Synthesis and XRPD studies of new barium dicarboxylates

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New salts of barium with dicarboxylic acids (glutaric, adipic, pimelic, suberic, sebacic, and dodecanedioic) were synthesized and characterized by powder diffraction techniques. In addition to the basic crystallographic data and chemical analyses of barium glutarate hexahydrate {1}, barium adipate {2}, barium pimelate {3}, barium disuberate {4}, barium sebacate {5}, and barium dodecanedioate {6}, the processes of their thermal decomposition were investigated by XRPD. All the compounds decompose to barium carbonate at temperatures between 400 and 500 °C. © *2011 International Centre for Diffraction Data.* [DOI: 10.1154/1.3548073]

Key words: XRPD, high-temperature XRPD, indexing of powder pattern

I. INTRODUCTION

Synthesis and study of new salts of dicarboxylic acids with metals can lead to new types of structures, which are of interest for the crystal engineering and practical applications. Compounds of this type can form layered materials, three-dimensional micro- and macroporous systems. Properly selected dicarboxylic acids may be substrates used in the synthesis of complex three-dimensional hierarchical materials. The poor solubilities of such salts of certain metals, e.g., calcium, may lead to practical applications in chemical analysis, ecology, and industry. In crystallographic databases CSD (Version 5.31, Nov. 2009), there are 28 entries describing uranium compounds of dicarboxylic or polycarboxylic acids (Borkowski and Cahill, 2006); similar salts of other heavy metal elements (e.g., Np) are also quite numerous.

The compounds obtained by us are similar to metal organic framework (MOF) materials, created by dicarboxylic acids and transition metals. Increasing interest in MOF materials is connected with their possible use similar to zeolites, including sorption and separation of gases, ion exchange, and catalytic properties. This paper presents synthesis and diffraction data for six new salts of barium and selected dicarboxylic acids with the number of carbon atoms from 5 to 12. The obtained salts were examined at room and elevated temperatures by powder diffraction methods.

II. EXPERIMENTAL

A. Synthesis

To synthesize six new compounds of barium—glutaric, adipic, pimelic, suberic, sebacic, and dodecanedioic acids—0.005 mol of barium carbonate and 0.005 mol of appropriate dicarboxylic acid were dissolved in 50 ml of water. In each synthesis, the solution was first boiled for 1 h. The hot solution was then filtered and left for crystallization. After about 24 h, white precipitates crystallized from each solution. The precipitates were filtered off, washed with warm mixture of water and propanol (1:1), and finally dried in air.

B. Diffraction measurements

The powder diffraction data were collected at room temperature using a Panalytical X'pert PRO MPD diffractometer working in the Bragg-Brentano geometry in the 2θ range from 4.0 (or 5.0) to 60°2θ with a step size of 0.02°2θ and 2.15 to 80 s/step. Radiation types Cu $K\alpha$ (1.541 87 Å) for compounds {1,3,4} and Cu Ka_1 (1.540 56 Å) for compounds {2,5,6} were used. Other experimental details are generator conditions of 40 kV, 30 mA, fixed divergence slit of 1/4°, secondary monochromator, and a PIXCEL detector. A rotated back-loaded sample was used during an XRPD measurement. Peak positions were determined with the use of the second derivative method using the program written by Sonneveld and Visser (1975). The unit-cell parameters were determined using indexing programs of the PROSZKI package (Łasocha and Lewiński, 1994).

In the case of barium glutarate {1}, pimelate {3}, suberate {4}, and sebacate {5}, additional *in situ* X-ray diffraction investigations of thermal decomposition were performed. The *in situ* measurements were carried out in air at a temperature range from 27 to 600 °C in the 2θ range from 4.0 to 60°2θ, with a step size of 0.025°2θ and count time of 1.35 s/step. The X-ray radiation source was a Cu tube. The XRPD vs temperature investigations were carried out using an X'pert PRO diffractometer equipped with an XRK 900 (Anton Paar) reaction chamber.

III. RESULTS AND DISCUSSION

A. Room-temperature XRPD analysis

Figure 1 shows X-ray diffraction patterns for all six investigated compounds and XRPD data for the compounds

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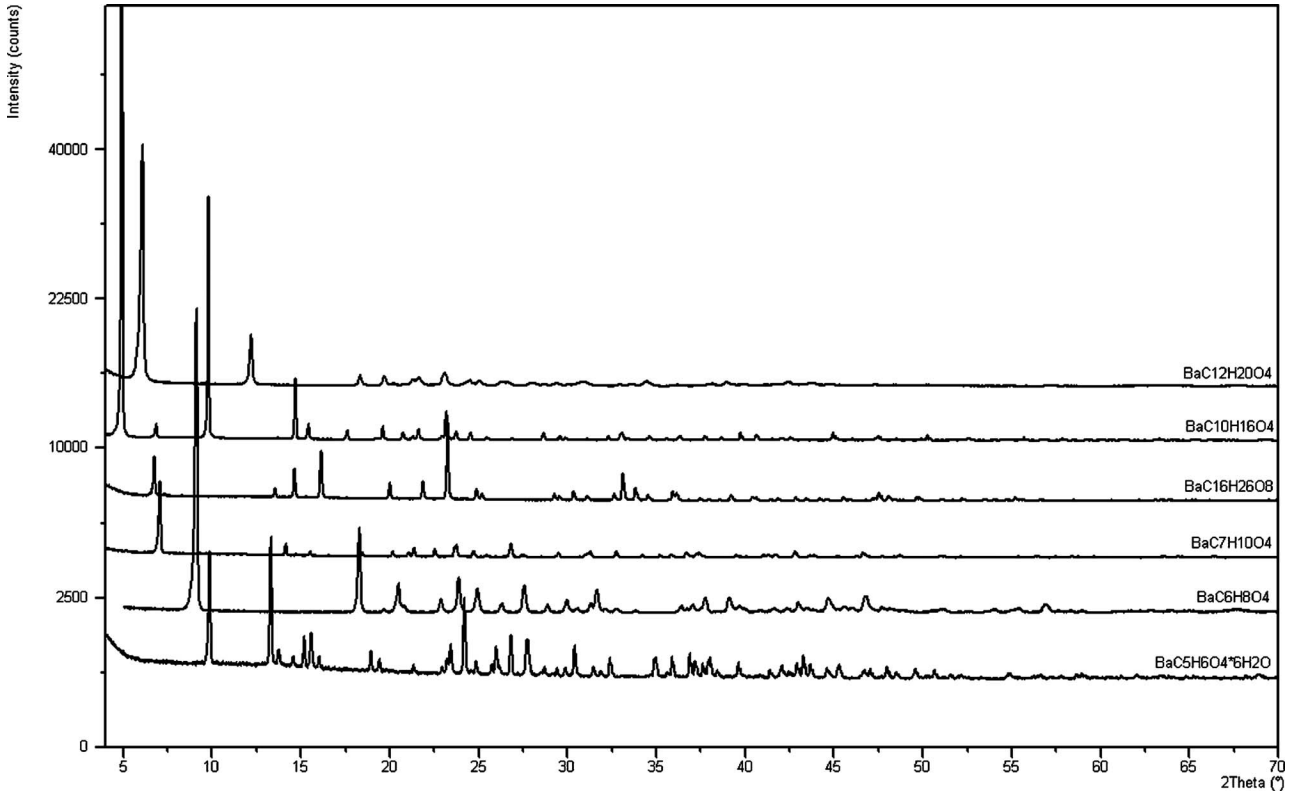

Figure 1. Diffraction patterns for barium dicarboxylates.

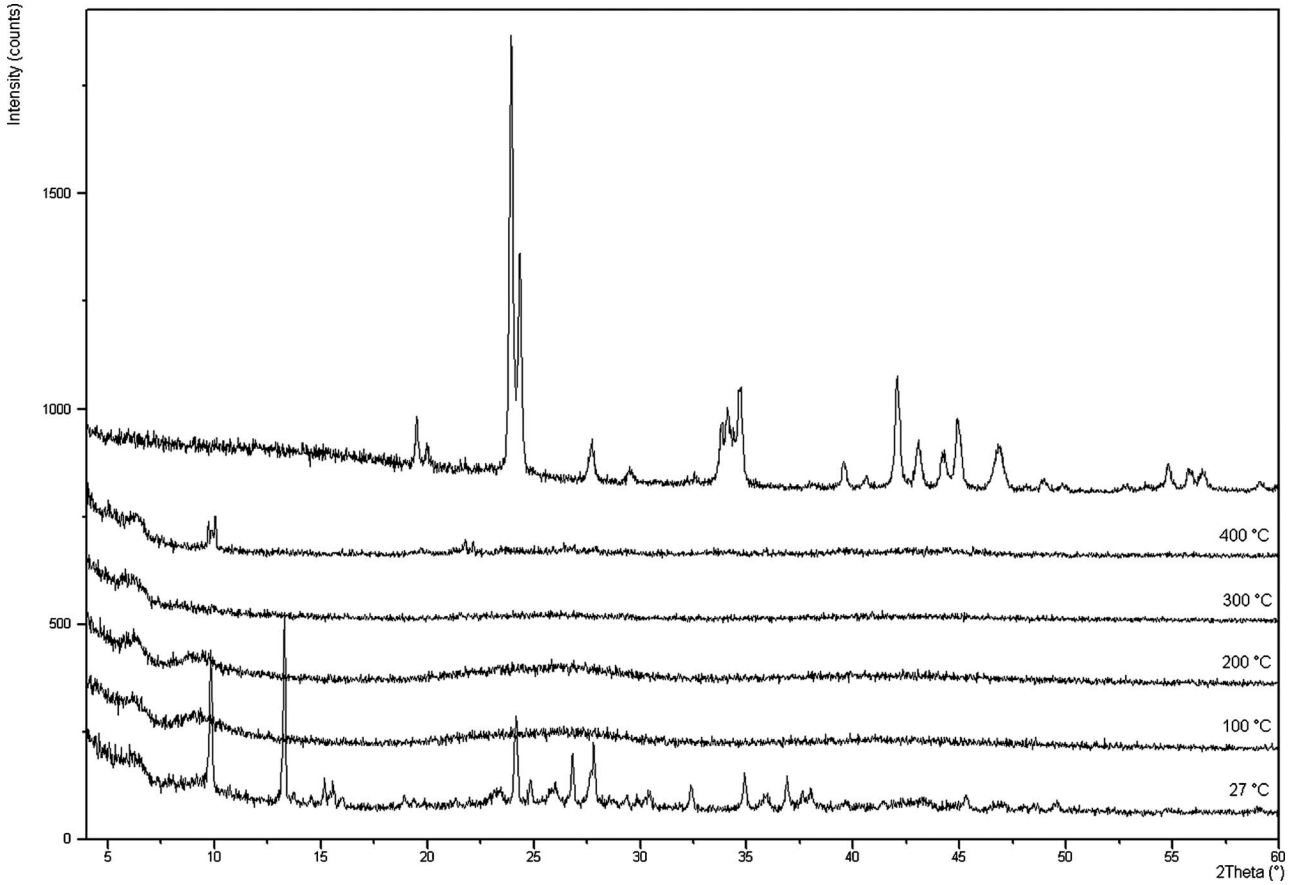

Figure 2. High-temperature XRPD patterns for $BaC_5H_6O_4 \cdot 6H_2O$ {1}.

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TABLE I. Powder diffraction data for $BaC_5H_6O_4 \cdot 6H_2O$ {1}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
9.851	9.855	78	8.9713	8.9682	1	0	1	−0.004
13.307	13.309	100	6.6481	6.6472	0	0	2	−0.002
13.743	13.752	7	6.4381	6.4342	0	1	1	−0.009
14.566	14.571	5	6.0762	6.0744	2	0	0	−0.005
15.179	15.181	15	5.8321	5.8314	1	0	2	−0.002
15.568	15.572	18	5.6873	5.6860	1	1	1	−0.004
16.025	16.029	5	5.5261	5.5250	2	0	1	−0.004
18.935	18.935	10	4.6829	4.6830	2	1	0	0.000
19.412	19.412	6	4.5689	4.5689	1	1	2	0.000
21.328	21.325	4	4.1626	4.1632	1	0	3	0.003
22.940	22.939	3	3.8736	3.8739	3	0	1	0.001
23.212	23.215	7	3.8288	3.8283	2	1	2	−0.003
23.421	23.420	14	3.7951	3.7954	0	1	3	0.001
24.191	24.190	52	3.6760	3.6763	0	2	0	0.001
24.541	24.553	3	3.6244	3.6228	1	1	3	−0.012
24.856	24.850	6	3.5792	3.5800	2	0	3	0.006
25.743	25.740	4	3.4578	3.4584	3	0	2	0.003
25.981	25.977	14	3.4267	3.4273	3	1	1	0.004
26.175	26.176	4	3.4017	3.4016	1	2	1	−0.001
26.801	26.802	24	3.3237	3.3236	0	0	4	−0.001
27.704	27.692	17	3.2174	3.2188	2	1	3	0.012
	27.707			3.2171	0	2	2	−0.003
27.804	27.806	9	3.2060	3.2058	1	0	4	−0.002
28.479	28.499	1	3.1315	3.1295	3	1	2	−0.020
28.686	28.682	4	3.1094	3.1099	1	2	2	0.004
29.382	29.384	4	3.0373	3.0372	4	0	0	−0.002
29.867	29.865	4	2.9891	2.9894	3	0	3	0.003
30.397	30.393	16	2.9382	2.9386	1	1	4	0.004
31.446	31.441	5	2.8425	2.8430	2	2	2	0.005
31.854	31.854	3	2.8070	2.8071	4	1	0	0.000
32.387	32.382	10	2.7620	2.7625	4	0	2	0.005
34.923	34.895	9	2.5670	2.5691	3	0	4	0.028
	34.955			2.5648	2	2	3	−0.032
35.614	35.613	2	2.5188	2.5190	3	2	2	0.001
35.891	35.886	11	2.5000	2.5004	0	1	5	0.005
36.880	36.872	13	2.4352	2.4358	2	0	5	0.008
37.185	37.182	8	2.4159	2.4162	1	2	4	0.003
37.606	37.602	7	2.3898	2.3902	5	0	1	0.004
37.913	37.911	7	2.3712	2.3714	4	1	3	0.002
38.031	38.030	8	2.3641	2.3642	1	3	1	0.000
38.416	38.414	4	2.3413	2.3415	4	2	0	0.002
39.622	39.617	8	2.2728	2.2731	5	1	1	0.005
	39.621			2.2729	2	3	0	0.001
41.394	41.389	4	2.1795	2.1798	1	0	6	0.005
	41.394			2.1795	5	1	2	0.000
41.976	41.977	4	2.1506	2.1506	2	3	2	0.000
42.091	42.097	4	2.1450	2.1447	0	3	3	−0.006
	42.101			2.1446	4	1	4	−0.009
42.445	42.454	2	2.1279	2.1275	3	1	5	−0.009
42.913	42.912	7	2.1058	2.1059	3	2	4	0.001
43.265	43.257	12	2.0894	2.0899	1	1	6	0.008
43.671	43.667	6	2.0710	2.0712	3	3	1	0.004
	43.688			2.0703	4	2	3	−0.017
44.598	44.588	4	2.0300	2.0305	2	2	5	0.010
45.250	45.213	6	2.0023	2.0039	5	2	1	0.036
	45.238			2.0029	2	1	6	0.012
	45.265			2.0017	6	0	1	−0.015
					*	*	*	
46.656	46.692	3	1.9452	1.9438	3	0	6	−0.036
47.035	47.010	4	1.9304	1.9314	6	1	1	0.025

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TABLE I. (*Continued.*)

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
	47.036			1.9304	4	1	5	−0.001
47.965	47.960	6	1.8951	1.8953	3	3	3	0.004
	47.963			1.8952	5	1	4	0.001
48.489	48.475	3	1.8758	1.8764	1	0	7	0.014
	48.483			1.8761	2	3	4	0.006
	48.514			1.8750	1	2	6	−0.025
49.550	49.531	4	1.8381	1.8389	0	1	7	0.019
	49.550			1.8382	0	4	0	0.000
50.628	50.611	4	1.8015	1.8021	0	3	5	0.017
	50.652			1.8007	1	4	1	−0.024
51.542	51.543	2	1.7717	1.7717	0	4	2	−0.001
54.819	54.783	2	1.6733	1.6743	3	1	7	0.036
58.639	58.619	2	1.5730	1.5736	6	1	5	0.020
	58.641			1.5730	4	1	7	−0.002
	58.659			1.5726	4	4	0	−0.020
58.930	58.925	2	1.5660	1.5661	2	1	8	0.005
	58.937			1.5658	3	4	3	−0.007
62.033	62.001	0.5	1.4949	1.4956	5	2	6	0.032
	62.032			1.4949	3	4	4	0.001
	62.042			1.4947	6	0	6	−0.009
63.378	63.336	2	1.4663	1.4672	2	4	5	0.042
	63.379			1.4664	1	0	9	−0.001
	63.383			1.4663	5	1	7	−0.005
68.886	68.882	3	1.3619	1.3620	1	2	9	0.004
	68.918			1.3614	5	3	6	−0.032
	68.925			1.3613	6	1	7	−0.039

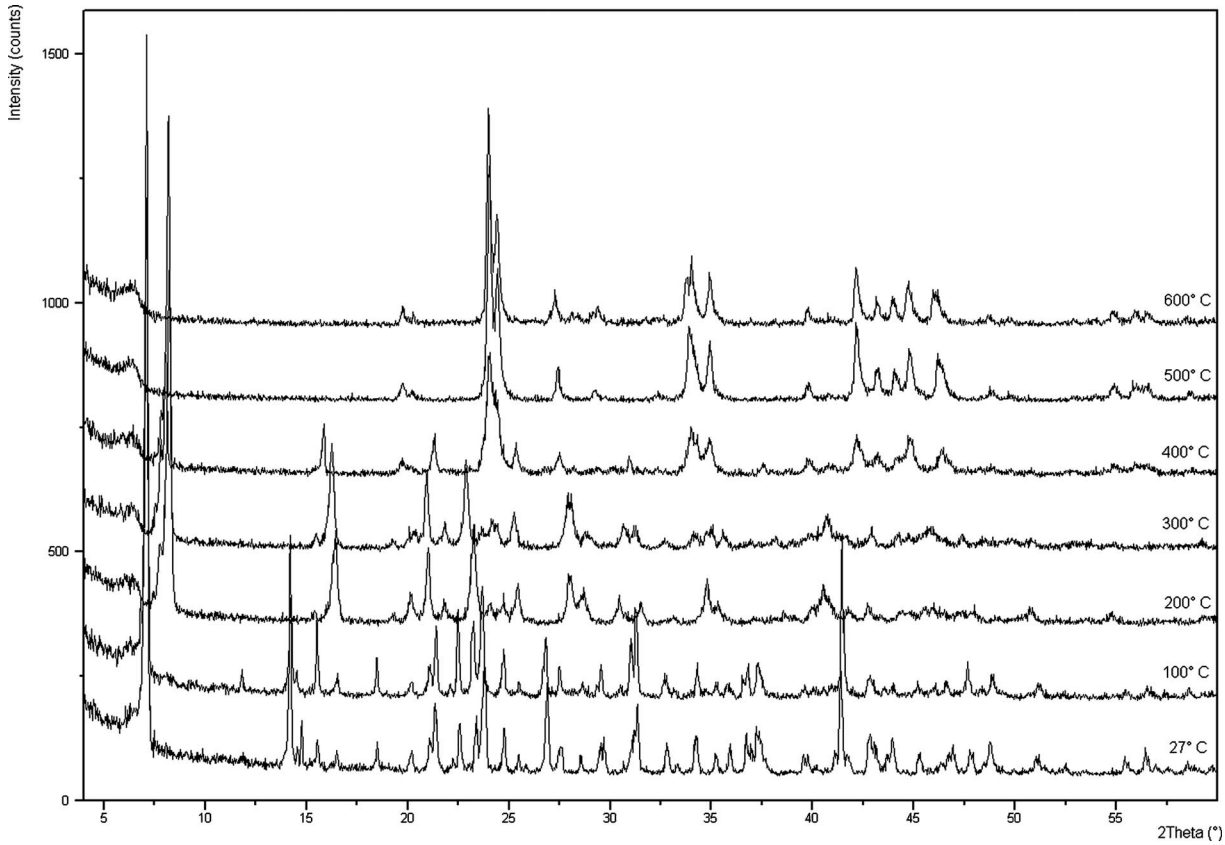

Figure 3. High-temperature XRPD patterns for $BaC_7H_{10}O_4$ {3}.

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TABLE II. Powder diffraction data for $BaC_6H_8O_4$ {2}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
9.120	9.108	100	9.6965	9.7095	0	1	0	0.012
18.285	18.274	17	4.8518	4.8548	0	2	0	0.011
19.670	19.659	0.5	4.5132	4.5156	1	0	0	0.010
20.480	20.473	5	4.3365	4.3380	−1	1	0	0.007
20.811	20.796	1	4.2682	4.2712	0	−1	1	0.014
22.884	22.874	2	3.8860	3.8878	1	1	0	0.010
23.886	23.877	6	3.7253	3.7266	0	1	1	0.008
24.936	24.939	4	3.5707	3.5703	−1	2	0	−0.004
26.302	26.290	1	3.3883	3.3898	−1	0	1	0.012
27.570	27.559	5	3.2352	3.2365	0	3	0	0.011
	27.571			3.2351	−1	−1	1	−0.001
28.867	28.860	1	3.0928	3.0935	1	2	0	0.007
29.963	29.925	2	2.9820	2.9858	1	−1	1	0.038
	29.960			2.9824	0	2	1	0.004
30.537	30.534	1	2.9274	2.9277	1	0	1	0.003
31.303	31.304	1	2.8574	2.8574	0	−3	1	−0.001
31.657	31.630	4	2.8262	2.8287	−1	3	0	0.028
	31.669			2.8252	−1	−2	1	−0.012
32.143	32.134	0.5	2.7846	2.7855	1	−2	1	0.010
32.758	32.735	1	2.7337	2.7356	−1	2	1	0.023
33.809	33.822	0.5	2.6511	2.6502	1	1	1	−0.013
36.402	36.387	1	2.4680	2.4690	1	3	0	0.015
36.699	36.705	0.5	2.4487	2.4484	1	−3	1	−0.005
37.030	37.034	1	2.4276	2.4274	0	4	0	−0.004
37.499	37.522	0.5	2.3983	2.3969	0	3	1	−0.023
37.746	37.765	2	2.3831	2.3821	−1	−3	1	−0.018
39.121	39.135	2	2.3025	2.3018	−1	3	1	−0.014
39.658	39.673	1	2.2725	2.2718	−2	1	0	−0.014
40.809	40.819	0.5	2.2111	2.2106	0	−1	2	−0.009
41.629	41.638	0.5	2.1694	2.1690	−2	2	0	−0.009
42.349	42.320	0.5	2.1342	2.1356	0	−2	2	0.029
	42.328			2.1353	−2	0	1	0.022
	42.375			2.1330	2	1	0	−0.026
42.997	42.994	1	2.1035	2.1037	1	−4	1	0.004
43.445	43.449	1	2.0828	2.0827	−1	−1	2	−0.004
	43.456			2.0824	−1	0	2	−0.011
43.839	43.826	0.5	2.0650	2.0656	−2	−1	1	0.013
44.821	44.843	1	2.0220	2.0211	1	4	0	−0.022
46.019	46.001	0.5	1.9721	1.9729	0	4	1	0.019
	46.053			1.9708	1	3	1	−0.033
46.791	46.770	3	1.9414	1.9423	−1	4	1	0.021
	46.779			1.9419	0	5	0	0.012
47.709	47.691	0.5	1.9062	1.9069	0	−5	1	0.019
48.299	48.302	0.5	1.8843	1.8842	−1	5	0	−0.002
48.879	48.878	0.5	1.8632	1.8633	0	2	2	0.001
50.529	50.512	0.5	1.8062	1.8068	1	−5	1	0.017
51.053	51.026	0.5	1.7889	1.7898	0	−4	2	0.027
54.019	53.997	0.5	1.6975	1.6981	1	5	0	0.022
	54.000			1.6981	1	4	1	0.020
55.339	55.321	0.5	1.6601	1.6606	−1	5	1	0.018
	55.341			1.6600	−2	1	2	−0.002
56.922	56.898	1	1.6176	1.6183	0	6	0	0.024
	56.924			1.6176	−2	−2	2	−0.002
58.949	58.990	0.5	1.5667	1.5658	1	−6	1	−0.041

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TABLE III. Powder diffraction data for $BaC_7H_{10}O_4$ {3}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
7.063	7.060	100	12.5051	12.5103	0	2	0	0.003
11.828	11.813	1	7.4759	7.4857	1	1	0	0.015
14.146	14.147	15	6.2556	6.2552	0	4	0	−0.001
15.499	15.494	5	5.7125	5.7143	−1	3	0	0.005
18.435	18.443	4	4.8088	4.8069	−1	1	1	−0.008
20.140	20.140	7	4.4054	4.4055	0	0	1	0.000
21.042	21.017	6	4.2185	4.2236	−1	3	1	0.025
	21.041			4.2189	−1	5	0	0.001
21.354	21.366	11	4.1576	4.1554	0	2	1	−0.012
22.530	22.534	11	3.9431	3.9426	−2	0	1	−0.004
23.631	23.642	11	3.7619	3.7603	−2	2	1	−0.011
23.747	23.753	14	3.7437	3.7428	2	2	0	−0.006
24.700	24.698	9	3.6014	3.6018	0	4	1	0.002
25.423	25.425	3	3.5006	3.5004	−1	5	1	−0.002
26.802	26.806	18	3.3235	3.3232	2	4	0	−0.004
27.390	27.398	3	3.2535	3.2527	−1	7	0	−0.008
27.536	27.537	3	3.2366	3.2366	1	1	1	−0.001
29.462	29.470	5	3.0292	3.0285	0	6	1	−0.008
30.945	30.946	4	2.8874	2.8873	−1	7	1	−0.001
31.102	31.095	4	2.8732	2.8738	−3	1	1	0.007
31.265	31.281	7	2.8585	2.8572	−2	6	0	−0.016
32.738	32.731	9	2.7332	2.7338	1	5	1	0.007
	32.739			2.7332	−3	3	1	−0.001
34.189	34.191	4	2.6205	2.6204	−1	9	0	−0.002
35.169	35.161	3	2.5496	2.5503	0	8	1	0.008
35.828	35.824	4	2.5043	2.5046	−3	5	1	0.004
	35.861			2.5021	0	10	0	−0.033
36.673	36.646	6	2.4485	2.4502	−2	8	1	0.027
	36.664			2.4491	−2	0	2	0.009
36.927	36.889	1	2.4322	2.4347	2	0	1	0.038
37.163	37.156	4	2.4173	2.4178	−1	9	1	0.007
37.278	37.234	4	2.4101	2.4129	−1	1	2	0.044
	37.276			2.4103	1	7	1	0.002
37.390	37.386	7	2.4031	2.4035	−2	2	2	0.004
37.611	37.607	3	2.3895	2.3898	2	2	1	0.004
39.483	39.483	3	2.2804	2.2805	−2	4	2	0.000
39.715	39.694	2	2.2676	2.2689	2	4	1	0.021
40.058	40.025	2	2.2490	2.2509	−3	1	2	0.033
	40.065			2.2487	−3	7	1	−0.007
41.017	41.045	3	2.1986	2.1972	−4	0	1	−0.028
41.303	41.293	4	2.1841	2.1846	−1	11	0	0.010
41.608	41.597	3	2.1688	2.1694	0	2	2	0.011
41.733	41.703	3	2.1625	2.1641	−4	2	1	0.031
42.779	42.770	8	2.1121	2.1126	−2	10	1	0.009
	42.785			2.1118	−2	6	2	−0.006
	42.813			2.1105	3	7	0	−0.034
43.584	43.626	2	2.0749	2.0731	−4	4	1	−0.042
43.866	43.849	4	2.0622	2.0630	−1	11	1	0.017
45.183	45.156	2	2.0051	2.0063	−1	7	2	0.027
	45.198			2.0045	−3	9	1	−0.015
45.992	46.004	1	1.9717	1.9713	−4	0	2	−0.012
46.267	46.253	3	1.9606	1.9612	4	0	0	0.014
46.622	46.593	8	1.9465	1.9477	0	6	2	0.029
	46.604			1.9473	−4	2	2	0.018
46.868	46.851	2	1.9369	1.9376	4	2	0	0.017
47.702	47.708	2	1.9049	1.9048	−3	9	0	−0.006
48.359	48.373	1	1.8806	1.8801	−4	4	2	−0.014
48.668	48.673	4	1.8694	1.8692	1	13	0	−0.005
50.972	50.937	2	1.7901	1.7913	−1	13	1	0.035
52.114	52.112	2	1.7536	1.7537	−3	9	2	0.002

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TABLE III. (*Continued.*)

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
52.406	52.394	1	1.7445	1.7449	2	10	1	0.012
	52.431			1.7438	−5	1	1	−0.025
55.331	55.341	1	1.6590	1.6588	−1	11	2	−0.010
	55.372			1.6579	1	13	1	−0.041
56.346	56.328	4	1.6315	1.6320	2	0	2	0.018
	56.344			1.6316	−1	15	0	0.002
56.598	56.580	1	1.6248	1.6253	−2	2	3	0.018
57.459	57.433	1	1.6025	1.6032	−3	11	2	0.026
	57.463			1.6024	−3	13	1	−0.004
	57.468			1.6023	−3	3	3	−0.009
58.397	58.392	3	1.5790	1.5791	2	4	2	0.005
	58.398			1.5790	−1	15	1	−0.001
58.770	58.743	1	1.5698	1.5705	3	9	1	0.027
	58.753			1.5703	−5	7	1	0.017
59.630	59.586	2	1.5492	1.5503	−1	3	3	0.044
	59.596			1.5501	−3	13	0	0.034
	59.658			1.5486	−4	2	3	−0.028
					*	*	*	
61.165	61.154	1	1.5140	1.5143	0	12	2	0.011
	61.157			1.5142	−4	4	3	0.008
61.454	61.464	2	1.5076	1.5074	−1	13	2	−0.010
62.512	62.478	1	1.4845	1.4853	1	15	1	0.034
	62.487			1.4851	−3	7	3	0.025
63.431	63.429	2	1.4652	1.4653	−3	13	2	0.002
63.674	63.701	1	1.4602	1.4597	3	11	1	−0.027
64.358	64.335	3	1.4464	1.4469	2	8	2	0.023
	64.349			1.4466	1	17	0	0.008
	64.353			1.4465	−6	0	2	0.004
66.355	66.341	2	1.4076	1.4079	−3	9	3	0.013
69.317	69.277	1	1.3545	1.3552	1	13	2	0.040
	69.291			1.3550	−5	11	2	0.026

are given in Tables I–VI. Basic crystallographic data such as unit-cell parameters, V, Z, space groups, and densities are presented in Table VII. The unit-cell parameters for compounds {1} and {4} were confirmed by single-crystal studies (Grzesiak *et al.*, 2010).

In barium glutarate {1}, infinite hybrid inorganic-organic layers are present. They are built of infinite barium-oxygen slabs connected by dicarboxylic linkers. Thanks to the single-crystal analysis, it was found that using subaric acid, barium disuberate with formula $Ba(COOC_6H_{12}COOH)_2$ was obtained. For simplicity its formula is written as $Ba(C_8H_{13}O_4)_2$ and it is named barium suberate {4}. This compound can be considered as tridimensional coordination polymer in which barium-oxygen nodes are connected by dicarboxylic linkers. Complete structural data for these compounds will be the subject of our future publications.

Most of the obtained salts crystallize as anhydrous compounds, only barium glutarate $BaC_5H_6O_4 \cdot 6H_2O$ {1} contains six water molecules. Barium suberate $Ba(C_8H_{13}O_4)_2$ {4} and barium dodecanediate $BaC_{12}H_{20}O_4$ {6} crystallize in the tetragonal system, barium glutarate hexahydrate in orthorhombic {1}, and barium pimelate $BaC_7H_{10}O_4$ {3} in monoclinic. Barium adipinate $BaC_6H_8O_4$ {2} and barium sebacate $BaC_{10}H_{16}O_4$ {5} crystallize in the triclinic system.

B. High-temperature XRPD analysis

Evolution of the diffraction patterns obtained during thermal decompositions in air is presented in Figures 2–5. The thermal decomposition study by XRPD methods of barium glutarate {1} was limited to low temperatures because during heating in higher temperatures the sample bulged, which made high-temperature XRPD measurements impossible (see Figure 2). Please note that we used the flat-sample Bragg-Brentano geometry. Diffraction data obtained for barium glutarate {1}, reloaded after thermal decomposition, show that the compound decomposed to barium carbonate.

As shown in Figure 3 for the case of barium pimelate ($BaC_7H_{10}O_4$) {3}, the thermal decomposition clearly shows that the phase of barium pimelate disappeared because of heating and is replaced by a new compound stable at a temperature range from 200 to 300 °C. At 400 °C, this compound disappears and at 500 °C barium carbonate is the only phase present in the sample. In the case of barium subarate $Ba(C_8H_{13}O_4)_2$ {4} similar observations as for barium pimelate can be made (see Figure 4).

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TABLE IV. Powder diffraction data for $BaC_{16}H_{26}O_8$ {4}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
6.753	6.757	39	13.0787	13.0713	0	0	1	−0.004
13.539	13.537	8	6.5348	6.5357	0	0	2	0.001
14.641	14.641	32	6.0453	6.0453	2	0	0	0.000
16.135	16.141	53	5.4888	5.4869	2	0	1	−0.006
19.990	19.991	17	4.4381	4.4379	2	0	2	−0.002
21.856	21.858	21	4.0633	4.0629	2	2	1	−0.002
23.246	23.246	100	3.8233	3.8234	3	1	0	0.000
24.870	24.869	11	3.5772	3.5774	2	2	2	0.001
25.171	25.174	6	3.5351	3.5347	2	0	3	−0.004
29.242	29.234	7	3.0516	3.0524	1	1	4	0.008
	29.244			3.0514	2	2	3	−0.003
29.528	29.529	5	3.0227	3.0226	4	0	0	−0.001
30.329	30.326	11	2.9446	2.9449	4	0	1	0.002
31.085	31.085	5	2.8746	2.8747	2	0	4	0.000
	31.095			2.8738	3	1	3	−0.010
32.608	32.613	7	2.7438	2.7434	4	0	2	−0.005
33.115	33.109	34	2.7030	2.7035	4	2	0	0.006
33.830	33.830	16	2.6474	2.6475	4	2	1	0.000
34.523	34.520	7	2.5958	2.5961	2	2	4	0.003
35.915	35.892	11	2.4984	2.5000	1	1	5	0.023
	35.918			2.4982	4	2	2	−0.003
36.140	36.129	9	2.4833	2.4841	3	1	4	0.011
	36.138			2.4835	4	0	3	0.002
37.447	37.450	3	2.3996	2.3995	2	0	5	−0.002
37.916	37.915	2	2.3710	2.3712	5	1	0	0.002
39.179	39.183	7	2.2974	2.2972	4	2	3	−0.004
40.403	40.411	5	2.2306	2.2302	2	2	5	−0.008
	40.435			2.2290	5	1	2	−0.031
40.621	40.626	4	2.2191	2.2190	4	0	4	−0.004
41.420	41.413	2	2.1781	2.1786	0	0	6	0.007
41.821	41.826	2	2.1582	2.1580	3	1	5	−0.004
42.835	42.801	4	2.1094	2.1111	1	1	6	0.035
	42.838			2.1093	4	4	1	−0.003
43.398	43.406	4	2.0833	2.0831	4	2	4	−0.007
	43.413			2.0827	5	1	3	−0.015
44.153	44.153	2	2.0494	2.0495	2	0	6	0.001
	44.190			2.0479	5	3	1	−0.036
44.557	44.566	2	2.0318	2.0315	4	4	2	−0.009
45.510	45.509	4	1.9914	1.9916	6	0	1	0.002
45.861	45.856	2	1.9770	1.9773	4	0	5	0.006
	45.877			1.9764	5	3	2	−0.016
47.158	47.138	3	1.9256	1.9265	3	3	5	0.020
	47.159			1.9256	6	0	2	−0.001
47.336	47.328	2	1.9188	1.9192	5	1	4	0.008
	47.335			1.9189	4	4	3	0.001
47.524	47.525	10	1.9116	1.9117	6	2	0	0.000
48.054	48.027	6	1.8918	1.8928	3	1	6	0.027
	48.062			1.8916	6	2	1	−0.008
48.379	48.395	2	1.8798	1.8793	4	2	5	−0.015
49.646	49.647	4	1.8348	1.8348	6	2	2	−0.001
49.810	49.817	2	1.8291	1.8290	6	0	3	−0.006
51.002	51.017	1	1.7891	1.7887	4	4	4	−0.015

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TABLE IV. (*Continued.*)

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
51.146	51.117	2	1.7845	1.7855	6	3	1	0.030
	51.157			1.7842	2	0	7	−0.010
52.190	52.204	2	1.7512	1.7508	5	3	4	−0.014
	52.210			1.7506	6	2	3	−0.020
53.369	53.372	1	1.7153	1.7152	6	0	4	−0.003
53.529	53.507	1	1.7105	1.7112	2	2	7	0.022
	53.552			1.7099	5	5	0	−0.023
54.009	54.013	2	1.6964	1.6963	4	2	6	−0.004
	54.045			1.6954	5	5	1	−0.036
54.698	54.656	2	1.6767	1.6779	3	1	7	0.042
	54.700			1.6767	6	4	0	−0.002
55.182	55.186	4	1.6631	1.6630	6	4	1	−0.004
55.616	55.657	1	1.6511	1.6501	6	2	4	−0.041
56.616	56.609	2	1.6243	1.6246	5	3	5	0.007
	56.628			1.6241	6	4	2	−0.012
63.073	63.086	2	1.4727	1.4725	8	0	2	−0.013
63.372	63.346	2	1.4665	1.4670	5	1	7	0.026
	63.387			1.4662	8	2	0	−0.015
63.833	63.831	2	1.4570	1.4571	8	2	1	0.002

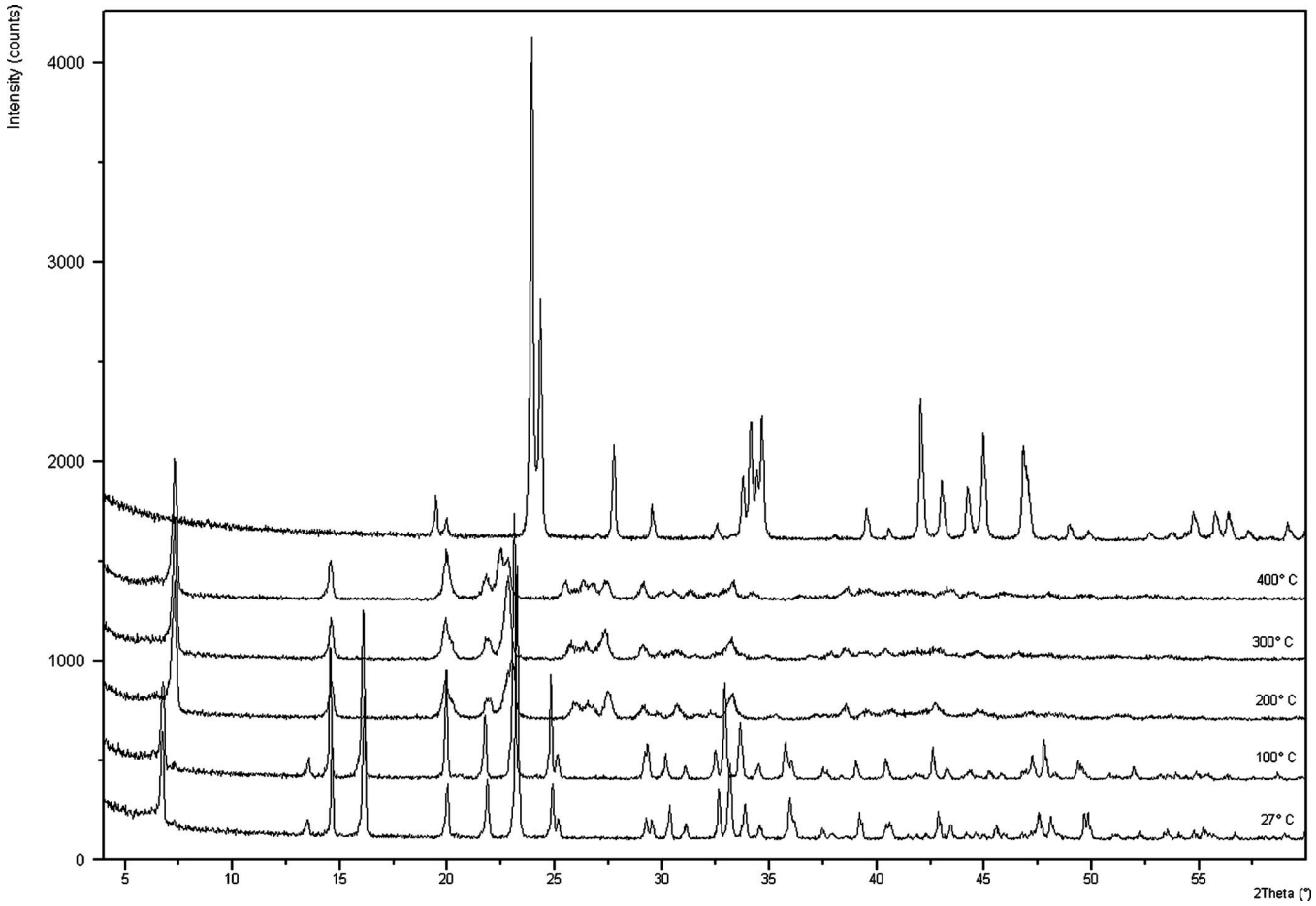

Figure 4. High-temperature XRPD for $Ba(C_8H_{13}O_4)_2$ {4}.

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TABLE V. Powder diffraction data for $BaC_{10}H_{16}O_4$ {5}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
6.066	6.090	100	14.5707	14.5138	0	1	0	−0.024
12.191	12.197	17	7.2604	7.2569	0	2	0	−0.006
18.338	18.339	3	4.8382	4.8379	0	3	0	−0.001
19.695	19.689	3	4.5078	4.5091	2	0	0	0.006
	19.722			4.5016	0	0	1	−0.028
20.250	20.212	0.5	4.3855	4.3937	−1	0	1	0.038
20.777	20.795	0.5	4.2754	4.2717	−1	1	1	−0.019
21.280	21.261	2	4.1755	4.1792	−2	2	0	0.019
21.440	21.455	2	4.1447	4.1418	−1	−1	1	−0.015
21.645	21.658	2	4.1059	4.1035	2	1	0	−0.013
23.087	23.074	4	3.8526	3.8547	−1	2	1	0.013
24.449	24.465	2	3.6410	3.6386	−2	3	0	−0.017
25.049	25.005	2	3.5551	3.5613	−2	0	1	0.044
	25.043			3.5559	2	2	0	0.005
	25.049			3.5552	−2	1	1	0.000
26.611	26.576	1	3.3499	3.3541	−2	2	1	0.034
	26.612			3.3497	0	−3	1	−0.002
	26.638			3.3466	−1	3	1	−0.027
27.921	27.917	1	3.1956	3.1960	1	2	1	0.003
28.199	28.187	0.5	3.1646	3.1661	−1	−3	1	0.013
28.730	28.694	0.5	3.1075	3.1113	−2	4	0	0.036
29.383	29.373	1	3.0399	3.0408	−2	3	1	0.009
	29.392			3.0390	2	3	0	−0.009
30.077	30.078	0.5	2.9713	2.9712	−3	2	0	−0.001
30.741	30.742	1	2.9085	2.9085	2	0	1	−0.001
31.080	31.082	1	2.8776	2.8775	−1	4	1	−0.002
32.032	32.026	0.5	2.7942	2.7948	−3	1	1	0.007
32.939	32.909	0.5	2.7193	2.7217	−2	−3	1	0.030
	32.918			2.7210	−3	2	1	0.021
33.599	33.602	0.5	2.6674	2.6672	−2	5	0	−0.003
34.379	34.382	2	2.6086	2.6085	2	4	0	−0.002
36.189	36.188	0.5	2.4822	2.4823	1	4	1	0.001
38.098	38.097	1	2.3621	2.3622	−1	−5	1	0.002
38.986	38.985	1	2.3103	2.3104	−2	6	0	0.001
39.989	39.991	0.5	2.2547	2.2546	4	0	0	−0.002
42.431	42.387	1	2.1304	2.1325	−2	−5	1	0.044
	42.392			2.1323	2	4	1	0.040
	42.409			2.1315	1	−6	1	0.023
					*	*	*	
43.726	43.712	1	2.0703	2.0709	−1	−6	1	0.014
	43.712			2.0709	−2	−2	2	0.014
44.729	44.729	0.5	2.0261	2.0261	−2	7	0	0.000
47.289	47.257	0.5	1.9223	1.9235	3	5	0	0.033
48.404	48.450	0.5	1.8805	1.8789	2	−1	2	−0.046
57.389	57.419	0.5	1.6057	1.6049	−5	−3	1	−0.030

As shown in Figure 5, barium sebacate ($BaC_{10}H_{16}O_4$) {5} is stable at a temperature range from 27 to 100 °C. It is replaced by a new unknown compound, which is stable at a temperature range from 200 to 400 °C. This compound can be tentatively indexed with another triclinic cell very similar to the original one shown in Table VII: a=9.1385, b=14.9888, c=4.6877 Å, α=99.2394, β=100.8070, γ=79.5253°, V=614.86 Å^3, and $F(20)$=18.0. This phase,

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TABLE VI. Powder diffraction data for $BaC_{12}H_{20}O_4$ {6}.

$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I (%)	d_{obs} (Å)	d_{calc} (Å)	h	k	l	$\Delta 2\theta$ (deg)
4.850	4.859	100	18.2052	18.1724	0	0	1	−0.009
9.718	9.726	78	9.0939	9.0862	0	0	2	−0.009
14.604	14.612	17	6.0606	6.0575	0	0	3	−0.008
15.330	15.346	4	5.7751	5.7694	1	1	1	−0.016
17.510	17.529	2	5.0607	5.0554	1	1	2	−0.019
19.522	19.524	4	4.5435	4.5431	0	0	4	−0.002
20.656	20.629	2	4.2965	4.3021	2	0	0	0.027
	20.675			4.2927	1	1	3	−0.019
21.194	21.206	1	4.1887	4.1864	2	0	1	−0.012
22.840	22.853	1	3.8904	3.8883	2	0	2	−0.013
23.093	23.096	8	3.8483	3.8479	2	1	0	−0.003
23.633	23.615	2	3.7616	3.7645	2	1	1	0.018
24.444	24.433	2	3.6386	3.6402	1	1	4	0.010
	24.472			3.6345	0	0	5	−0.029
25.371	25.373	0.5	3.5077	3.5075	2	0	3	−0.002
28.556	28.552	2	3.1233	3.1238	2	0	4	0.004
	28.586			3.1202	1	1	5	−0.030
29.467	29.468	1	3.0288	3.0287	0	0	6	−0.001
29.798	29.753	0.5	2.9958	3.0003	2	2	1	0.045
30.982	30.975	0.5	2.8840	2.8847	2	2	2	0.007
32.203	32.216	1	2.7773	2.7764	2	0	5	−0.013
32.899	32.891	2	2.7202	2.7209	3	1	0	0.008
	32.921			2.7185	2	2	3	−0.022
33.007	33.010	1	2.7115	2.7114	1	1	6	−0.003
33.278	33.268	0.5	2.6900	2.6909	3	1	1	0.010
34.530	34.521	1	2.5953	2.5961	0	0	7	0.009
	34.574			2.5922	3	0	3	−0.044
35.492	35.485	0.5	2.5272	2.5277	2	2	4	0.007
36.204	36.161	1	2.4791	2.4820	3	1	3	0.043
	36.243			2.4766	2	0	6	−0.039
37.639	37.641	1	2.3878	2.3878	1	1	7	−0.001
	37.663			2.3864	3	2	0	−0.024
38.550	38.537	0.5	2.3334	2.3343	3	1	4	0.013
	38.563			2.3328	2	2	5	−0.013
39.653	39.645	2	2.2710	2.2716	0	0	8	0.008
40.546	40.554	2	2.2231	2.2227	2	0	7	−0.007
41.421	41.421	0.5	2.1781	2.1782	3	1	5	0.000
41.948	41.947	0.5	2.1519	2.1521	2	1	7	0.002
	41.967			2.1511	4	0	0	−0.019
42.430	42.443	1	2.1286	2.1281	1	1	8	−0.012
44.859	44.853	2	2.0188	2.0192	0	0	9	0.006
47.406	47.401	1	1.9161	1.9164	1	1	9	0.005
50.169	50.160	1	1.8169	1.8172	0	0	10	0.009

however, will be the subject of our further investigations. At 500 °C, we observed the disappearance of diffraction pattern of this phase due to an increase in the sample volume. A control experiment performed after the end of heating (the sample was reloaded into a sample holder) showed that the sample decomposed to $BaCO_3$.

IV. CONCLUSION

Six new salts of barium and dicarboxylic acids were synthesized and characterized by X-ray powder diffraction methods. Most of the obtained salts crystallize as anhydrous compounds, and only barium glutarate {1} contains six water molecules. Barium suberate and dodecanedioate {4 and 6}

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TABLE VII. Unit-cell parameters for barium dicarboxylates.

Code formula and compound name	Crystal system, space group	Density D_x (g/cm^3)	Unit-cell data (Å)	Unit-cell data (deg)	Volume (Å^3)	Volume per non-H atom (Å^3)	Z	Figures of merit: FM value[a]	Figures of merit: de Wolff's[b]
{1} $BaC_5H_6O_4 \cdot 6H_2O$, barium glutarate hexahydrate	Orthorhombic, *Pnma*(62)	2.09	a=12.149(1) b=7.352(1) c=13.294(1)	α=90.0 β=90.0 γ=90.0	1187.5 (2)	18.5	4	203.92	74.30
{2} $BaC_6H_8O_4$, barium adipate	Triclinic, *P*-1(2)	2.365	a=4.5972(9) b=9.945(2) c=4.4592(9)	α=99.45(2) β=97.06(2) γ=96.86(2)	197.53 (4)	17.96	1	67.92	34.31
{3} $BaC_7H_{10}O_4$, barium pimelate	Monoclinic, *C*2/*m*(12)	2.025	a=8.789(1) b=25.021(3) c=4.9357(7)	α=90.0 β=116.80(1) γ=90.0	968.8 (1)	20.18	4	105.55	44.00
{4} $Ba(C_8H_{13}O_4)_2$, barium disuberate	Tetragonal, *P*-4*b*2(117)	1.68	a=12.0906(4) b=12.0906(4) c=13.0713(5)	α=90.0 β=90.0 γ=90.0	1910.8 (1)	19.11	4	122.85	64.38
{5} $BaC_{10}H_{16}O_4$, barium sebacate	Triclinic, *P*-1(2)	1.83	a=9.349(2) b=14.751(3) c=4.5942(9)	α=89.79(2) β=101.38(2) γ=100.13(2)	611.2 (1)	20.37	2	20.61	13.25
{6} $BaC_{12}H_{20}O_4$, barium dodecanedioate	Tetragonal, *P*-4*b*2(117)	1.82	a=8.604(1) b=8.604(1) c=18.172(2)	α=90.0 β=90.0 γ=90.0	1345.0 ()	19.78	4	45.23	24.33

[a]Smith and Snyder, 1979.
[b]de Wolff, 1968.

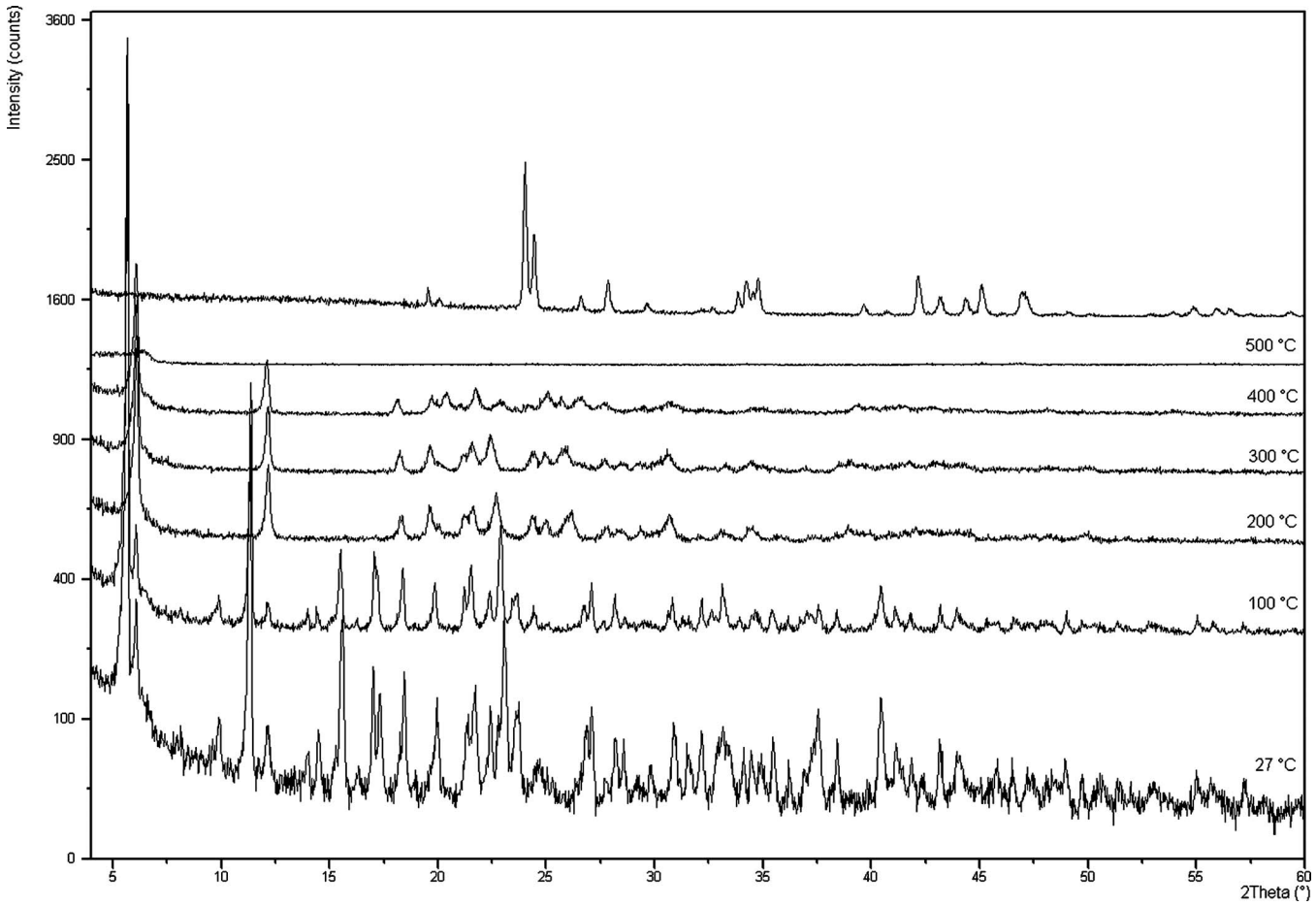

Figure 5. High-temperature XRPD for $BaC_{10}H_{16}O_4$ {5}.

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crystallize in the tetragonal system, barium glutarate hexahydrate {1} in the orthorhombic system, barium pimelate {3} in monoclinic, and barium adipinate and sebacate {2 and 5} in the triclinic system.

During the thermal treatment all the compounds decompose to barium carbonate at temperatures between 400 and 500 °C. Investigations of thermal behavior of the investigated salts were hampered by the formation of copious products, which caused attenuation of the X-ray beam in the Bragg-Brentano geometry.

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