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Synthesis and spectroscopic properties of large single-crystals of Pb(II), Hg(II) and Sr(II) methanesulfonato 1D coordination polymers

Milena Đorđević [a], Dejan Jeremić [a,*], Goran N. Kaluđerović [b], Santiago Gómez-Ruiz [c], Boban Anđelković [a], Dušanka Radanović [d], Ilija Brčeski [a]

[a] Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, 11000 Belgrade, Serbia
[b] Department of Bioorganic Chemistry, Leibniz Institute of Plant Biochemistry, Weinberg 3, D-06120 Halle (Saale), Germany
[c] Departamento de Química Inorgánica y Analítica, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain
[d] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, P.O. Box 815, 11000 Belgrade, Serbia

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

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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.

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 $[Mg(H_2O)_6]\cdot(CH_3SO_3)_2\cdot 6H_2O$ [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, 4000–400 and 700–240 cm^{-1} using the

* Corresponding author. Tel.: +381 113336737.
E-mail address: djeremic@chem.bg.ac.rs (D. Jeremić).

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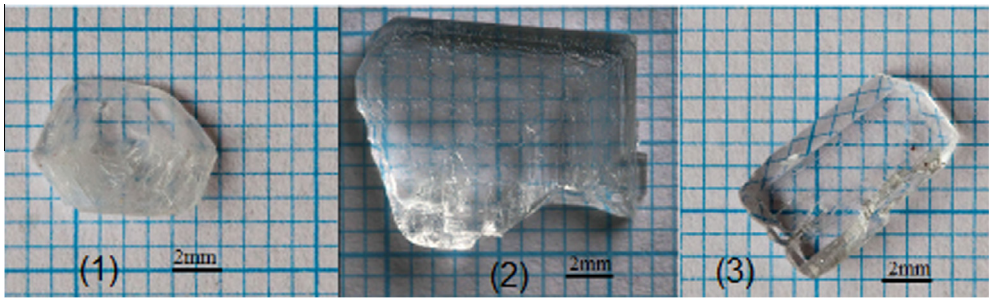

Fig. 1. Photographs of (**1**) lead(II), (**2**) mercury(II) and (**3**) strontium(II) methanesulfonate crystals.

ATR technique with a Smart Orbit accessory (diamond crystal). Elemental analyses were realized with an Elemental Vario EL III microanalyser. The ^{1}H 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 ^{1}H and ^{13}C chemical shifts were scaled relative to the chemical shifts of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.

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 (Å^3)	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 (mm^3)	0.1 × 0.03 × 0.02	0.13 × 0.02 × 0.02	0.2 × 0.03 × 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
T (K)	130	130	130
θ Range (°)	2.9–26.4	3.3–30.7	3.4–30.4
Index range	$-10 \leqslant h \leqslant 10$ $-12 \leqslant k \leqslant 8$ $-11 \leqslant l \leqslant 13$	$-5 \leqslant h \leqslant 5$ $-7 \leqslant k \leqslant 7$ $-10 \leqslant l \leqslant 10$	$-11 \leqslant h \leqslant 8$ $-8 \leqslant k \leqslant 6$ $-8 \leqslant l \leqslant 11$
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 (GOF) 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 $P = (F_o^2 + 2F_c^2)/3$.

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 min. 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 (Fig. 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%. ^{1}H NMR

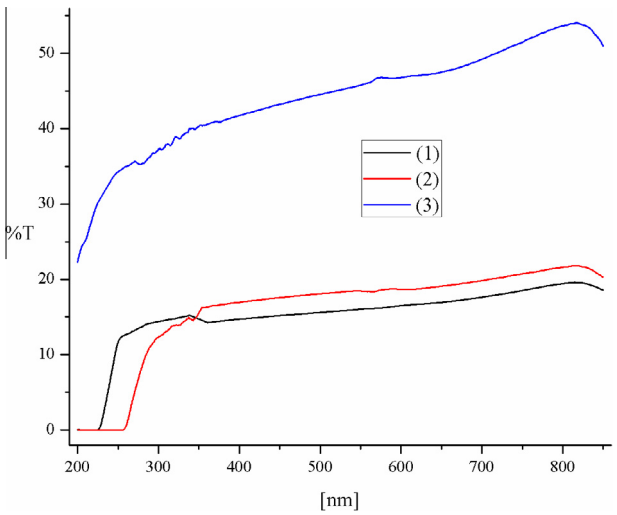

Fig. 2. UV–Vis spectra of monocrystals of lead(II) methanesulfonate (**1**), mercury(II) methanesulfonate (**2**) and strontium(II) methanesulfonate (**3**).