Ca2	O22[b]	2.67(2)

Transformation of the asymmetric unit: [a] $-1+x,y,z$; [b] $1+x,y,z$

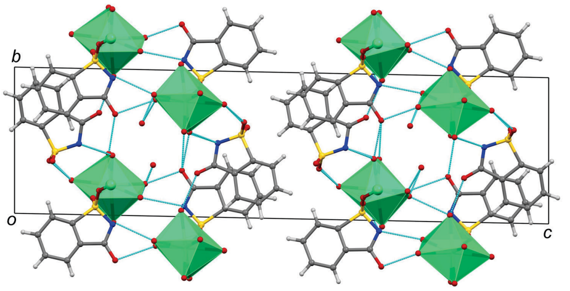

Figure 5. Projection of the structure of $Ca(sac)_2 \cdot 7H_2O$ down the *a*-axis (in the *b*-*c* plane). The polyhedra around the calcium ions are shown in green color and the probable hydrogen bonds between donors and acceptors in light blue color.

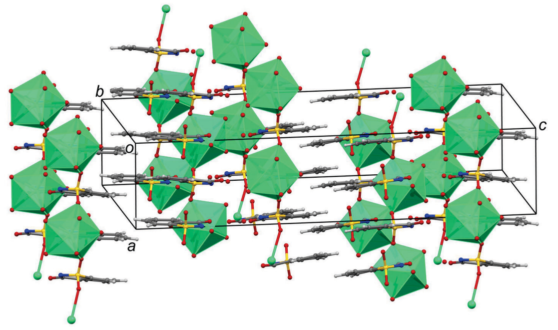

Figure 6. Packing of the structural moieties $(Ca(sac)(H_2O)_6)$, (sac) and (H_2O) in $Ca(sac)_2 \cdot 7H_2O$. The polyhedra around the calcium ions are shown in green color.

Stacking of the saccharinate anions along the *a*-axis can be seen in Figure 6. There are π···π interactions between the six-membered saccharinate rings. The perpendicular distances of the center of gravity of one ring to the adjacent ring are in the range 3.306(9) to 3.568(10) Å (Supplementary Table S7).

Crystal Structure of $Ba(sac)_2 \cdot 4.5H_2O$

The crystal structure consists of two crystallographically different Ba^{2+} cations, four structurally different saccharinate anions and eleven different water molecules (four of them laying at special positions: O2W, O8W, O10W and O11W) (Figures 7 – 10). The moieties present in the asymmetric unit are $(Ba_2(sac)_3(H_2O)_7)$, (sac) and $2(H_2O)$, Figure 9. Both cations Ba1 and Ba2 are irregularly nine-coordinated. Thereby, Ba1 is surrounded by one carbonyl O atom, two sulfonyl O atoms, one N atom and five water O atoms (Figure 7), whereas Ba2 is coordinated by two carbonyl O atoms, two sulfonyl O atoms and five water O atoms (Figure 8). All bond lengths, angles, hydrogen bond parametrers and short ring-ring interactions, are given in the Supplementary Tables S9 – S12, respectively.

Almost perpendicularly to the chains formed by Ba1 and Ba2 coordination polyhedra are the saccharinate anions laying almost parallel to the *a*-*c* unit cell plane (Figures 10 and 11). The saccharinate anions are planar, within experimental errors. The interatomic distances and angles within saccharinate ions are close to the values found in Na and Mg saccharinates[3] in mixed K_2Na saccharinate,[23] in Mn saccharinate[4] and the corresponding isomorphous saccharinates of Mn, Co, Ni, Zn, Cu, Cd and Cr[8–10] as well as in lithium saccharinate.[20]

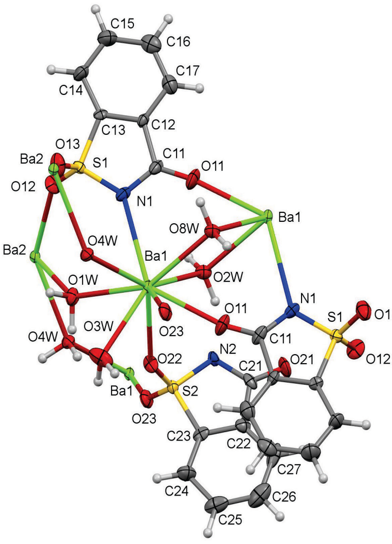

Figure 7. Coordination of the Ba1 ion in $Ba(sac)_2 \cdot 4.5H_2O$ with the atom-numbering scheme.

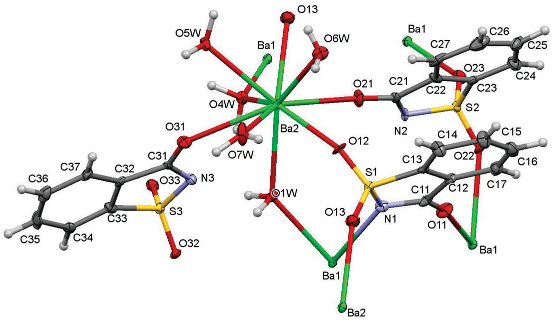

Figure 8. Coordination of the Ba2 ion in $Ba(sac)_2 \cdot 4.5H_2O$ with the atom-numbering scheme.

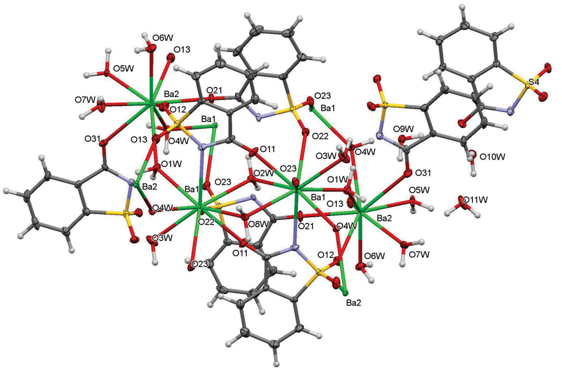

Figure 9. Connectivity of the structural moieties $(Ba_2(sac)_3(H_2O)_7)$, (sac) and $2(H_2O)$ in $Ba(sac)_2 \cdot 4.5H_2O$. The saccharinate anion not included in coordination is shown with the label S4 for the corresponding sulfur atom. Other atoms in this saccharinate have the same labeling scheme as in other saccharinates but starting with 4 (C41, O41...).

Table 3. Bond lengths in the coordination spheres of Ba cations (*d* / Å).

Ba1	O11	2.629(6)	Ba2	O12	2.740(7)
Ba1	O22	2.853(7)	Ba2	O13	2.711(7)
Ba1	O23$^{(b)}$	2.917(7)	Ba2	O21$^{(a)}$	2.705(7)
Ba1	N1	3.048(7)	Ba2	O31	3.015(7)
Ba1	O1W	2.842(6)	Ba2	O1W	2.918(7)
Ba1	O2W	2.807(6)	Ba2	O4W	2.894(6)
Ba1	O3W	2.788(7)	Ba2	O5W	2.859(7)
Ba1	O4W$^{(b)}$	2.843(6)	Ba2	O6W	2.821(7)
Ba1	O8W	2.795(6)	Ba2	O7W	2.692(7)

Transformation of the asymmetric unit: $^{(a)}$ $1-x,y,½-z$; $^{(b)}$ $x,1+y,z$

The role of the water molecules in the structure of Ba saccharinate is diverse. Four of them lie at special positions. Water molecules O2W and O8W which are coordinated to Ba1 lie on 2-fold axes (positions 2*f*: ½, *y*, ¼; ½. –*y*, ¾). Solvent water molecules O10W and O11W also lie on 2-fold axes (positions 2*e*: 0, *y*, ¼; 0, –*y*, ¾) but do not participate in coordination of Ba cations. In addition, molecule O9W also does not participate in the mentioned coordination spheres. Since these four water molecules are in special positions, and in spite of the existence of even eleven crystallographically different water molecules, the chemical formula describing the asymmetric unit is $Ba_2(sac)_4 \cdot 9H_2O$, and the empirical formula is $Ba(sac)_2 \cdot 4.5H_2O$. Regardless of either being coordinated or not to Ba1 or Ba2 cations, all water molecules are included in the hydrogen bonding (Figure 10, Supplementary Table S11) forming layers parallel to (001). The hydrogen bonds are of the O–H···O and O–H···N type and are weak to medium strong, the O···O and O···N distances range from 2.702(9) Å to 2.837(10) Å, and from 2.793(10) Å to 2.882(10) Å, respectively. There are only weak hydrogen bonds of the C–H···O type between the layers, as well as van der Waals interactions. Stacking of the bonded and free saccharinate anions can be seen in Figures 10 and 11. The distance from the centers of gravity of the saccharinate six-membered rings to the best plane of the neighboring saccharinates (calculated through the six-membered ring) are in the range 3.453(4) Å to 3.692(4) Å (Supplementary Table S12).

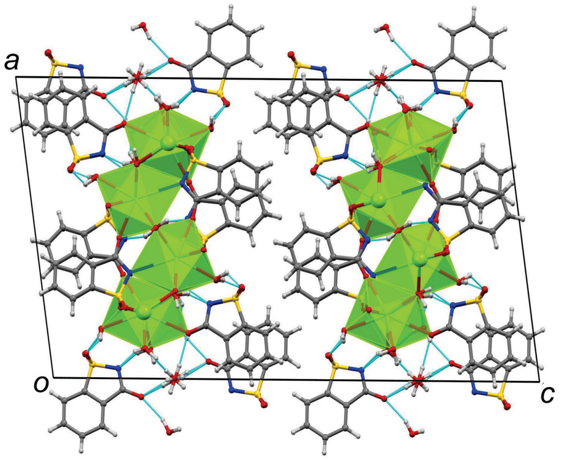

Figure 10. Projection of the structure of $Ba(sac)_2 \cdot 4.5H_2O$ down the *b*-axis (in the *a*-*c* plane). The polyhedra around the barium ions are shown in light green color and the hydrogen bonds between donors and acceptors in light blue color.

The values of the C–O distances in the four crystallographically different saccharinate ions range from 1.211(11) Å to 1.246(11) Å, the longest distance being in the free saccharinate anion. These C–O distances are similar to other in the ionic saccharinates.[13] These results are in a very good agreement with the study of the infrared spectra of Ca, Sr and Ba saccharinates in the region of the CO stretching vibrations which strongly indicated that the metal-to-saccharin bonds in these compounds are mainly ionic in character.[19]

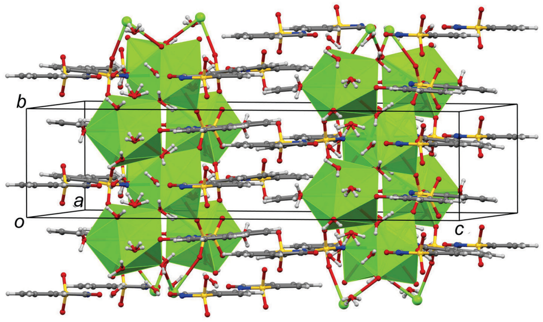

Figure 11. Packing of the structural the structural moieties ($Ba_2(sac)_3(H_2O)_7$), (sac) and $2(H_2O)$ in $Ba(sac)_2 \cdot 4.5H_2O$. The polyhedra around the barium ions are shown in light green color.

Thermogravimetric Analysis

Results of the thermogravimetric analysis of $Mg(sac)_2 \cdot 7H_2O$, $Ca(sac)_2 \cdot 7H_2O$, $Sr(sac)_2 \cdot 4H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$ are shown in Table 4 and Figure 12. Water loss and the mass fraction of the metal in calcium, strontium and barium saccharinates are consistent with the theoretical values. By thermogravimetric analysis it was found that the strontium compound probably has the formula $Sr(sac)_2 \cdot 4H_2O$. All compounds except $Mg(sac)_2 \cdot 7H_2O$ lose water molecules in two consecutive steps starting at 30 – 56 °C. Decomposition of compounds starts at temperatures 390 – 449 °C and proceeds in several consecutive steps. It was found that the stability of the anhydrous saccharinates decreases as radius of metal ion increases. Calcium, strontium and barium saccharinates decompose completely to the respective metal sulfates.

The formula $Ca(sac)_2 \cdot 4H_2O$ was previously proposed from electrometric Karl Fisher titration.[19] Now we have found that this hydrate starts to lose water already at 30 °C so the compound analyzed previously has already lost some water molecules.

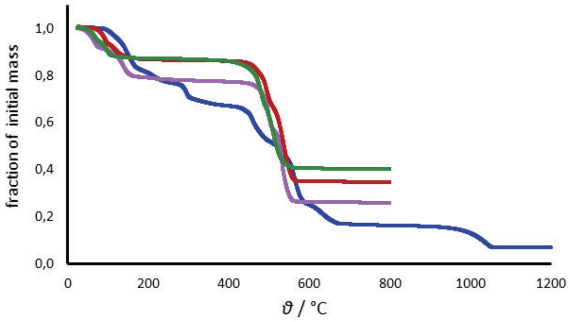

Figure 12. TGA curves of $Mg(sac)_2 \cdot 7H_2O$ (blue), $Ca(sac)_2 \cdot 7H_2O$ (purple), $Sr(sac)_2 \cdot 4H_2O$ (red) and $Ba(sac)_2 \cdot 4.5H_2O$ (green).

$Mg(sac)_2 \cdot 7H_2O$ has a different mechanism of decomposition, it starts losing water at 76 °C in several consecutive steps which are overlapped with decomposition of the saccharinate ions. At around 700 °C an unknown compound is formed. We supposed it to be magnesium sulfate, however the experimental and theoretical values were not in agreement. $MgSO_4$ is very hygroscopic and the powder patterns did not correspond to the powder pattern of the anhydrous compound nor with any known hydrate. Another analysis was carried out to 1200 °C and the decomposition to magnesium oxide started at 950 °C and was completed at 1050 °C.

CONCLUSION

$Mg(sac)_2 \cdot 7H_2O$ forms well diffracting crystals and the room temperature structure was determined previously. The data presented here was collected at 170 °C. The crystals of other alkaline earth metals Ca – Ba crystallize in the form of very thin needle-like crystals and it was difficult to find well diffracting crystals. After many crystallization and data collection trials the crystal structures of $Ca(sac)_2 \cdot 7H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$ were successfully determined. The formula for $Sr(sac)_2 \cdot 4H_2O$ was proposed from the thermogravimetric experiment and is in agreement with the previously proposed formula from the IR spectral analysis and from electrometric Karl Fisher titration.[19]

The structures are characterized by bonding of the saccharinate anion (or anions) and water molecules to the metal cation, free saccharinate ions involved in stacking and π···π interactions, and water molecules of

Table 4. Thermogravimetric data of $Ca(sac)_2 \cdot 7H_2O$, $Sr(sac)_2 \cdot 4H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$.

Compound	Water loss			Compound decomposition		
	θ / °C	$w_{\text{theor}}(H_2O)$ / %	$w_{\text{exp}}(H_2O)$ / %	θ / °C	$w_{\text{theor}}(M)$ / %	$w_{\text{exp}}(M)$ / %
$Mg(sac)_2 \cdot 7H_2O$	76	24,50	/ [(a)]	/ [(a)]	4,72	4,23
$Ca(sac)_2 \cdot 7H_2O$	30	23.77	23.30	449	7.55	7.61
$Sr(sac)_2 \cdot 4H_2O$ [(b)]	56	13.75	14.01	428	16.72	16.50
$Ba(sac)_2 \cdot 4.5H_2O$	35	13.91	13.25	390	23.57	23.62

(a) water and saccharinate decomposition are overlapped

(b) theoretical values are calculated for the formula $Sr(sac)_2 \cdot 4H_2O$

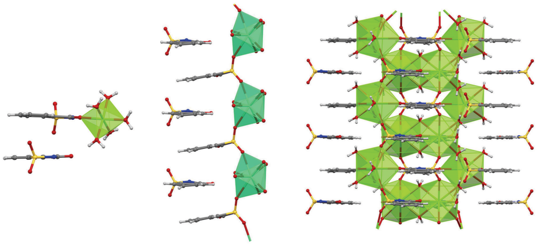

Figure 13. Connectivity of the polyhedra in the structural moieties (Mg(sac)(H_2O)$_5$)(sac) (left); (Ca(sac)(H_2O)$_6$)(sac) (middle) and (Ba$_2$(sac)$_3$(H_2O)$_7$)(sac) (right). The Mg and Ba coordination polyhedra are shown in light green color, and green color for the Sr polyhedra.

crystallization. In the (Mg(sac)(H_2O)$_5$) moiety the Mg ion is six-coordinated forming an octahedron, in (Ca(sac)(H_2O)$_6$) the two Ca ions are irregularly eight-coordinated with the polyhedra bridged by saccharinate ions into chains, and in (Ba$_2$(sac)$_3$(H_2O)$_7$) both Ba ion are irregularly nine-coordinated with the polyhedra sharing both edges and corners through bridging water molecules and bridging saccharinate ions into double chains (Figure 13). All water molecules are involved in hydrogen bonding forming layers with only weak van der Waals and C–H···O interactions between them. The needle-like crystals of Ca(sac)$_2$·7H_2O and Ba(sac)$_2$·4.5H_2O are elongated in the direction of the chains, along [100] and [010], respectively.

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REFERENCES

[1] J. C. J. Bart, *J. Chem. Soc. B Phys. Org.* **1968**, 376–382. https://doi.org/10.1039/j29680000376

[2] Y. Okaya, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1969**, *25*, 2257–2263. https://doi.org/10.1107/S056774086900553X

[3] G. Jovanovski, B. Kamenar, *Cryst. Struct. Commun.* **1982**, *11*, 247–255.

[4] B. Kamenar, G. Jovanovski, *Cryst. Struct. Commun.* **1982**, *11*, 257–261.

[5] E. J. Baran, V. T. Yilmaz, *Coord. Chem. Rev.* **2006**, *250*, 1980–1999. https://doi.org/10.1016/j.ccr.2005.11.021

[6] D. P. Karothu, I. Jahović, G. Jovanovski, B. Kaitner, P. Naumov, *CrystEngComm* **2017**, *19*, 4338–4344. https://doi.org/10.1039/C7CE00627F

[7] B. Kamenar, G. Jovanovski, D. Grdenić, *Cryst. Struct. Commun.* **1982**, *11*, 263–268.

[8] S. Z. Haider, K. M. A. Malik, K. J. Ahmed, H. Hess, H. Riffel, M. B. Hursthouse, *Inorganica Chim. Acta* **1983**, *72*, 21–27. https://doi.org/10.1016/S0020-1693(00)81689-8

[9] S. Z. Haider, K. M. A. Malik, S. Das, M. B. Hursthouse, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1984**, *40*, 1147–1150.

[10] F. A. Cotton, G. E. Lewis, C. A. Murillo, W. Schwotzer, G. Valle, *Inorg. Chem.* **1984**, *23*, 4038–4041. https://doi.org/10.1021/ic00192a038

[11] F. A. Cotton, L. R. Falvello, R. Llusar, E. Libby, C. A. Murillo, W. Schwotzer, *Inorg. Chem.* **1986**, *25*, 3423–3428. https://doi.org/10.1021/ic00239a021

[12] G. Jovanovski, A. Hergold-Brundić, B. Kamenar, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1988**, *44*, 63–66. https://doi.org/10.1107/S0108270187009120

[13] P. Naumov, G. Jovanovski, *Struct. Chem.* **2000**, *11*, 19–33. https://doi.org/10.1023/A:1009264221838

[14] P. Naumov, G. Jovanovski, O. Grupče, B. Kaitner, A. D. Rae, S. W. Ng, *Angew. Chemie Int. Ed.* **2005**, *44*, 1251–1254. https://doi.org/10.1002/anie.200461043

[15] G. Jovanovski, *Croat. Chem. Acta* **2000**, *73*, 843–868.

[16] P. Naumov, G. Jovanovski, *J. Coord. Chem.* **2001**, *54*, 63–79. https://doi.org/10.1080/00958970108022630

[17] E. Kleinpeter, D. Ströhl, G. Jovanovski, B. Šoptrajanov, *J. Mol. Struct.* **1991**, *246*, 185–188. https://doi.org/10.1016/0022-2860(91)80025-Y

[18] N. Suzuki, H. Suzuki, *Cancer Res.* **1995**, *55*, 4253–4256. https://doi.org/10.1049/ip-opt:19951669

[19] G. Jovanovski, D. Spasov, S. Tančeva, B. Šoptrajanov, *Acta Chim. Slov.* **1996**, *43*, 41–50.

[20] P. Naumov, G. Jovanovski, S. Tančeva, S. W. Ng, *Zeitschrift für Anorg. und Allg. Chemie* **2006**, *632*, 454–460. https://doi.org/10.1002/zaac.200500433

[21] R. Banerjee, P. M. Bhatt, M. T. Kirchner, G. R. Desiraju, *Angew. Chemie Int. Ed.* **2005**, *44*, 2515–2520. https://doi.org/10.1002/anie.200462967

[22] G. Jovanovski, B. Kaitner, O. Grupče, P. Naumov, *Open Chem.* **2004**, *2*, 254–275. https://doi.org/10.2478/BF02476195

[23] K. M. A. Malik, S. Z. Haider, M. A. Hossain, M. B. Hursthouse, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1984**, *40*, 1696–1698. https://doi.org/10.1107/S0108270184009197

[24] A. Y. Nazarenko, *IUCrData* **2018**, *3*, x180867. https://doi.org/10.1107/S2414314618008672

[25] P. Naumov, L. Pejov, G. Jovanovski, T. Stafilov, M. Taseska, E. Stojanovska, *Cryst. Growth Des.* **2008**, *8*, 1319–1326.

[26] O. E. Piro, E. E. Castellano, E. J. Baran, *Zeitschrift für Anorg. und Allg. Chemie* **2002**, *628*, 612–619. https://doi.org/10.1002/1521-3749(200203)628:3%3C612::AID-ZAAC612%3E3.0.CO;2-G

[27] S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steedk, D. C. Waddelli, *Chem. Soc. Rev.* **2012**, *41*, 413-447. https://doi.org/10.1039/C1CS15171A

[28] T. Friščić, L. Fábián, *CrystEngComm* **2009**, *11*, 743–745. https://doi.org/10.1039/b822934c

[29] T. Friščić, S. L. Childs, S. A. A. Rizvi, W. Jones, *CrystEngComm* **2009**, *11*, 418–426. https://doi.org/10.1039/B815174A

[30] D. Vušak, B. Prugovečki, D. Milić, M. Marković, I. Petković, M. Kralj, D. Matković-Čalogović, *Cryst. Growth Des.* **2017**, *17*, 6049–6061. https://doi.org/10.1021/acs.cgd.7b01157

[31] J. Pejić, D. Vušak, G. Szalontai, B. Prugovečki, D. Mrvoš-Sermek, D. Matković-Čalogović, J. Sabolović, *Cryst. Growth Des.* **2018**, *18*, 5138–5154. https://doi.org/10.1021/acs.cgd.8b00589

[32] D. Vušak, K. Ležaić, J. Jurec, D. Žilić, B. Prugovečki, *Heliyon* **2022**, *8*, e09556. https://doi.org/10.1016/j.heliyon.2022.e09556

[33] M. Tašner, D. Mrvoš-Sermek, E. Hajdarpašić, D. Matković-Čalogović, *Contrib. Sect. Nat. Math. Biotech. Sci.* **2018**, *39*, 91–101. https://doi.org/10.20903/csnmbs.masa.2018.39.2.122

[34] T. Degen, M. Sadki, E. Bron, U. König, G. Nénert, *Powder Diffr.* **2014**, *29*, S13–S18. https://doi.org/10.1017/S0885715614000840

[35] CrysAlisPro 1.171.41.123a, Rigaku Oxford Diffraction, **2022**.

[36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341. https://doi.org/10.1107/S0021889808042726

[37] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053273314026370

[38] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053229614024218

[39] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13. https://doi.org/10.1107/S0021889802022112

[40] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854. https://doi.org/10.1107/S0021889812029111

[41] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Crystallogr.* **2020**, *53*, 226–235. https://doi.org/10.1107/S1600576719014092