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Dedicated to Professor Vukadin Leovac on the occasion of his 70th birthday.

Abstract

Three new 1D coordination polymers, $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$, $[Hg(CH_3SO_3)_2(H_2O)_2]_n$ and $[Sr(CH_3SO_3)_2(H_2O)]_n$, were synthesized as large single crystals. The crystals were analyzed and characterized by the means of X-ray analysis, IR and NMR spectroscopy, elemental analysis and solid state UV-Vis spectroscopy. The formation of 1D polymeric chains in the crystal structures of the title compounds is affected by the various bonding modes of the bridging methanesulfonate groups. The studied compounds showed no decomposition in the air.

Keywords: lead(II), mercury(II), strontium(II), methanesulfonates, large single crystals, solid state UV-Vis, X-ray crystallography.

1. Introduction

The synthesis and structural characterization of some methanesulfonates have been reported since the 1960s. In hitherto published papers, the crystal structures of many methanesulfonates were described. Thus, the following have been studied: the alkali metals, cesium methanesulfonate $CsCH_3SO_3$ [1] and $NaCH_3SO_3$ [2]; the alkaline earth metals, hexaaquamagnesium(II) bis(methanesulfonate) hexahydrate $[Mg(H_2O)_6]\cdot(CH_3SO_3)_2\cdot6H_2O$ [3], calcium methanesulfonate $Ca(CH_3SO_3)_2$ [4] and barium methanesulfonate $Ba(CH_3SO_3)_2$ [5]; the transition metals, scandium(III) methanesulfonate $[Sc(OH_2)_6][Sc(CH_3SO_3)_6]$ [6], copper(II) methanesulfonate $[Cu(CH_3SO_3)_2(H_2O)_4]$ [7], silver(I) methanesulfonate $AgCH_3SO_3$ [8], cadmium(II)-methanesulfonate $[Cd(CH_3SO_3)_2(H_2O)_2]$ [9], mercury(I) methanesulfonate $Hg_2(CH_3SO_3)_2$ [10], and zinc(II) methanesulfonate $[Zn(CH_3SO_3)_2(H_2O)_4]$ [11]; the lanthanides, lanthanum(III), neodymium(III) and erbium(III) methanesulfonate $[M(CH_3SO_3)_3(H_2O)_2]$ M = La(III), Nd(III), Er(III) [12] and the actinides, neptunium(IV) methanesulfonate $[Np_2(C_2O_4)_2(CH_3SO_3)_6(H_2O)_4)]^{2-}$ [13] and uranium(VI) methanesulfonate $[UO_2(CH_3SO_3)_2(H_2O)]$ [14]. In addition, the properties of iron(II) and iron(III) methanesulfonates [15] and cobalt(II) methanesulfonate [16] were thoroughly investigated.

In order to realize further research and to develop on previous studies [17–19], the physical properties of three newly synthesized crystalline compounds with methanesulfonate as the anion are presented herein. Since within the previous series of synthesized compounds, their purpose was not emphasized, possible applications of the newly synthesized compounds as wide-range, transparent and cheap optical materials are presented.

2. Materials and methods

2.1. Materials and physical measurements

Chemical reagents, unless otherwise stated, were used directly from commercial sources. All UV-Vis spectra of solid samples were recorded in range 200–850 nm on a GBC Cintra 40 instrument, using the double beam technique. The IR spectra were recorded on a Nicolet 6700 FT-IR instrument (Thermo Scientific), in the ranges of 11000-3800 cm^{-1}, 4000–400 cm^{-1} and 700-240 cm^{-1} using the ATR technique with a Smart Orbit accessory (diamond crystal). Elemental analyses were realized with an Elemental Vario EL III microanalyser. The ^1H and ^{13}C spectra, using D_2O as solvent, were recorded on a Varian Gemini 2000 instrument at 200 and 50 MHz, respectively. The values of the ^1H and ^{13}C chemical shifts were scaled relative to the chemical shifts of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.

2.2. Synthesis of the title methanesulfonates

To 20 cm^3 of a 50 % aqueous solution of methanesulfonic acid, 5 g of an adequate metal compound (carbonate in the case of strontium and lead, and oxide in the case of mercury) was added as a 50 % aqueous suspension, previously treated in an ultrasonic bath for 15 min. The suspension was added in portions over 30 min because of the intense reaction. The solution was left for 2 h at room temperature and then refluxed for 20 minutes. The mixture was then vacuum filtered and the acidity of the clear solution was adjusted to pH 2 with aqueous methanesulfonic acid. This method ensures that methanesulfonic acid remains in excess. The resulting clear solutions were left to crystallize for 30 days, without any movement, in a non-heated room at a temperature of 15 °C. A Platinum wire (0.5 mm diameter, 80 mm long) was added as a crystallization center. The obtained colorless crystals of **1–3** measured up to 2 cm and were transparent to the human eye (Figure 1). The crystals were dried between sheets of filter paper at room temperature for 48 h. All the obtained compounds were stable in air.

1: Yield 85 %. Anal. Calc. for lead(II) methanesulfonate: C, 5.78; H, 1.94; S, 15.44 %. Found: C, 6.32; H, 1.66; S, 16.50 %. ^1H NMR (100 MHz, D_2O): δ 2.82 (s, C*H*₃). ^{13}C NMR (50 MHz, D_2O): δ 41.3 (*C*H₃).

2: Yield 81 %. Anal. Calc. for mercury(II) methanesulfonate: C, 5.63; H, 2.36; S, 15.03 %. Found: C, 5.71; H, 3.28; S, 14.23 %. ^{1}H NMR (100 MHz, D_2O): δ 2.67 (s, CH_3). ^{13}C NMR (50 MHz, D_2O): δ 40.3 (CH_3).

3: Yield 87 %. Anal. Calc. for strontium(II) methanesulfonate : C, 8.12; H, 2.73; S, 21.68 %. Found: C, 8.36; H, 2.61; S, 23.01 %. ^{1}H NMR (100 MHz, D_2O): δ 2.81 (s, CH_3). ^{13}C NMR (50 MHz, D_2O): δ 41.2 (CH_3).

Figure 1. Photographs of (**1**) lead(II), (**2**) mercury(II) and (**3**) strontium(II) methanesulfonate crystals

2.3. Crystal structure determination

The data of **1**, **2**, **3**, were collected with a CCD Oxford Xcalibur S and an Oxford Gemini S diffractometer, (λ(Mo Kα)=0.71073 Å) using the multiscan mode. Semi-empirical absorption corrections from equivalents were carried out with SCALE3 ABSPACK [20]. The structures were solved by direct methods [21] and refined on F^2 with SHELXL-97 [22]. The hydrogen atoms were refined isotropically. They were placed in calculated positions with fixed displacement parameters (Riding model), except for the hydrogen atoms attached to oxygen atoms, which were found in the electron density map and refined freely. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Anisotropic refinement of structure (**3**) in space group $P2_1/m$ gave the suspicious anisotropic displacement parameters for O(1). Accordingly, we have refined the structure in alternative space group $P2_1$ with aim to exclude the possibility of having an acentric crystal structure with pseudo symmetry. However, the results of anisotropic refinement in $P2_1$ were less satisfactory compared with those obtained in $P2_1/m$ especially due to complex and unrealistic anisotropic displacement parameters in the

main residue. The ORTEP-3 and MERCURY programs were used for the presentation of the structures [23,24]. The crystallographic details are listed in Table 1.

Table 1. Crystal data and structure refinement for the obtained compounds

Compound	(1)	(2)	(3)
Chemical formula	$C_4H_{16}O_{14}Pb_2S_4$	$C_2H_{10}HgO_8S_2$	$C_2H_8O_7S_2Sr$
Formula weight	830.82	426.81	295.83
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/m$
a (Å)	8.7593 (4)	4.7130 (3)	8.5633 (3)
b (Å)	9.7905 (5)	6.1837 (2)	6.0436 (2)
c (Å)	10.5886 (6)	8.0157 (4)	9.0002 (4)
α (°)	87.839 (4)	88.935 (4)	90
β (°)	86.191 (4)	87.157 (4)	112.786 (5)
γ (°)	71.327 (5)	85.510 (4)	90
V (Å³)	858.23 (8)	232.58 (2)	429.44 (3)
Z	2	1	2
D_{calc}(g cm^{-3})	3.200	3.047	2.272
μ (mm^{-1})	20.143	17.006	6.762
F(000)	752.0	198.0	288.0
Crystal size (mm³)	$0.1 \times 0.03 \times 0.02$	$0.13 \times 0.02 \times 0.02$	$0.2 \times 0.03 \times 0.01$
Data collection			
Diffractometer	Ccd oxford gemini diffractometer	Ccd xcalibur s diffractometer	Ccd oxford gemini diffractometer
Monochromator	graphite	graphite	graphite
Radiation, Mo Kα (Å)	0.71073	0.71073	0.71073
Temperature (K)	130	130	130
θ Range (°)	2.9-26.4	3.3–30.7	3.4–30.4
Index range	$-10 \leq h \leq 10$	$-5 \leq h \leq 5$	$-11 \leq h \leq 8$
	$-12 \leq k \leq 8$	$-7 \leq k \leq 7$	$-8 \leq k \leq 6$
	$-11 \leq l \leq 13$	$-10 \leq l \leq 10$	$-8 \leq l \leq 11$
T_{min}/ T_{max}	0.470/ 1	0.297/ 1	0.727/ 1
Number of measured reflections	6099	4662	3561
Number of independent reflections	3502	943	1156
Number of observed reflections	2961	943	1068
R_{int}	0.034	0.061	0.045

Refinement			
Refinement on	F^2	F^2	F^2
Data/restraints/parameters	3502 / 0 / 221	943 / 2 / 70	1156 / 0 / 69
$R[F^2 > 2\sigma(F^2)]$	0.033	0.020	0.032
$wR(F^2)$ [a]	0.068	0.050	0.068
Goodness-of-fit on F^2	1.002	1.04	1.11
$\Delta\rho_{min}/ \Delta\rho_{max}$ (e Å^{-3})	−1.97/ 1.39	−1.50/ 2.08	−0.59/ 0.71

[a] $w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.4067P]$ where $P = (F_o^2 + 2F_c^2)/3$

3. Results and discussion

As a continuation of ongoing studies of the optical properties of various metal salts of alkyl sulfonic acid [16–18], three compounds were prepared from the simplest possible alkyl sulfonate, methanesulfonate. The compounds **1**–**3** are obtained as crystalline solids in very good yields (81–87%). The quality of the obtained large crystals of the compounds makes them suitable for optical applications (Figure 1). All complexes were analyzed with elemental analysis to prove the composition.

Compounds **1**–**3** showed similar NMR spectra. The methyl protons of methanesulfonate group gave resonances in ^{1}H NMR spectra at 2.8 (for **1**, **3**) or 2.7 (for **2**) ppm. In ^{13}C NMR spectra chemical shift of the carbon atom was found at 41.3, 40.3 and 41.3 ppm for **1**–**3**, respectively. The upfielded chemical shifts in ^{1}H and ^{13}C NMR spectra for **2** in comparison to **1** and **3** might be due to the more covalent nature of the bonding as compared to the bonding of the other two compounds.

3.1. Optical and spectroscopic properties in the solid state

3.1.1. UV-Vis spectra

The UV-Vis spectra of single crystals are presented in Figure 2. And they were as follows: lead(II) methanesulfonate (**1**) had a maximum bandwidth of 815 nm and was transparent from 226 nm; mercury(II) methanesulfonate (**2**) had a maximum bandwidth of 818 nm and was transparent from 258 nm and strontium(II) methanesulfonate (**3**) had a maximum bandwidth of 818 nm and was transparent over the whole recorded spectral region.

The transparent spectrum of these compounds showed good overall permeability in the range 200–850 nm.
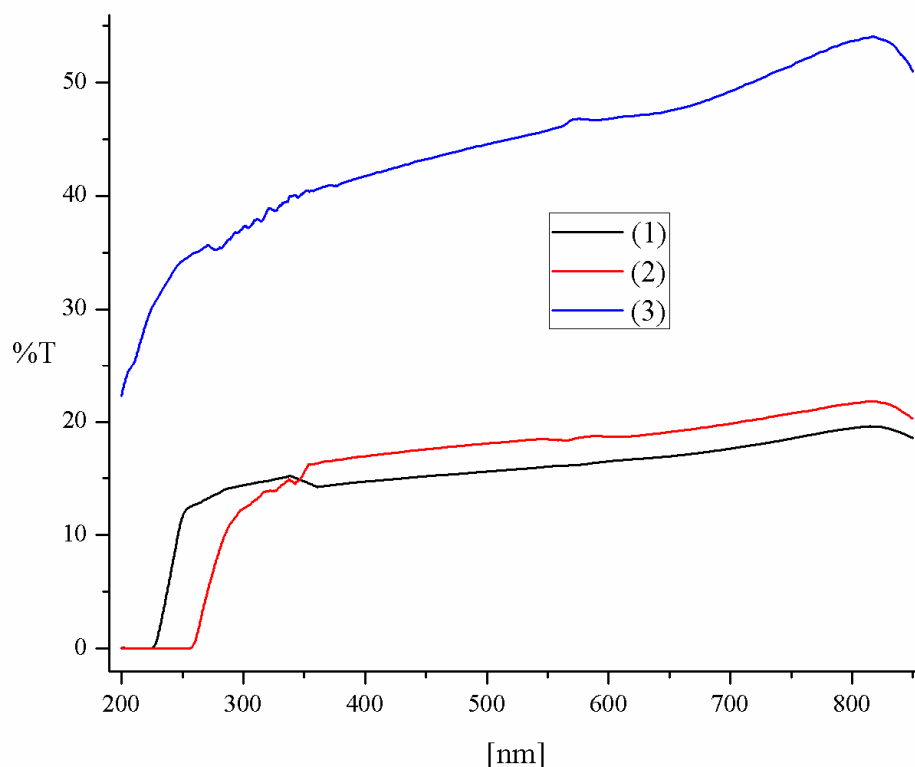
Figure 2. UV-Vis spectra of monocrystals of lead(II) methanesulfonate (**1**), mercury(II) methanesulfonate (**2**) and strontium(II) methanesulfonate (**3**)

3.1.2. NIR IR

All examined compounds were mostly transparent over the whole recorded NIR range (11000-3800 cm^{-1}). Only very weak bands (minor absorption) originating from overtones of –OH at around 5340 cm^{-1} (first overtone) and 7230 cm^{-1} (second overtone), and CH groups at around 5339 cm^{-1} (first overtone) and 7230 cm^{-1} (second overtone) could be detected.

3.1.3. MID IR

1: A broad signal from hydrogen bonded νO-H at 3358 cm^{-1} was observed. The broadening was due to strong hydrogen bonding, which was the strongest of all three studied compounds. The medium bands from νC-H at 3026 cm^{-1} (ν_{as}C-H) and 2941 cm^{-1} (ν_{s}C-H) were shifted toward

higher energy values because of bonding to the heaviest heteroatom group. The same was true for the weak peaks of δC-H at 1418 cm^{-1} (δ_{as}) and 1325 cm^{-1} (δ_{as} - umbrella bending). Strong signals in the range of 1200–1020 cm^{-1} with multiple peaks arise from asymmetric and symmetric stretch of SO_3^-. The greater number of peaks in this spectral region could be explained since this compound has of lowest symmetry compared to the others. Medium signal at 975 cm^{-1} is δO-H out-of-plane wag in hydrogen bonding dimer and the signals at 1635 cm^{-1} and 777 cm^{-1} arise from δO-H. The medium intensity peaks at 540 and 517 cm^{-1} are from coordinatively bonded water.

2: A strong signal from non-hydrogen bonded νO-H at 3512 cm^{-1} and a broad signal from hydrogen bonded νO-H at 3328 cm^{-1} were present. The medium bands at 3033 and 2947 cm^{-1} from νC-H, which were shifted toward higher energy values for the same reasons as for **1**. Deformation bands were observed as follows: medium (1613 cm^{-1}) from δO-H groups and weak (δ_{as}1426, δ_s1332 cm^{-1}) from C-H groups. The spectrum exhibited very strong bands at 1195, 1122 and 1059 cm^{-1} that originated from the $-SO_3^-$ moiety. The medium intensity peaks at 558 and 527 cm^{-1} were from water in the water-metal complex. The signals were shifted toward higher energy values because of the water molecules were coordinatively bonded to the metals.

3: Narrow strong signal from non-hydrogen bonded νO-H at 3544 cm^{-1} was observed. The weak bands at 3047 and 2965 cm^{-1}, arising from νC-H, were shifted toward higher energy values because of bonding to the heavier heteroatom group. In addition, deformation bands were observed as follows: medium (1639 cm^{-1}) from O-H groups and weak (δ_{as}1433, δ_s1319cm^{-1}) from C-H group. Very strong bands at 1202 and 1063 cm^{-1} were observed, which originated from the $-SO_3^-$ moiety (this compound has the highest symmetry of the three observed compounds hence, only 2 bands were observed in this region). Medium intensity peaks at 552 and 524 cm^{-1} arise from water in the water-metal complex. The signals were shifted toward higher energy values because of bonding to the metal.

3.1.4. FAR IR

All compounds shows a wide band at around 350 cm^{-1} that originates from δ symmetric bend of the O-S-C vibration [25] and weak signals from δO-H at around 260 cm^{-1}, attributed to free shape out-of-plane deformation.

3.2. X-ray crystallography

The construction of 1D assemblies in the crystals of the coordination polymers $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$ (**1**), $[Hg(CH_3SO_3)_2(H_2O)_2]_n$ (**2**) and $[Sr(CH_3SO_3)_2(H_2O)]_n$ (**3**) is affected by variable bonding modes of the methanesulfonate groups. As a cutoff criterion of the methanesulfonate coordination, the sum of the corresponding ionic radii provided by Shannon [26] (1.28 Å for oxygen and mercury(II) and 1.58 and 1.63 Å for strontium(II) and lead(II), respectively) was used.

In the crystal structure of **1**, each lead(II) ion is coordinated with five oxygen atoms from different methanesulfonate groups and one water molecule. The Pb1 ion is bound to O2, O3, O4, O5 and O10[a] (where "a" stands for 1–x, 1–y, 2–z) oxygens from the methanesulfonate groups and O1 water molecule at distances between 2.412(6)–2.862(5) Å (Table 2, Fig. 3).

The Pb2 ion is bound to O3, O9, O6[b], O7[c] and O13[c] (where "b" and "c" stand for 1–x, –y, 2–z and x, –1+y, z, respectively) oxygens from methanesulfonate groups and O8 water molecule at distances between 2.441(6)–2.716(6) Å (Table 2, Fig. 3). The polyhedra formed about the Pb1 and Pb2 ions are irregular in shape.

Table 2. Selected geometric parameters (Å, °) for complexes **1**, **2** and **3**.

(1)		(2)	(3)
Bond lengths			
Pb1–O1 2.412(6)	S1–O2 1.445(5)	Hg1–O1 2.299(3)	Sr1–O1^g 2.497 (3)
Pb1–O2 2.590(5)	S1–O7 1.481(6)	Hg1–O3 2.327(3)	Sr1–O3 2.542 (3)
Pb1–O3 2.623(6)	S1–O10 1.469(6)	Hg1–O4^d 2.399(3)	Sr1–O4^h 2.560 (2)
Pb1–O4 2.498(5)	S2–O3 1.483(5)	S1–O1 1.474(4)	Sr1–O2^i 2.565 (2)
Pb1–O5 2.515(6)	S2–O6 1.446(6)	S1–O2 1.446(4)	Sr1–O5 2.604 (3)
Pb1–O10^a 2.862(5)	S2–O11 1.456(6)	S1–O4 1.475(4)	S1^j–O2^j 1.458 (2)
	S3–O4 1.475(5)	S1–C1 1.762(5)	S1–O1 1.459 (3)
Pb2–O3 2.606(5)	S3–O9 1.468(6)		S1–C1 1.746 (4)
	S3–O12 1.452(6)		S2–O5 1.458 (3)
Pb2–O6^b 2.690(5)	S4–O5 1.467(6)		S2–O4 1.458 (2)
Pb2–O7^c 2.468(6)	S4–O13 1.454(5)		S2–C2 1.762 (4)
Pb2–O8 2.441(6)	S4–O14 1.465(6)		
Pb2–O9 2.716(6)			
Pb2–O13^c 2.530(6)	S1–C1 1.749(9)		
	S2–C2 1.752(9)		
	S3–C3 1.751(9)		O1^g–Sr1–O3 153.5 (1)
	S4–C4 1.741(9)		O1^g–Sr1–O4^h 83.2 (1)
Bond angles			O3–Sr1–O4^h 78.1 (1)
O1–Pb1–O2 80.4(2)		O1–Hg1–O4^e 88.6(1)	O4^h–Sr1–O4^g 89.9 (1)
O1–Pb1–O4 75.5(2)		O3–Hg1–O1 96.5(1)	O1^g–Sr1–O2 122.4 (1)
O1–Pb1–O5 84.1(2)		O3–Hg1–O1^f 83.5(1)	O3–Sr1–O2 74.2 (1)
O1–Pb1–O10^a 140.2(2)		O1^f–Hg1–O4^e 91.4(1)	O4^h–Sr1–O2 152.2 (1)
O1–Pb1–O3 80.8(2)		O3–Hg1–O4^e 92.6(1)	O4^g–Sr1–O2 83.4 (1)
O2–Pb1–O3 115.0(2)		O3–Hg1–O4^d 87.5(1)	O2–Sr1–O2^i 90.0 (1)
O2–Pb1–O4 154.9(2)	O3–Pb2–O9 111.3(2)	O1–Hg1–O1^f 180.0(1)	O1^g–Sr1–O5 70.9 (1)
O2–Pb1–O5 96.0(2)	O13^c–Pb2–O9 71.4(2)	O4^e–Hg1–O4^d 180.0(1)	O3–Sr1–O5 135.6(1)
O2–Pb1–O10^a 135.5(2)	O7^c–Pb2–O9 158.2(2)	O3–Hg1–O3^f 180.0(1)	O4^g–Sr1–O5 128.4(1)
O3–Pb1–O4 67.8(2)	O2–S1–C1 107.3(4)	O1–S1–O2 112.9(2)	O2–Sr1–O5 74.9 (1)
O3–Pb1–O5 142.3(2)	O7–S1–C1 107.5(4)	O2–S1–O4 111.2(2)	
O3–Pb1–O10^a 69.1(2)	O10–S1–C1 106.8(4)	O1–S1–O4 111.7(2)	
O4–Pb1–O5 75.0(2)	O2–S1–O7 112.0(4)	O2–S1–C1 108.0(2)	
O5–Pb1–O10^a 104.1(2)	O2–S1–O10 112.1(3)	O1–S1–C1 105.1(2)	O2–S1–O2^k 111.9(2)
O4–Pb1–O10^a 69.5(2)	O7–S1–O10 110.8(4)	O4–S1–C1 107.5(2)	O2–S1–O1 111.3(1)
	O3–S2–C2 104.7(4)		O2–S1–C1 107.7(1)
	O6–S2–C2 106.4(4)		O1–S1–C1 106.7(2)
	O11–S2–C2 108.6(4)		O5–S2–O4 112.5(1)
	O3–S2–O6 113.9(3)		O4^i–S2–O4 112.6(2)
	O3–S2–O11 109.3(3)		O5–S2–C2 105.9(2)
	O6–S2–O11 113.5(4)		O4–S2–C2 106.3(1)
	O12–S3–C3 107.2(4)		
	O9–S3–C3 106.8(4)		
	O4–S3–C3 107.7(4)		
	O9–S3–O4 109.0(3)		
	O12–S3–O4 113.2(3)		
	O12–S3–O9 112.6(4)		
	O13–S4–C4 109.0(4)		
	O14–S4–C4 106.0(4)		
O6^b–Pb2–O9 103.8(2)	O5–S4–C4 105.9(4)		
O8–Pb2–O6^b 140.9(2)	O13–S4–O14 112.7(3)		
O8–Pb2–O7^c 77.7(2)	O13–S4–O5 112.1(4)		
O8–Pb2–O13^c 72.2(2)	O14–S4–O5 110.8(4)		
O7^c–Pb2–O13^c 91.8(2)			
O8–Pb2–O3 77.1(2)			
O7^c–Pb2–O3 75.7(2)			
O13^c–Pb2–O3 148.8(2)			
O7^c–Pb2–O6^b 84.1(2)			
O13^c–Pb2–O6^b 74.1(2)			
O3–Pb2–O6^b 131.2(2)			
O8–Pb2–O9 83.7(2)			

Symmetry codes: a = 1−x, 1−y, 2−z; b = 1−x, −y, 2−z and c = x, −1+y, z for (**1**), d = 1+x, y, z; e = 1−x, −y, 2−z and f = 2−x, −y, 2−z for (**2**) and g = 2−x, 1−y, 2−z; h = 2−x, 1/2+y, 2−z; i = x, 3/2−y, z; j = x, 1+y, z and k = x, 1/2−y, z for (**3**).
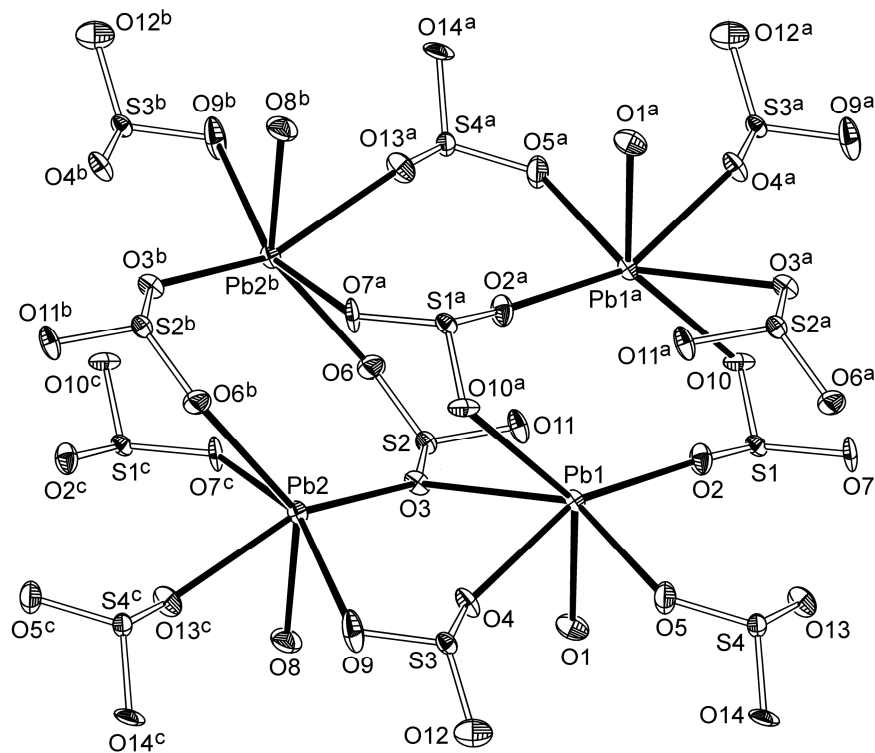
Figure 3. Perspective view of the crystal structure of (**1**) showing the coordination environment of Pb1 and Pb2 and the system of fused rings generated by bridging methanesulfonate groups. The thermal ellipsoids are shown at the 50 % probability level. The hydrocarbon groups are omitted for clarity. Symmetry codes: a = 1–x, 1–y, 2–z, b = 1–x, –y, 2–z and c = x, –1+y, z.

The Pb1 and Pb2 ions and the respective atoms at the symmetry equivalent positions 1–x, 1–y, 2–z and 1–x, –y, 2–z are bridged through methanesulfonate groups S1 and S2, thereby forming centrosymmetric eight-membered rings (Pb1–O2–S1–O10–)$_2$ and (Pb2–O3–S2–O6–)$_2$ around the symmetry centers at ½ ½ 0 and ½ 0 0, respectively (Fig. 3). The connectivity between the Pb1 and Pb2 centers from neighboring centrosymmetric eight-membered rings is acquired through a common oxygen atom (O3 from S2) and through a tridentate bridging methanesulfonate group (S1). The coordination of O7 (S1) to Pb2 at x, 1+y, z and O3 to both Pb1 and Pb2 enables the formation of a non-centrosymmetric eight-membered ring (Pb1–O3–S2–O6–Pb2^b–O7^a–S1^a–O10^a–), which shares two common edges with (Pb1–O2–S1–O10–)$_2$ and

three edges with the other centrosymmetric ring (Pb2–O3–S2–O6–)$_2$. The Pb1 and Pb2 ions are additionally bridged by the methanesulfonate groups S3 and S4, which act as bridging bidentate ligands. As a result, additional rings (six- and eight-membered rings) are formed, which together with the above-mentioned eight-membered rings constitute a system of fused rings (Fig. 3). The system of fused rings expand parallel to the *b*-direction, building a columnar motif based on the eight-membered rings [(Pb1–O2–S1–O10–)$_2$, (Pb2–O3–S2–O6–)$_2$ and Pb1–O3–S2–O6–Pb2^b–O7^a–S1^a–O10^a–] (Fig. 4).
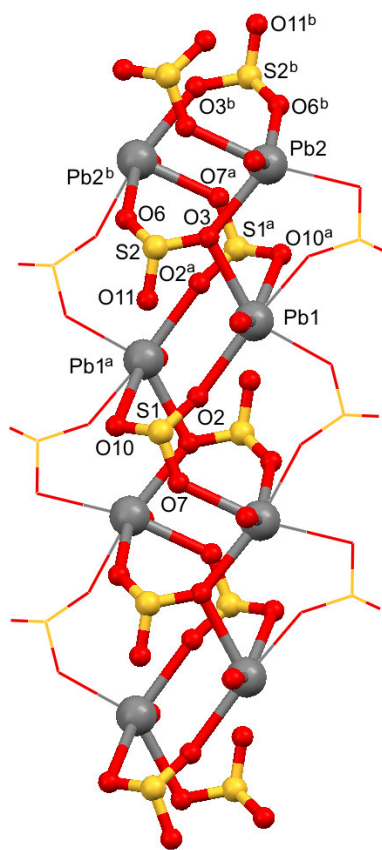
Figure 4. A view of the columnar motif observed in the crystal structure of compound **1**. The hydrocarbon groups are omitted for clarity.

Coordinated water molecules (O1 and O8) are involved in strong intermolecular hydrogen bonding with the oxygen atoms from methanesulfonate groups (Table 3 lists the O···O contacts). The neighboring 1D polymeric chains of [Pb$_2$(CH$_3$SO$_3$)$_4$(H$_2$O)$_2$]$_n$ are connected *via* O···O hydrogen bonds that involve coordinated water molecules as hydrogen bond donors and methanesulfonate oxygens as acceptors, thereby forming a 2D assembly parallel to the (1 0 0) lattice plane (Fig. 5a and Table 3). Furthermore, the lateral methyl groups, serving as hydrogen

bond donors, are involved in non-classical hydrogen bonds with methanesulfonate oxygens, serving as acceptors (C2-H2C···O11 and C3-H3A···O9), thereby furnishing a 3D supramolecular network of $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$ (Fig. 5b and Table 3).

(a)

(b)
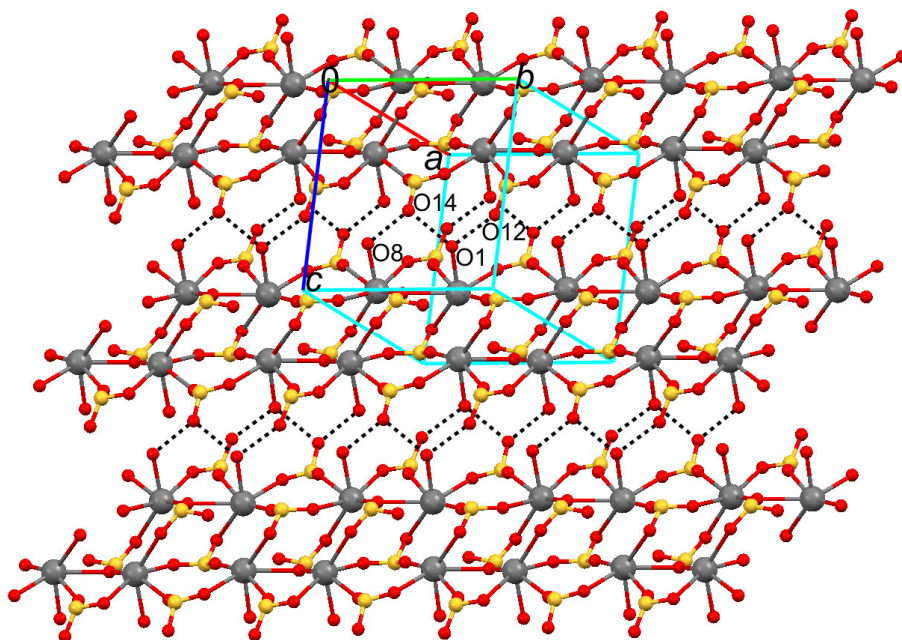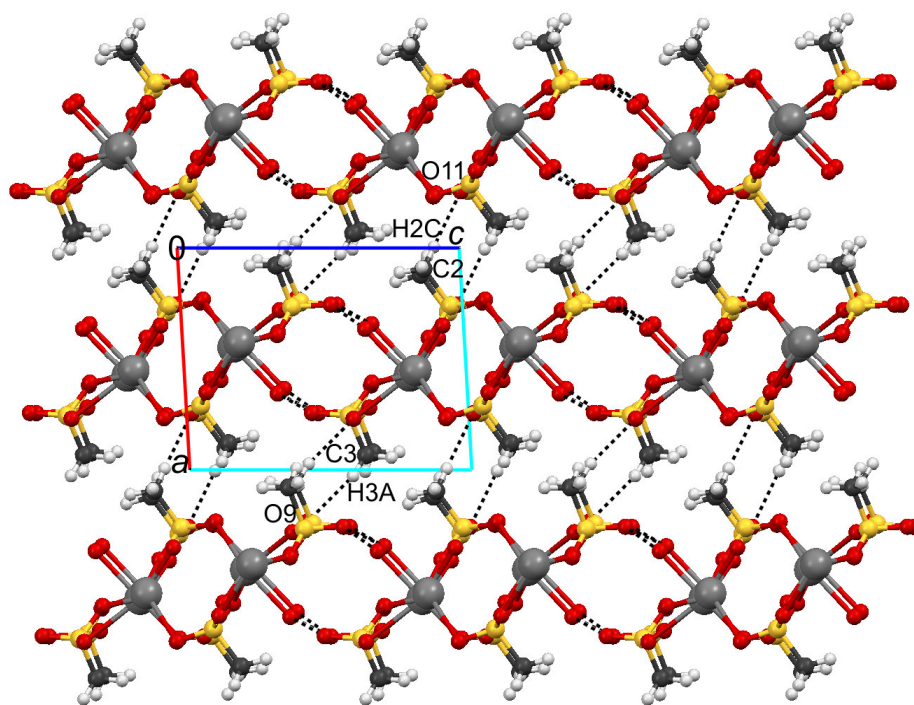
Figure 5. (a) The 2D assembly of $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$ parallel to (1 0 0) generated by O···O intermolecular hydrogen bonding. (b) A view along the [0 1 0] direction illustrates the non-classical hydrogen bonding between successive 2D assemblies of $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$. Donor-acceptor contacts are presented with dashed lines.

Table 3. Hydrogen bond parameters (Å, °) for complexes **1**, **2** and **3**.

Donor...Acceptor (symmetry code)			D···A (Å)	
(1) − classical H-bonds				
O1···O12 (1−x, 1−y, 1−z)			2.751(8)	
O1···O14 (1−x, 1−y, 1−z)			2.754(9)	
O8···O14 (1−x, 1−y, 1−z)			2.765(8)	
Donor−H...Acceptor (symmetry code)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
(1) − non-standard H-bonds				
C1−H1A···O12 (1−x, 1−y, 1−z)	0.98	2.42	3.357(11)	159
C2−H2C···O11 (−x, 1−y, 2−z)	0.98	2.41	3.385(11)	175
C3−H3A···O9 (2−x, −y, 1−z)	0.98	2.49	3.455(11)	167
C3−H3B···O10 (1−x, 1−y, 2−z) (intra)	0.98	2.52	3.319(10)	139
C3−H3C···O5 (intra)	0.98	2.48	3.248(11)	136
C4−H4A···O9 (x, 1+y, z) (intra)	0.98	2.54	3.295(10)	134
C4−H4C···O6 (x, 1+y, z) (intra)	0.98	2.38	3.220(10)	143
Donor−H...Acceptor (symmetry code)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
(2) - classical H-bonds				
O3−H3A···O4 (intra)	1.0(1)	2.2(1)	3.060(5)	147(9)
O3−H3A···O4 (1−x, −1−y, 2−z)	1.0(1)	2.6(1)	3.152(5)	121(9)

Donor...Acceptor (symmetry code)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O3–H3B···O2 (2–x, –1–y, 2–z)	0.94(6)	1.78(6)	2.716(5)	172(7)
(3) - classical H-bonds				
O3–H3WA···O2 (2–x, 1–y, 3–z)	0.88(4)	2.32(3)	3.082(4)	146(2)
Donor−H...Acceptor (symmetry code)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
(3) − non-standard H-bonds				
C(1)–H(1A)···O(5) (1–x, –1/2+y, 2–z)	0.98	2.48	3.442(5)	167

In compound **2**, the coordination polyhedron about Hg1 is described as a nearly regular octahedron with four in-plane coordinated sulfonate oxygens O1, O4^d (d = 1+x, y, z), O4^e (e = 1–x, –y, 2–z), and O1^f (f = 2–x, –y, 2–z), and two out-of-plane coordinated water molecules O3 and O3^f (Fig. 6).
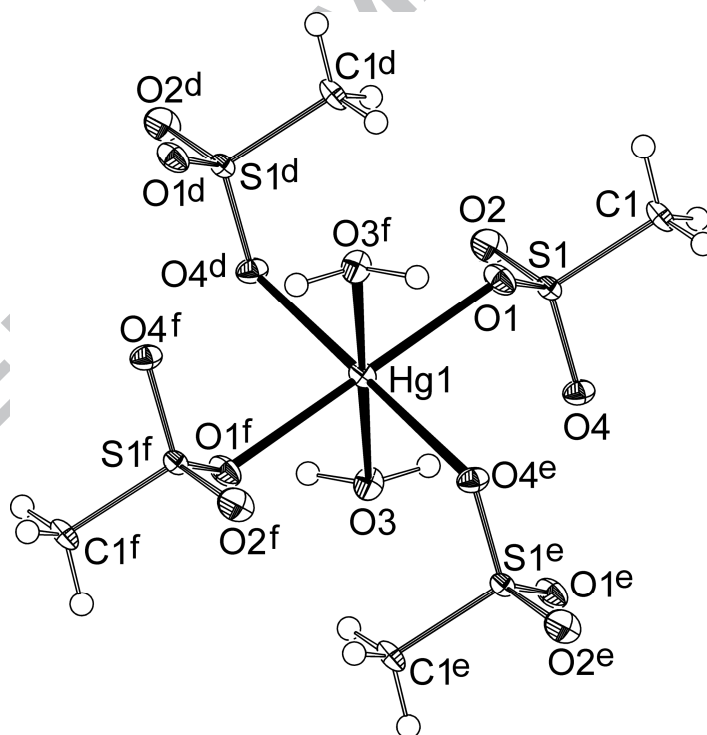
Figure 6. The coordination environment of the Hg(II) ion in [Hg(CH$_3$SO$_3$)$_2$(H$_2$O)$_2$]$_n$. Thermal ellipsoids are shown at the 50 % probability level. Symmetry codes: d = 1+x, y, z, e = 1–x, –y, 2–z and f = 2–x, –y, 2–z.

The average ΔO_h value sums to 3.5° (the average ΔO_h is defined as the mean deviation of twelve octahedral angles from the ideal 90°). The formation of a 1D assembly in (**2**) was affected by the bridging bidentate methanesulfonate group S1. The Hg1 atom lies at the inversion center (Wyckoff position 1*a*). The Hg1 and Hg1 at −1+*x*, *y*, *z* with the bridging bidentate methanesulfonate group S1 form a centrosymmetric eight-membered ring (Hg1–O1–S1–O4–)$_2$ around the symmetry center at ½ 0 0. The ring motif [(Hg1–O1–S1–O4–)$_2$] propagates in the *a*-direction forming a 1D polymeric chain. Intermolecular hydrogen bonding interactions (Table 3) between the coordinated water molecules and the oxygen atoms from methanesulfonate anions extend the polymeric chains into a 2D supramolecular network (Fig. 7).
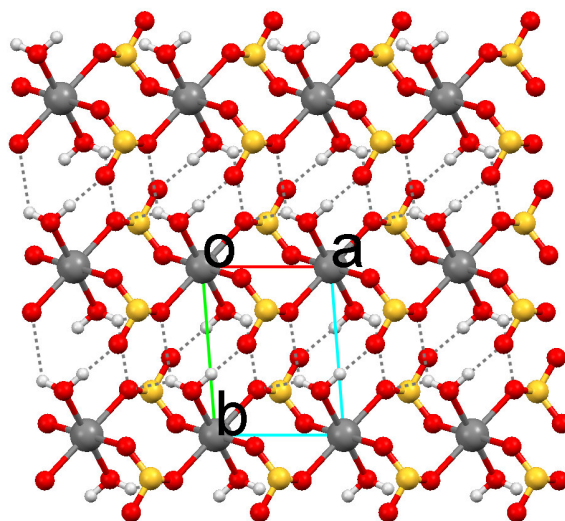
Figure 7. The 2D supramolecular network of [Hg(CH$_3$SO$_3$)$_2$(H$_2$O)$_2$]$_n$ viewed along *c*. The hydrocarbon groups are omitted for clarity.

In compound **3**, Sr1 is seven-coordinated with six oxygen atoms from methanesulfonate groups and one water molecule forming a nearly regular capped trigonal prism. The six ligating atoms: O2, O2^i, O5, O1^h, O4^h and O4^g occupy the vertices of the trigonal prism and the additional atom O3 (water molecule) is placed outside the center of the vertical rectangular face, Fig. 8.
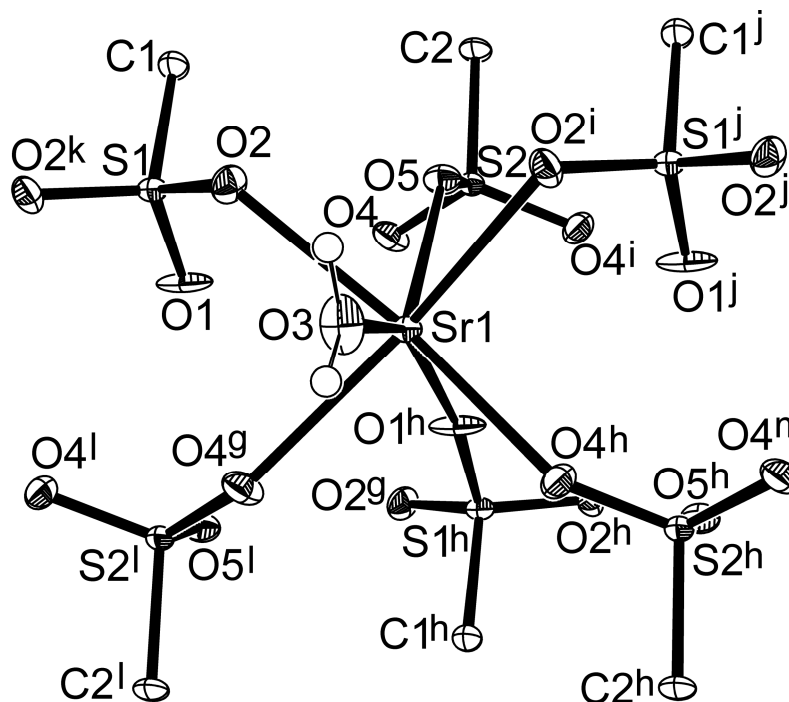
Figure 8. The coordination environment of the Sr(II) ion in $[Sr(CH_3SO_3)_2(H_2O)]_n$. Thermal ellipsoids are shown at the 50 % probability level. Symmetry codes: g = 2–x, 1–y, 2–z; h = 2–x, 1/2+y, 2–z; i = x, 3/2–y, z; j = x, 1+y, z; k = x, 1/2–y, z, l = 2–x, −1/2+y, 2–z and m = 2–x, 2–y, 2–z.

The central metal ion (Sr1), C–S–O atoms from methanesulfonate groups (C1, S1, O1, C2, S2 and O5) and coordinated water molecule (O3) lie in the mirror plane of symmetry (Wyckoff position 2e). Three strontium ions Sr1, Sr1^h and Sr1^l (h and l stand for 2–x, 1/2+y, 2–z and 2–x, −1/2+y, 2–z, respectively) with bridging tridentate methanesulfonate groups (S1^h and S2) form a system of fused rings analogous to bicyclo[3.3.3]undecane, which has a mirror plane of symmetry passing through S1^h, O1^h, Sr1, O5 and S2. The system of fused rings propagates in the b-direction forming a 1D polymeric chain (Fig. 9a).
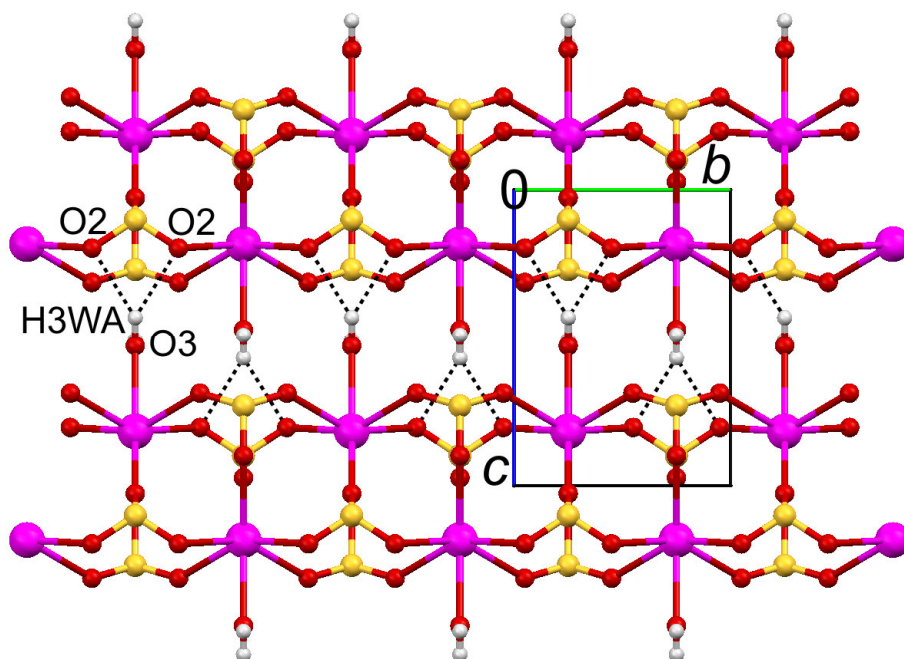
(a)
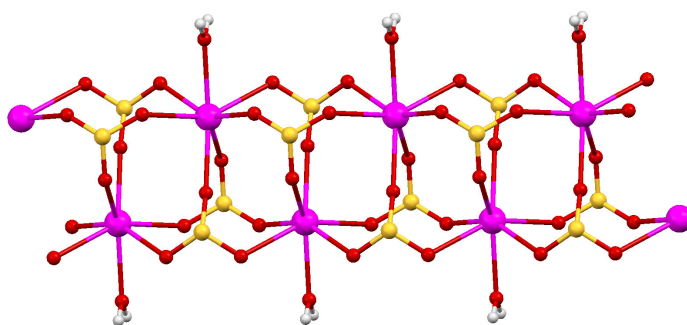
(b)

Figure 9. Packing diagram of **3** showing (a) 1D assembly generated by bridging tridentate methanesulfonate groups.
(b) 2D assembly parallel to (1 0 0) generated by O−H···O hydrogen bonding. The hydrocarbon groups are omitted
for clarity.

In the crystal structure of compound **3**, the 1D polymeric chains are self-assembled into a 2D layer parallel to (1 0 0) *via* O–H···O hydrogen bonds between the coordinated water molecules and methanesulfonate oxygens (Fig. 9b and Table 3). The non-classical hydrogen bonds C–H···O that involve lateral methyl groups as hydrogen bond donors and methanesulfonate oxygens as hydrogen bond acceptors serve to furnish a 3D supramolecular network of $[Sr(CH_3SO_3)_2(H_2O)]_n$.

4. Conclusions

The studied coordination polymers $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$ (**1**), $[Hg(CH_3SO_3)_2(H_2O)_2]_n$ (**2**) and $[Sr(CH_3SO_3)_2(H_2O)]_n$ (**3**) were obtained as large single crystals. The metal centers in **1**, **2** and **3** are connected *via* bridging methanesulfonate groups into 1D polymeric chains. In the crystals of **1** and **3**, the 1D polymeric chains are assembled into a 3D supramolecular network by a system of intermolecular hydrogen bonds, while in **2**, the system of intermolecular hydrogen bonds generates a 2D supramolecular network. The 1D polymeric chains observed in **1**, **2** and **3** are of different topology. The various electromagnetic (optical) spectra of the investigated compounds showed good overall transparency over a broad spectral region, especially in the UV-Vis and NIR ranges.

Acknowledgements

Appendix A. Supplementary data

Crystallographic data for $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$ (**1**), $[Hg(CH_3SO_3)_2(H_2O)_2]_n$ (**2**) and $[Sr(CH_3SO_3)_2(H_2O)]_n$ (**3**) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publications CCDC 934299–934301. A copy of the data can be obtained, free of charge, *via* www.ccdc.cam.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

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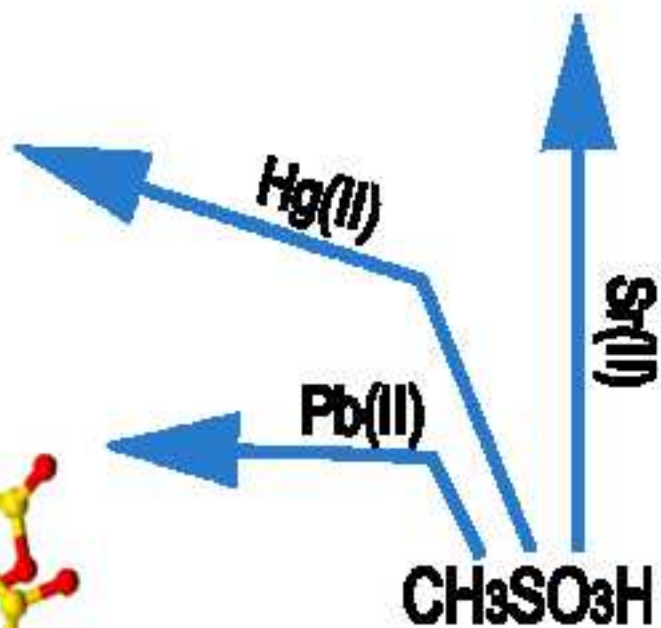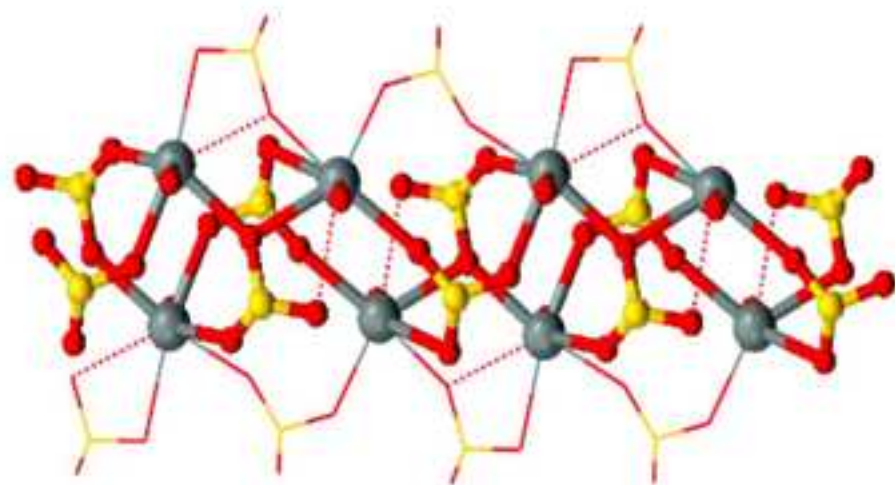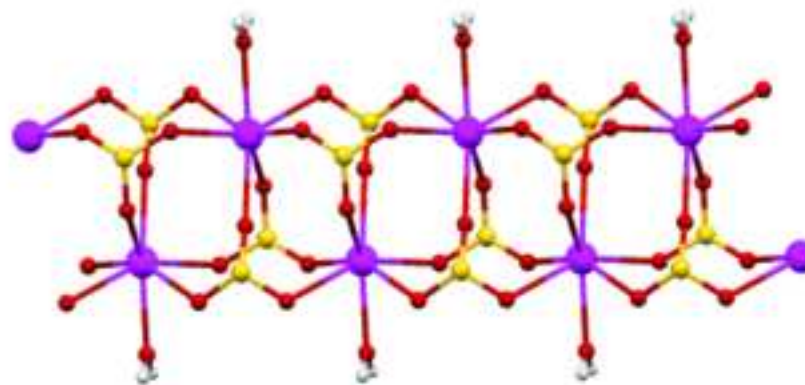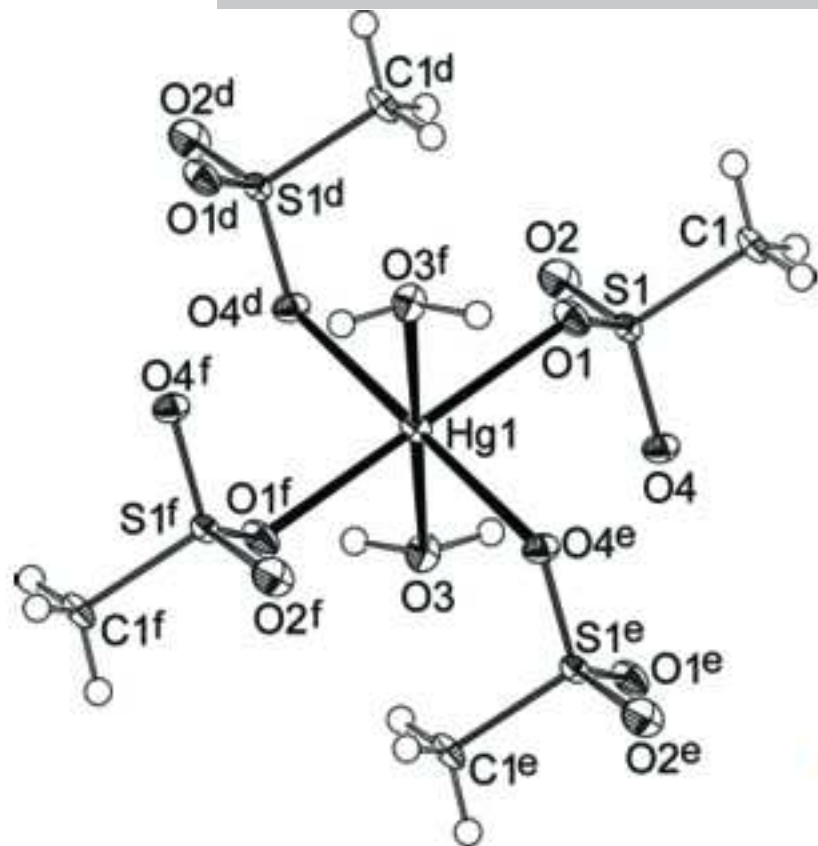
Three new 1D coordination polymers, $[Pb_2(CH_3SO_3)_4(H_2O)_2]_n$, $[Hg(CH_3SO_3)_2(H_2O)_2]_n$ and $[Sr(CH_3SO_3)_2(H_2O)]_n$, were synthesized as large single crystals. The low price of starting materials and the facile methods used for the preparation of title compounds and their UV-Vis and broad range IR spectrums imply the studied compounds could potentially be used as optical materials.