Synthesis and structure of chiral coordination polymers of Co^{II}, Cu^{II}, and Mg^{II} saccharates*

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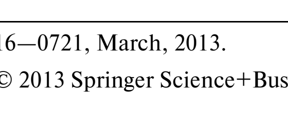
Chiral metal-organic coordination polymers $[Co_2(sacch)_2]\cdot 1/2H_2O\cdot CH_3OH$ (**1**), $[Cu(sacch)(H_2O)_2]\cdot 3H_2O$ (**2**), and $[Mg(H_2O)_3(sacch)]$ (**3**) (H_2sacch is D-saccharic acid) were synthesized from aqueous or water-methanol solutions of potassium hydrogen saccharate and a salt of the corresponding metal. The compositions and structures of the resulting compounds were determined by single-crystal X-ray diffraction and confirmed by X-ray powder diffraction, IR spectroscopy, thermogravimetry, and elemental analysis.

Key words: coordination polymers, chiral complexes, saccharic acid, magnesium complexes, copper(II) complexes, cobalt(II) complexes, X-ray diffraction.

The chemistry of enantiomerically pure (homochiral) porous coordination polymers has attracted great interest since these compounds show promise for applications in stereoselective processes.[1—3] A number of interesting studies on the stereoselective catalysis,[4,5] adsorption,[6,7] and enantiomeric separation[8] with the use of homochiral porous coordination frameworks were published in recent years. The recently shown[9] possibility of the synthesis of cyclodextrin-based homochiral porous coordination frameworks gave a new impetus to the development of the chemistry of such important compounds. Due to high biocompatibility of such "edible" homochiral porous coordination structures, these compounds can be considered as new promising drug carriers. The possibility of applying porous coordination polymers based on abiogenic terephthalates for the drug storage and delivery was examined in the recent past.[10] However, the problem of the toxicity of the drug carrier or its biodegradation products can be eliminated only with the use of porous compounds based on biocompatible compounds. Sugars, amino acids, and their simplest derivatives that are present in living systems are the most convenient and evident reagents for the synthesis of homochiral coordination polymers with high biocompatibility. Due to the availability of such biomolecules, numerous biomolecule-based coordination compounds were synthesized.[11] However, only a few of them have a porous nature.[12—15] We characterized a series of new homochiral porous frameworks based on aspartic,[16] malic,[17] lactic,[18] mandelic,[19] camphoric,[20,21] and tartaric acids.[22] Nevertheless, a search for new biocompatible and (or) biodegradable porous coordination structures remains a topical and important problem.

D-Saccharic acid (H_2sacch) is a product of the partial oxidation of glucose and a promising ligand for the preparation of biocompatible homochiral porous frameworks. Only four frameworks of metal saccharates were described in the literature,[23—26] whereas 13 coordination polymers are known for sterically isomeric galactaric acid (a product of the partial oxidation of galactose). However, since all galactarates are achiral diastereomers, they have attracted little interest. In the present study, we report the synthesis and structural characterization of three new homochiral coordination polymers, cobalt(II) saccharate $[Co_2(sacch)_2]\cdot 1/2H_2O\cdot MeOH$ (**1**), copper(II) saccharate $[Cu(sacch)(H_2O)_2]\cdot 3H_2O$ (**2**), and magnesium(II) saccharate $[Mg(H_2O)_3(sacch)]$ (**3**). Compound **3** is particularly interesting from the point of view of biocompatibility, because the magnesium cation is virtually safe for the body and is a component of many drugs and food additives.



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Results and Discussion

The coordination polymer complexes $[Co_2(sacch)_2] \cdot 1/2H_2O \cdot MeOH$ (**1**), $[Cu(sacch)(H_2O)_2] \cdot 3H_2O$ (**2**), and $[Mg(H_2O)_3(sacch)]$ (**3**) were prepared by the precipitation of crystalline products from aqueous or water-methanol solutions of the corresponding metal salt and potassium hydrogen saccharate KHsacch. The compositions and structures of the compounds were determined by single-crystal X-ray diffraction and confirmed by elemental analysis (C, H, N), thermogravimetry (TG), and IR spectroscopy.

The structural model of compound **1** was established by X-ray diffraction study. The crystal structure contains two crystallographically independent cobalt(II) cations. Both cations are in an octahedral environment formed by four α-carboxylate oxygen atoms and two β-hydroxyl oxygen atoms of the saccharate anion in *cis* positions. The Co(1) and Co(2) atoms are nonequivalent because they are surrounded by groups with different configurations (Fig. 1). The oxygen atoms of the OH groups are coordinated in a monodentate fashion, whereas the carboxylate oxygen atoms act as μ_2-bridges between the adjacent cobalt cations to form chains running along the crystallographic axis *c*. The chains are linked *via* the saccharate bridges in the perpendicular directions *a* and *b* to form a chiral framework containing two types of channels arranged in the staggered order (Fig. 2). Thus, there are small hydrophilic zigzag channels of variable diameter (1.8—2.6 Å), with the uncoordinated γ-hydroxyl groups of the saccharate anions pointing inside the channels. These channels are occupied by disordered methanol and H_2O molecules. The distance between the hydroxyl groups of the adjacent anions along the channel is 2.74 Å, which is indicative of hydrogen bonding. Besides, there are empty hydrophobic channels of a diameter of 5.2 Å, where disordered methanol molecules are located. Compound **1** is isostructural to the earlier described[23] zinc saccharate $[Zn_2(sacch)_2] \cdot 2H_2O$ (Fig. 3). The thermogravimetric analysis of compound **1** revealed a 5% weight loss in the temperature range of 20—220 °C. This fact can be assigned to the removal of guest water and methanol molecules (calculated 7% for 1/2 H_2O + MeOH).

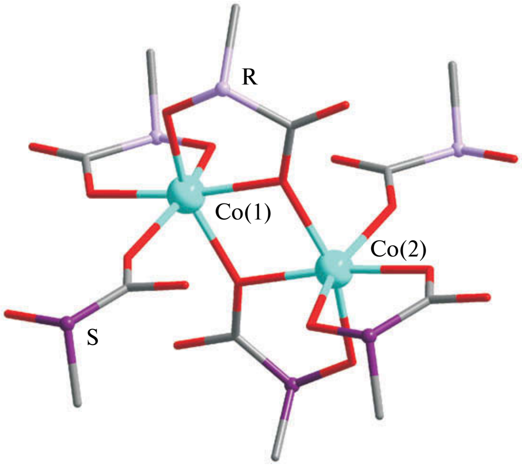

Fig. 1. Coordination environment of the cobalt cations in compound **1**. The carbon atoms in the *R* and *S* configurations are presented in lilac and violet, respectively. The hydrogen atoms are not shown.

Note. Figures 1, 4, and 6 are available in full color in the on-line version of the journal (http://www.springerlink.com).

In the crystal structure of compound **2**, the copper(II) cations are in an octahedral environment formed by oxygen atoms of two different carboxylate groups, two nonequivalent β-hydroxyl groups (related by a mirror plane), and two water molecules in *trans* positions with respect to each other (Fig. 4). The $Cu-OH_2$ distances (2.303(2) and 2.548(2) Å) are much longer than the Cu—OH (1.989(2) Å) and Cu—OCO distances (1.929(3) Å). This is typical of the Cu^{2+} (d^9) cation and results from the Jahn-Teller distortion. The copper(II) cations and saccharate anions form chains running along the body diagonal of the unit cell (Fig. 5). Cystallization water molecules are located between the chains. The distance between the oxygen atoms of the crystallization and coordinated water molecules corresponds to standard hydrogen bonds (2.71—2.86 Å). Shorter contacts are observed between the crystallization water molecules and the carboxyl oxygen atom (2.55 Å), which is attributed to stronger hydrogen-acceptor properties of the COO group. In addition, there are hydrogen bonds (2.75 and 2.77 Å) between the adjacent chiral chains. An extensive hydrogen bond network in the crystal structure of **2** can serve as a proton transport channel and promote the proton conductivity of the compound. The thermogravimetric analysis of compound **2** showed that a 18% weight loss occurs in the temperature range of 20—150 °C. This can be assigned to the removal of two guest crystallization water molecules and two coordinated water molecules (calculated 20% for 4 H_2O).

Compound **3** also has a chain structure. The magnesium cations are in a distorted octahedral environment formed by three meridional water molecules, two carboxylate oxygen atoms of the saccharate anions in *cis* positions with respect to each other, and one hydroxyl group (Fig. 6). In compound **3**, only three donor groups of the saccharate anions (2α + β) are involved in the formation of coordination bonds, as opposed to compounds **1** and **2** possessing four such groups (2α + 2β). Therefore, the carboxylate groups of the saccharate anion in compound **3** are coordinated to different metal cations in different fashion to form chelating coordination (α + β) with one Mg cation and monodentate coordination (α) with another Mg cation. The coordination chains [Mg(sacch)] are arranged along the *b* axis of the unit cell, the saccharate anions being oriented in the same direction in a head-to-tail manner. In the crystal packing of **3**, the chains are in an antiparallel arrangement (Fig. 7). There are short hydrogen bonds

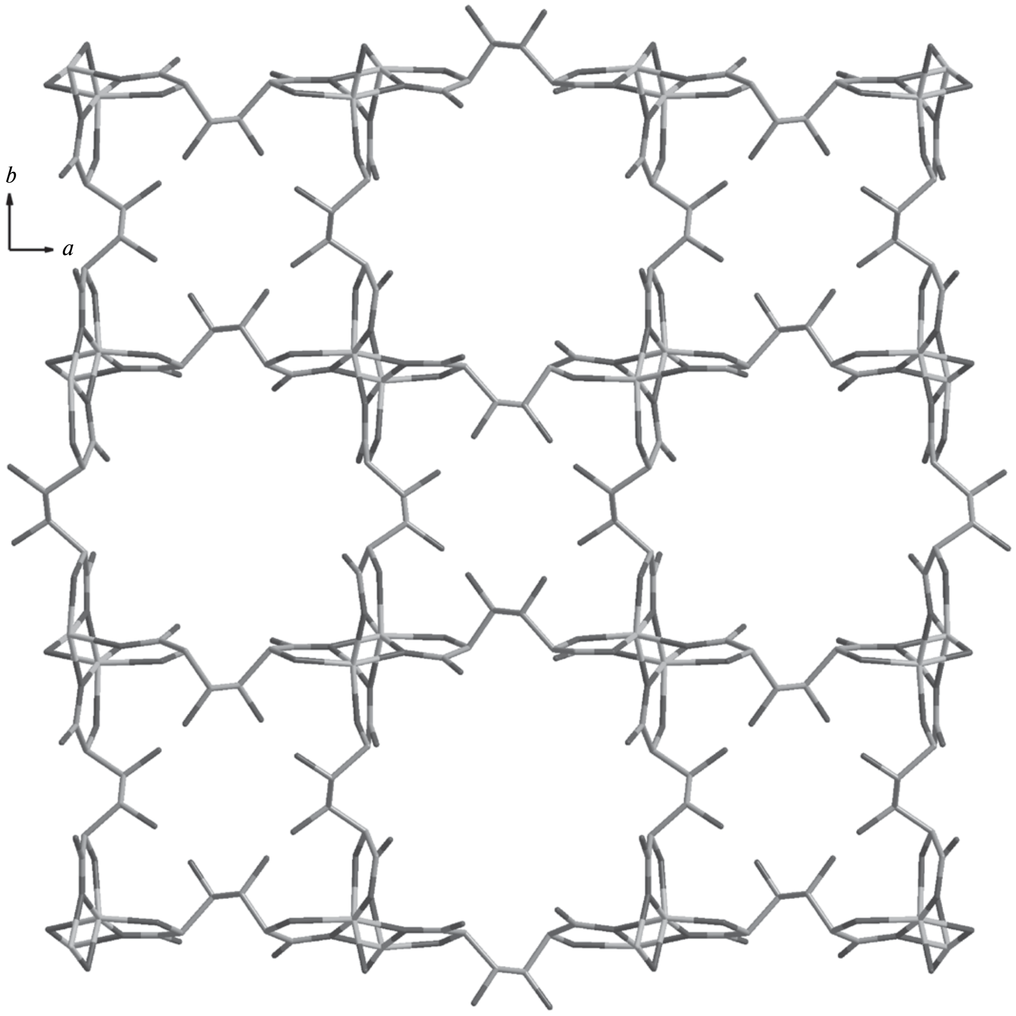

Fig. 2. Structure of the framework of compound **1**. The hydrogen atoms are not shown.

(2.66 and 2.70 Å) and several longer bonds (2.90—3.06 Å) between the chains. The chains form a close packing, where the solvent molecules of solvation are absent.

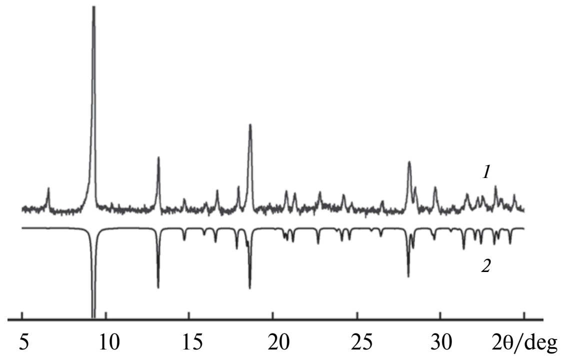

Fig. 3. Comparison of the experimental X-ray powder diffraction pattern of compound **1** (*1*) and the calculated pattern for $[Zn_2(sacch)_2] \cdot 2H_2O$ (*2*).

A comparison of our data and the earlier results shows that the bridging mode of coordination is typical of the saccharate ligand. The carboxylate groups of saccharic acid are always coordinated to different metal cations, resulting in the formation of homochiral coordination polymers. The β-hydroxyl groups adjacent to the carboxyl groups are usually also involved in the coordination to the

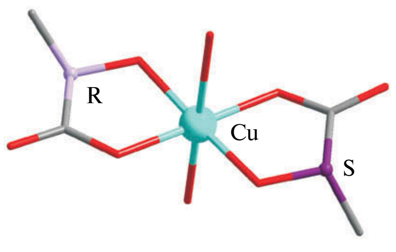

Fig. 4. Coordination environment of the copper cation in compound **2**. The carbon atoms in the *R* and *S* configurations are presented in lilac and violet, respectively. The hydrogen atoms are not shown.

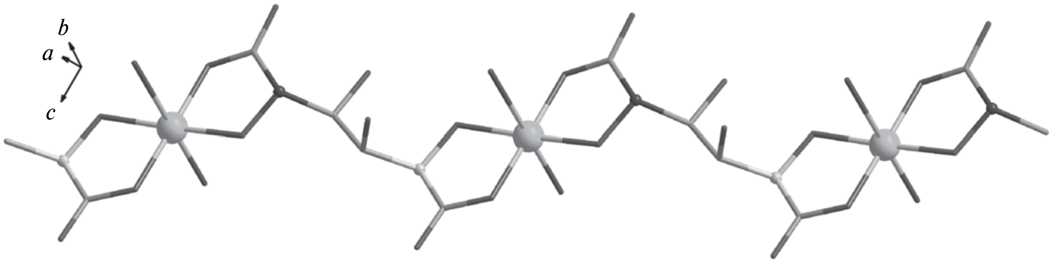

Fig. 5. Structure of the chains in compound **2**. The hydrogen atoms are not shown.

cation to form strong chelate complexes. The γ-hydroxyl groups are not involved in the coordination. However, they can serve as potential active sites for the stereospecific recognition or catalytic activation. The conformational flexibility of the saccharate ligand decreases the possibility of the formation of porous structures and hinders the directed design of coordination frameworks with a specified topology. In our opinion, the conformational lability can be partially compensated by means of additional bridging ligands having rigid geometry in the synthesis of heteroligand coordination polymers.

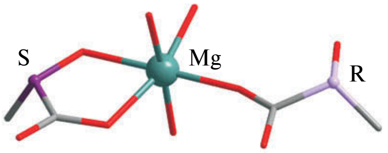

Fig. 6. Coordination environment of the magnesium cation in molecule **3**. The carbon atoms in the *R* and *S* configurations are presented in lilac and violet, respectively. The hydrogen atoms are not shown.

Experimental

Potassium hydrogen saccharate, magnesium(II) chloride, magnesium(II) perchlorate, copper(II) nitrate, cobalt(II) chloride, and methanol used as the starting compounds were at least of reagent grade. The IR spectra were recorded on a Scimitar FTS 2000 instrument in KBr pellets. The thermogravimetric analysis was performed on a TG 209 F1 thermobalance (Natzsch); samples were decomposed under an argon atmosphere at a heating rate of 10 deg min^{-1}. The elemental analysis for C, H, and N was carried out on an EURO EA 3000 instrument (EuroVector) in

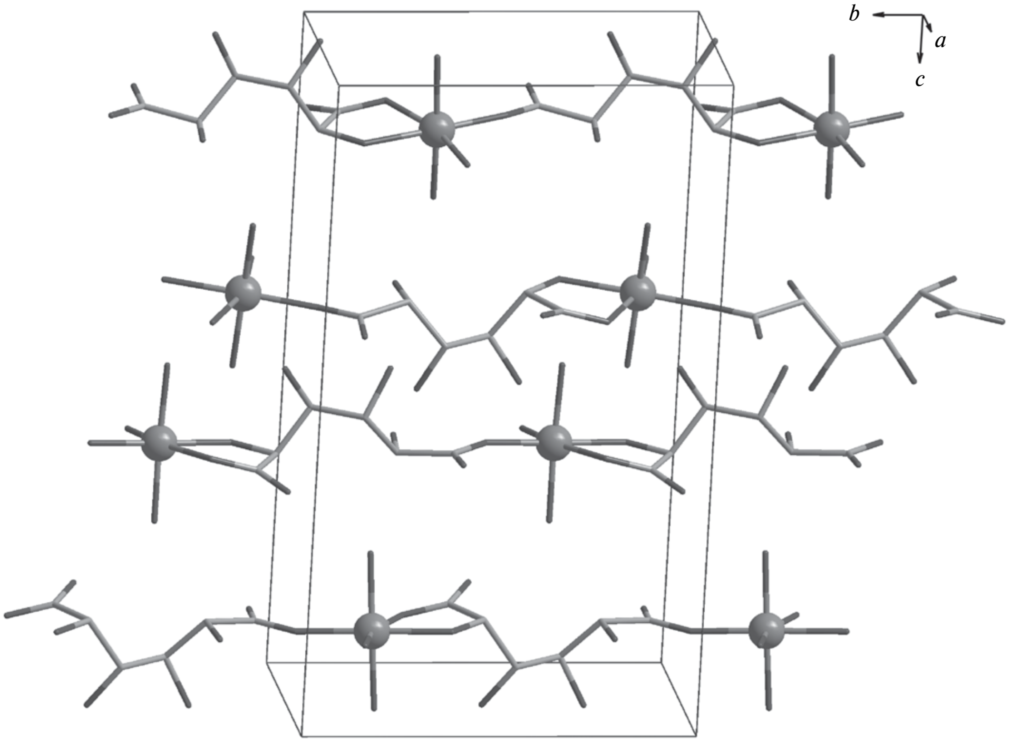

Fig. 7. Arrangement of the chains in the structure of compound **3**. The hydrogen atoms are not shown.

Table 1. Crystallographic characteristics and the X-ray data collection and structure refinement statistics for compounds **1**—**3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{13}H_{21}Co_2O_{17.5}$	$C_6H_{18}CuO_{13}$	$C_6H_{14}MgO_{11}$
M/g mol^{-1}	575.16	361.74	286.48
Crystal system	Tetragonal	Triclinic	Orthorhombic
Space group	$P4_12_12$	$P1$	$P2_12_12_1$
a/Å	18.968(1)	6.6359(2)	5.8180(2)
b/Å	18.968(1)	7.1541(2)	10.4281(3)
c/Å	5.773(1)	7.4077(2)	17.9763(6)
α/deg	90	100.120(1)	90
β/deg	90	103.445(1)	90
γ/deg	90	108.058(1)	90
V/Å^3	2077.0(4)	313.294(15)	1090.63(6)
Z	4	1	4
ρ_{calc}/g cm^{-3}	1.839	1.917	1.745
μ/mm^{-1}	4.245	1.814	0.220
F(000)	1172	187	600
Crystal size/mm	0.10×0.06×0.02	0.50×0.29×0.21	0.30×0.22×0.08
θ-Angle scan range/deg	2.14—35.41	2.93—30.96	2.26—28.33
hkl range	$-21 \le h \le 21$, $-21 \le k \le 21$, $-6 \le l \le 6$	$-8 \le h \le 8$, $-10 \le k \le 6$, $-9 \le l \le 9$	$-7 \le h \le 7$, $-8 \le k \le 13$, $-23 \le l \le 23$
N_{hkl} of measured/unique	10036/1681	3947/2636	8956/2706
N_{hkl} with $I > 2\sigma(I)$	1672	2628	2655
R_{int}	0.1126	0.0141	0.0285
Goodness of fit on F^2	1.199	1.225	1.088
R factors [$I > 2\sigma(I)$]			
R_1	0.1862	0.0191	0.0215
wR_2	0.3972	0.0610	
R factors (based on all reflections)			
R_1	0.1867	0.0194	0.0220
wR_2	0.3975	0.0686	0.0603
Absolute structure parameter	0.23(10)	0.016(8)	0.09(16)
Residual electron density (max/min), e Å^{-3}	3.025/–2.875	0.381/–0.315	0.329/–0.246

the Analytical Laboratory of the A. V. Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The X-ray powder diffraction data were obtained on a Philips PW 1820/PW 1710 powder diffractometer (Cu-Kα, λ = 1.54056 Å).

Synthesis of catena{bis(D-saccharate)dicobaltate(II)} hemihydrate methanol solvate, [Co$_2$(sacch)$_2$] · 1/2H$_2$O · CH$_3$OH (1). The compounds $CoCl_2 \cdot 6H_2O$ (0.335 g, 1.4 mmol) and KHsacch (0.252 g, 1.00 mmol) in a mixture of methanol and water (1 : 1, v/v, 3.00 mL) were placed in a sealed glass tube and kept under temperature-controlled conditions at 60 °C for 48 h. After cooling, the pink crystals that formed were separated from the mother liquor by decantation, washed several times with methanol, and dried in air. The yield was 0.098 g (36%). Found (%): C, 26.8; H, 3.8. $C_{13}H_{21}Co_2O_{17.5}$. Calculated (%): C, 27.1; H, 3.7. IR (KBr), ν/cm^{-1}: 528 (m), 566 (m), 632 (w), 686 (w), 738 (m), 850 (m), 895 (w), 1037 (m), 1120 (s, sh), 1232 (s), 1292 (s), 1352 (s), 1440 (s), 1645 (s), 2612 (w), 2934 (w), 3339 (m, sh). TG data: Δm = 5% (220 °C), calculated 7% for $1/2H_2O + CH_3OH$.

Synthesis of catena{D-saccharatediaquacopper(II)} trihydrate, [Cu(sacch)(H$_2$O)$_2$] · 3H$_2$O (2). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.20 mmol) and KHsacch (0.042 g, 0.17 mmol) in water (2.00 mL) was kept at room temperature for 48 h. The crystals that formed were washed several times with water and dried in air. The yield was 0.029 g (40%). Found (%): C, 21.3; H, 4.8. $C_6H_{16}CuO_{12}$ ([Cu(sacch)(H$_2$O)$_2$] · 2H$_2$O). Calculated: C, 21.0; H, 4.7. IR (KBr), ν/cm^{-1}: 400 (m), 512 (m), 589 (s), 687 (w), 716 (w), 807 (m), 835 (m), 962 (w), 1067 (m), 1123 (m), 1235 (m), 1291 (s), 1347 (s, sh), 2634 (w), 2612 (w), 2922 (m), 3413 (s, sh). TG data: Δm = 18% (150 °C), calculated 20% for 4 H_2O.

Synthesis of catena{D-saccharatetriaquamagnesium}, [Mg(H$_2$O)$_3$(sacch)] (3). A mixture of $MgCl_2 \cdot 6H_2O$ (0.020 g, 0.10 mmol) and KHsacch (0.025 g, 0.1 mmol) in water (1 mL) was placed in a sealed glass tube and kept under temperature-controlled conditions at 60 °C for 24 h. The crystals that formed were washed several times with water and dried in air. The yield was 0.002 g (7%). In the synthesis, an equivalent amount of magnesium perchlorate can be used instead of magnesium chloride. IR (KBr), ν/cm^{-1}: 473 (m), 498 (w), 629 (s), 701 (m), 790 (w), 843 (w), 887 (w), 947 (w), 1042 (s), 1097 (s), 1235 (m), 1286 (s), 1327 (s), 1388 (m), 1423 (m), 1474 (w), 1610 (s), 1646 (s), 2687 (w), 2612 (w), 2920 (m), 3179 (s, sh), 3477 (s).

X-ray diffraction study. Single-crystal X-ray diffraction data sets for compounds **2** and **3** were collected at 150 K on an automated Bruker X8Apex four-circle diffractometer equipped with an area detector (φ- and ω-scanning technique, λ(Mo-Kα) = = 0.71073 Å, graphite monochromator). Absorption corrections were applied based on comparison of redundant and equivalent

Table 2. Selected bond lengths in compounds **1**—**3**

Bond	*d*/Å		
	1	**2**	**3**
M—O(OH)	2.016(16), 2.069(17)	1.980(2), 1.989(2)	2.0924(8)
M—O(COO)	2.058(17), 2.077(17), 2.060(17), 2.128(18)	1.925(2), 1.929(3)	1.9963(9), 2.0421(9), 2.0832(9)
M—O(OH$_2$)	—	2.303(2), 2.548(2)	2.0476(9), 2.0783(10)

reflections using the SADABS software.[27] The single-crystal X-ray diffraction data for compound **1** were recorded at 90 K using a synchrotron source at the 2D Supramolecular Crystallography beamline of the Pohang Accelerator Laboratory equipped with a one-circle goniometer and the ADSC Quantum 210 area detector (λ = 1.00000 Å, silicon monochromator, φ-scanning technique). The X-ray data were collected, the frames were integrated, the data set was processed, and the absorption correction for the crystal of **1** was applied using the HKL2000 program package.[28] Structures **1**—**3** were solved by direct methods and refined anisotropically (except for the H atoms) by the full-matrix least-squares method using the SHELX-97 program package.[29] The hydrogen atoms were positioned geometrically and refined using a riding model. The positions of the hydrogen atoms of the water molecules in structures **2** and **3** were refined with constraints imposed on O—H bonds and atomic displacement parameters. Unfortunately, the low quality of the X-ray diffraction data for compound **1** did not allow us to perform the complete refinement of the crystal structure. According to the single-crystal X-ray diffraction data and the powder diffraction data (see Fig. 3), compound **1** is isostructural to the earlier described[23] $[Zn_2(sacch)_2] \cdot 2H_2O$. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics are given in Table 1. Selected interatomic distances are listed in Table 2. The complete tables of interatomic distances, bond angles, atomic coordinates, and displacement parameters were deposited to the Cambridge Crystallographic Data Centre (CCDC 926289 (**1**), 917000 (**2**), 917001 (**3**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif), and can be obtained from the authors.

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