

Article

Synthesis and Crystal Structures of 1,1'-Methylenebis(imidazolidine-2,4-dione) and Alkali Metal Salts

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Abstract: Single-crystal structures of 1,1'-methylenebis(imidazolidine-2,4-dione) and its sodium and dipotassium salts were determined. Powder X-ray diffraction was also employed to characterize the bulk materials and those phases which did not yield single-crystals. These compounds are of interest for intumescent coatings.

Keywords: hydantoin; intumescent; potassium salt; powder X-ray diffraction; sodium salt

1. Introduction

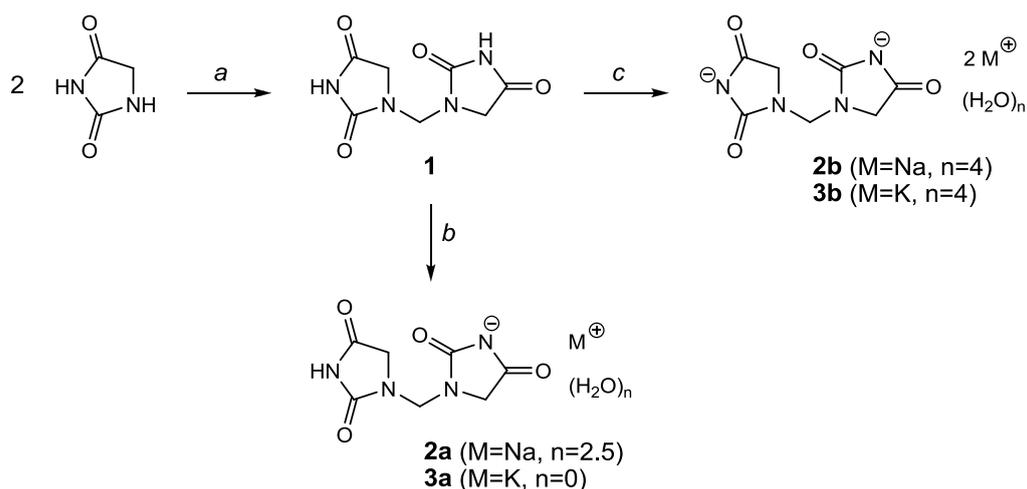
Intumescent coatings [1,2] are used as flame retardants for passive fire protection. Upon heating, they turn into an insulative foam. They typically consist of char-forming and gas-releasing constituents, often along with catalysts and binding resins. They should be non-toxic and inexpensive. It is also advantageous when they contain water as hydrates. The release of this water cools adjacent materials. We envisioned hydantoin derivatives as possible constituents of intumescent mixtures or intumescent

on their own. As a prerequisite, the decomposition temperature should be between 300 and 400 °C. The synthesis of methylene derivatives of hydantoin has been reported [3–5], and a crystal structure of a related methylene bis hydantoin tungstophosphate has been published previously [6]. Preparation of some salts of 1,1'-methylene-bis(imidazolidine-2,4-dione) was mentioned in a patent [5]. Salts were expected to have high melting or decomposition temperatures. Thus, we prepared a series of salts of the title compound (such as Na, K, Ca, Ba, tetramethylammonium, and tetramethylguanidinium) to be tested for their potential suitability as new intumescent materials. Single-crystals suitable for X-ray diffraction were obtained only from Na and K salts.

2. Results and Discussion

The preparation of the title compound **1** was essentially carried out according to the literature with minor modifications as described below. In our hands, it was not necessary to strictly limit the amount of water in the reaction mixture, in contrast to the patented method [5]. The synthesis of the mono-valent and di-valent salts of 1,1'-methylenebis(imidazolidine-2,4-dione) was expected to be straightforward, using one or two equivalents of sodium hydroxide or potassium hydroxide, respectively (Figure 1). However, we encountered several unexpected difficulties.

Figure 1. Synthesis of 1,1'-methylenebis(imidazolidine-2,4-dione) and its salts. Reagents and solvents: *a*: CH₂O/HCl/H₂O; *b*: 1 equivalent NaOH or KOH in H₂O/NH₃; *c*: 2 equivalents NaOH or KOH in H₂O.



Reaction of the title compound with one equivalent of sodium hydroxide in the presence of ammonia (which is needed to get a clear solution) yielded **2a** as an amorphous paste which was converted to a crystalline powder by prolonged stirring in ethanol. Surprisingly, this product was found by powder X-ray diffraction (PXRD) to consist of starting material **1** and disodium salt **2b**. The disodium salt **2b** was readily prepared by reaction of **1** with two equivalents of sodium hydroxide, but no single-crystals could be obtained. By serendipity, we found a single-crystal of the monosodium salt **2a** instead in the bulk of the disodium salt. The potassium salts also posed some problems. The purity of the monopotassium salt **3a** was better than that of the monosodium salt, but there was still contamination with the starting material. On the other hand, single-crystals of the dipotassium salt **3b**

were obtained which permitted the determination of their crystal structures. The crystallographic data and refinement details are summarized in Table 1.

Table 1. Crystal data and structure refinement details.

Compound	1	2a	3b
CCDC Number	950723	950724	950725
Chemical formula	C ₇ H ₈ N ₄ O ₄	C ₁₄ H ₂₄ N ₈ Na ₂ O ₁₃	C ₇ H ₁₄ K ₂ N ₄ O ₈
<i>M_r</i>	212.17	558.39	360.42
Crystal size/mm ³	0.21 × 0.13 × 0.09	0.43 × 0.20 × 0.08	0.30 × 0.30 × 0.20
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>C</i> 222 ₁	<i>C</i> 2/ <i>c</i>	<i>Pbcn</i>
<i>a</i> /Å	9.5263(3)	29.4742(12)	16.0906(6)
<i>b</i> /Å	20.6048(4)	7.8472(3)	7.5688(3)
<i>c</i> /Å	17.7875(6)	10.0477(4)	11.5890(4)
<i>α</i> /°	90	90	90
<i>β</i> /°	90	104.849(4)	90
<i>γ</i> /°	90	90	90
<i>V</i> /Å ³	3491.46(17)	2246.32(15)	1411.38(9)
<i>Z</i>	16	4	4
<i>D_x</i> /g cm ⁻³	1.62	1.65	1.70
<i>μ</i> /mm ⁻¹	0.14	0.18	0.72
<i>F</i> (000)/e	1760	1160	744
<i>T</i> /K	243	173	173
<i>θ</i> _{max} /°	25.0	25.7	25.7
<i>h, k, l</i> range	-10 ≤ <i>h</i> ≤ 11 -24 ≤ <i>k</i> ≤ 24 -21 ≤ <i>l</i> ≤ 21	-35 ≤ <i>h</i> ≤ 27 -9 ≤ <i>k</i> ≤ 9 -12 ≤ <i>l</i> ≤ 11	-19 ≤ <i>h</i> ≤ 16 -9 ≤ <i>k</i> ≤ 8 -14 ≤ <i>l</i> ≤ 13
Measured reflections	10711	6571	8168
Independent reflections (<i>R</i> _{int})	1721 (0.032)	2135 (0.027)	1335 (0.028)
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	1540	1836	1226
Restraints/parameters	0/320	9/190	6/112
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.048/0.117	0.031/0.075	0.024/0.061
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.054/0.121	0.038/0.080	0.026/0.062
Δρ _{max/min} /e Å ⁻³	0.19/-0.22	0.23/-0.24	0.26/-0.24

2.1. 1,1'-Methylenebis(imidazolidine-2,4-dione) (1)

Because of the absence of significant anomalous scattering effects [Flack parameter *x* around -2(2)], Friedel pairs were merged. All hydrogens were found, especially at nitrogen atoms, but were calculated because of a low data/parameter ratio. In the asymmetric unit, there is one complete molecule, half a molecule with C11 on a twofold rotation axis, and a disordered molecule with occupancy of 0.5 for each atom (Figure 2a). Moderate N-H...O hydrogen bonds are observed (Figure 2b). The disordered molecules produce a partially overlapping chain by symmetry elements of a twofold rotation axis along *a* and a twofold screw axis along *c*. In order to obtain reasonable bond lengths O9, C14, C15, and C16 were refined with isotropic displacement parameters (Figure 2c). The hydrogen bond parameters are summarized in Table 2.

Figure 2. (a) Asymmetric unit; (b) Hydrogen bonding of 1,1'-methylenebis(imidazolidine-2,4-dione) (**1**); (c) View of the disordered molecule; symmetry operation (i): $-x, y, 3/2 - z$; hydrogen atoms omitted for clarity.

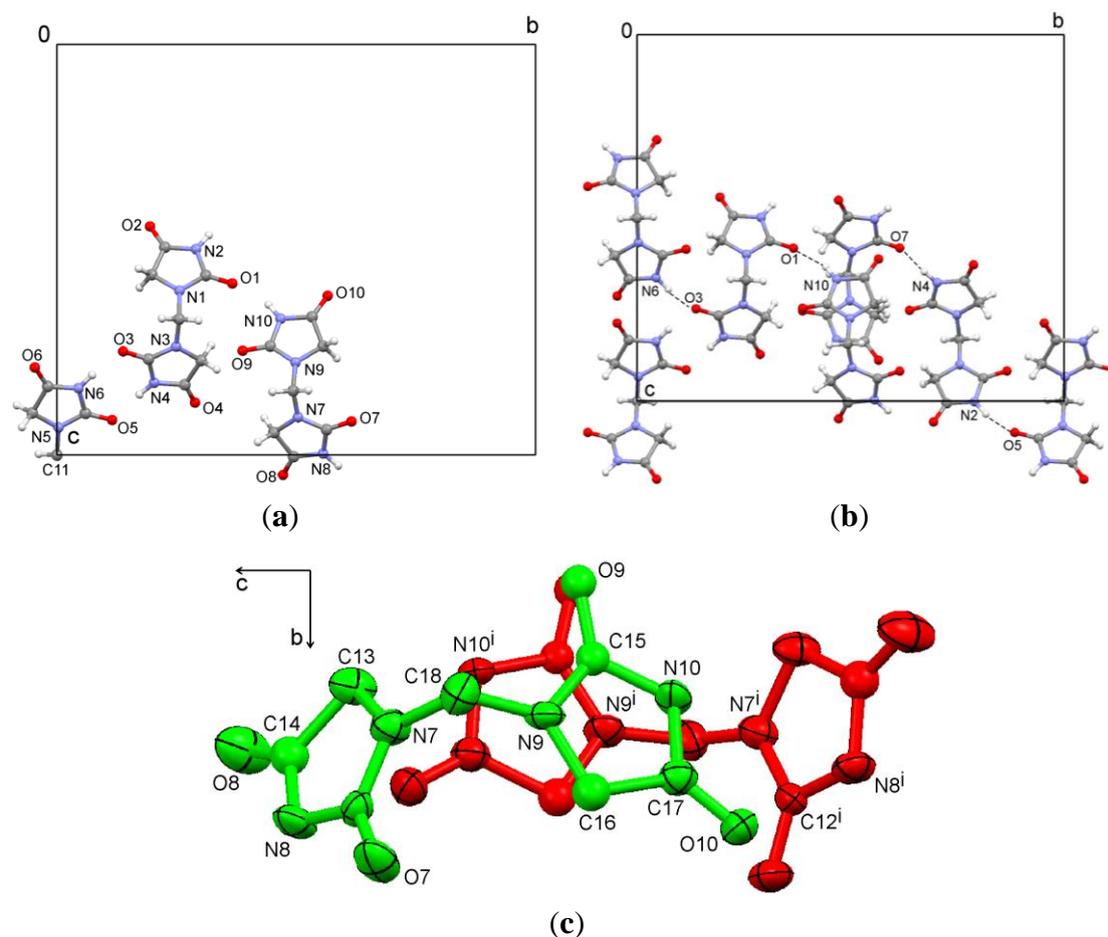


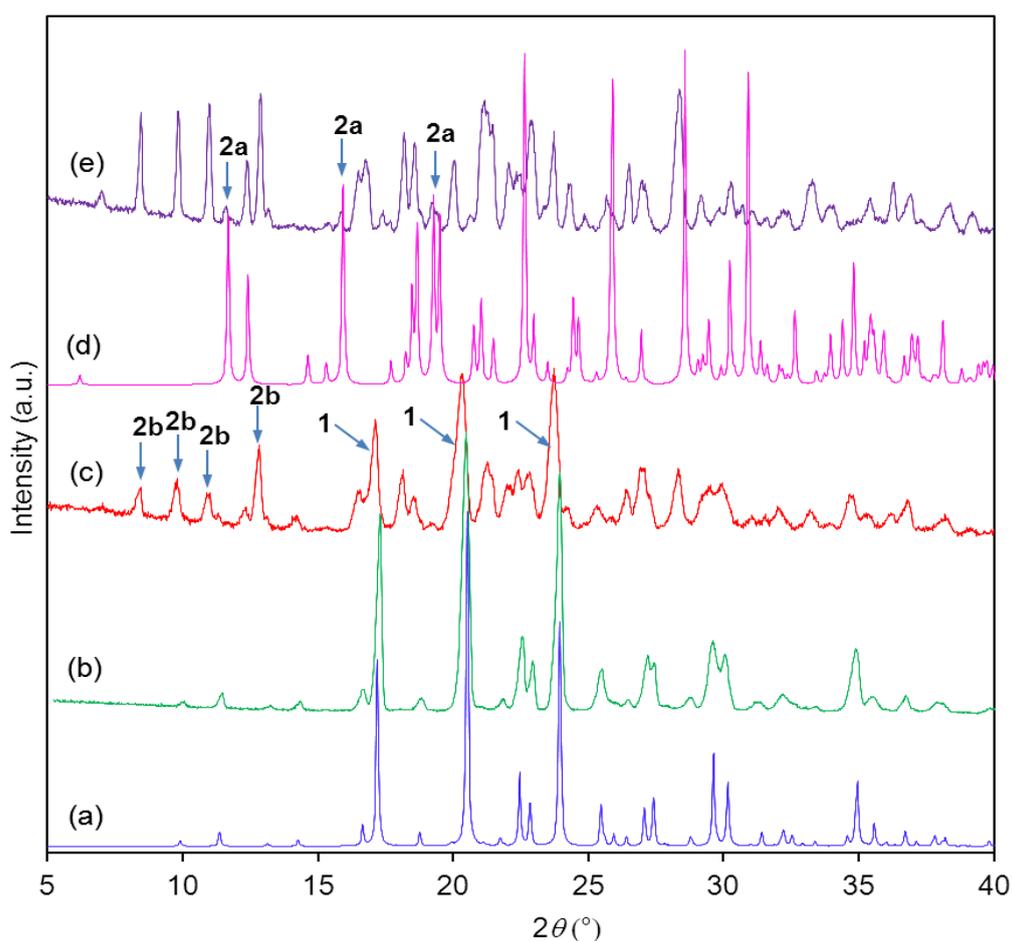
Table 2. Hydrogen bond parameters (\AA , $^\circ$).

Compound	Interaction	H \cdots A	D \cdots A	D–H \cdots A	Symmetry A
1	N2–H \cdots O5	1.951(3)	2.793(5)	162.5(3)	$1/2 - x, 1/2 - y, -1/2 + z$
	N4–H \cdots O7	1.797(7)	2.667(8)	175.4(3)	$1/2 + x, -1/2 + y, z$
	N6–H \cdots O3	1.897(3)	2.750(5)	166.2(3)	$-x, y, 3/2 - z$
	N10–H \cdots O1	2.085(3)	2.927(9)	162.7(6)	x, y, z
2a	N2–H \cdots O4	1.84(2)	2.707(2)	166(2)	$x, y, -1 + z$
	O7–H \cdots N4	2.07(1)	2.908(2)	169(1)	$1 - x, y, 5/2 - z$
	O6–H \cdots O3	1.90(1)	2.752(1)	173(2)	$x, -y, -1/2 + z$
3b	O3–H \cdots O1	2.065(14)	2.9085(16)	172.8(19)	$1/2 - x, 1/2 - y, 1/2 + z$
	O3–H \cdots N2	1.982(14)	2.8085(16)	170.0(18)	$x, 1 - y, 1/2 + z$
	O4–H \cdots O2	1.962(14)	2.7888(15)	172.9(17)	$1/2 - x, 1/2 - y, 1/2 + z$
	O4–H \cdots O2	1.981(15)	2.7756(15)	153.4(16)	$1/2 + x, 1/2 - y, 1 - z$

2.2. 1,1'-Methylenebis(imidazolidine-2,4-dione), Sodium Salt, 2.5-Hydrate (2a)

Powder X-ray diffractograms showed that the starting material was pure (Figure 3a,b). It can be clearly seen that the attempted synthesis of the monosodium salt gave only a mixture of starting material **1** and disodium salt **2b** (Figure 3c). The disodium salt contained traces of the monosodium salt **2a** (Figure 3d,e), no single-crystals were obtained.

Figure 3. (a) Calculated powder X-ray diffraction (PXRD) of starting material **1**; (b) Experimental PXRD of starting material **1**; (c) Experimental PXRD of the product from attempted synthesis of mono-sodium salt **2a**; (d) Calculated PXRD of monosodium salt **2a**; (e) Experimental PXRD of disodium salt **2b**. Impurities are indicated by arrows.



In the crystal structure of **2a**, the sodium ions are coordinated to two oxygen atoms of the title ligand and four water molecules (Figure 4a). The sodium ions are alternately linked by one (O6) or two (O7) μ_2 -aqua bridges (Figure 4b). The O6 atom of the single μ_2 -aqua bridge is located on a twofold rotation axis in *b* direction. An inversion center is situated in the bis(μ_2 -aqua) moiety. Hydrogen bonds between ligands (N–H \cdots O) and between ligand and water molecules (O–H \cdots N and O–H \cdots O) are observed (Table 2, Figure 4b). Sodium \cdots oxygen contacts are summarized in Table 3.

Figure 4. (a) Coordination environment of the ion pair; (b) Hydrogen bonding of the sodium salt **2a**.

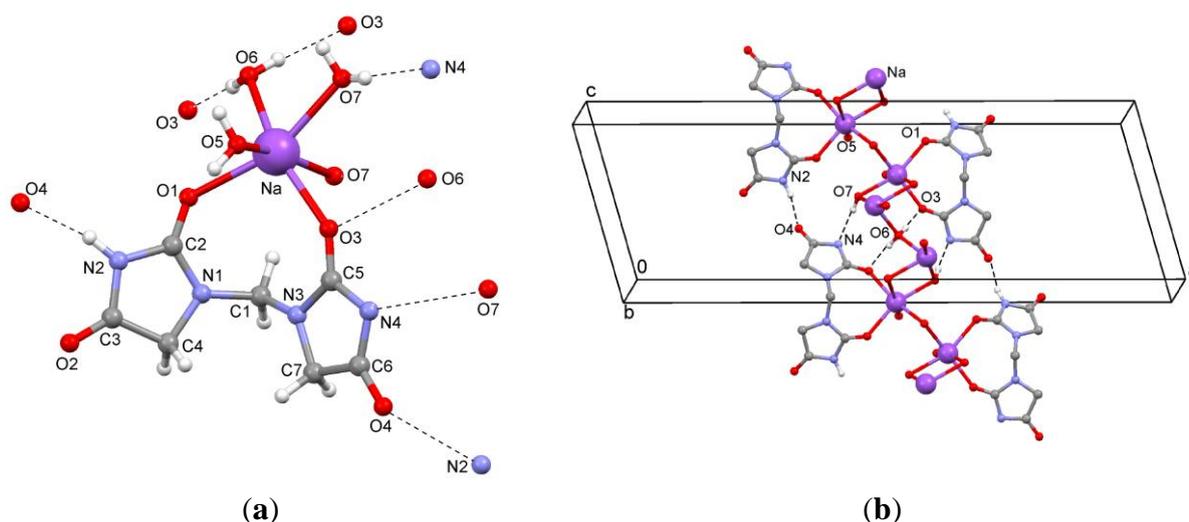


Table 3. Metal...oxygen bonds (Å) in salts **2a** and **3b**.

Compound	Bond	M...O	Symmetry O
2a	Na...O1	2.433(1)	x,y,z
	Na...O3	2.302(1)	x,y,z
	Na...O5	2.363(1)	x,y,z
	Na...O6	2.381(1)	x,y,z
	Na...O7	2.408(1)	x,y,z
	Na...O7	2.645(1)	$1-x,-y,2-z$
3b	K...O1	2.782(1)	x,y,z
	K...O1	2.737(1)	$1/2-x,1/2+y,z$
	K...O3	2.703(1)	x,y,z
	K...O3	2.821(1)	$1/2-x,-1/2+y,z$
	K...O4	2.783(1)	x,y,z
K...O4	2.782(1)	$1/2-x,1/2+y,z$	

2.3. 1,1'-Methylenebis(imidazolidine-2,4-dione), Dipotassium Salt, Tetrahydrate (**3b**)

Powder X-ray diffractograms showed that the bulk of the monopotassium salt **3a** contained considerable amounts of starting material **1** (Figure 5a,b), whereas the bulk of the dipotassium salt **3b** contained only traces of **1** (Figure 5b,c). Single-crystal and bulk material of the dipotassium salt were identical crystalline phases (Figure 5c,d).

The dipotassium salt **3b** is a typical coordination polymer. In the crystal structure of **3b**, there is half a ligand molecule in the asymmetric unit, C1 is located on a two-fold rotation axis in the direction of the b axis. Each potassium ion coordinates to two ligand molecules and four water molecules (Figure 6a). The potassium atoms are arranged in columns parallel to the b axis. They are linked by O1 of the ligand and two μ_2 -aqua bridges (O3 and O4), as shown in Figure 6b. Hydrogen bonds between ligand and water molecules (O–H...N and O–H...O) are observed (Table 2, Figure 6b). Potassium...oxygen contacts are summarized in Table 3.

3. Experimental Section

Hydantoin (purity 99%) was purchased from Alfa Aesar (Ward Hill, MA, USA). All other chemicals were obtained from Sigma-Aldrich, St. Louis, MO, USA (European affiliate Steinheim, Germany). Nuclear magnetic resonance (NMR) spectra were recorded with Bruker Avance DPX 300 (Billerica, MA, USA) and Bruker Avance II+ 600 spectrometers. IR spectra were obtained with a Bruker Alpha FT-IR instrument. Water content was determined by coulometric Karl Fischer titration using a Mettler Toledo C20 apparatus (Greifensee, Switzerland).

The powder X-ray diffraction patterns were measured with a Bruker D8 Discover diffractometer using Cu K α radiation. The patterns were recorded applying a step size of 0.02° with 1 s measuring time per step in the angular range of 2° to 40°.

Single-crystal diffraction intensity data were recorded by ϕ and ω scans with a Nonius KappaCCD diffractometer (Bruker) (for **1**) or by ω scans with an Oxford Diffraction Gemini-R Ultra diffractometer (Agilent, Santa Clara, CA, USA) (for **2a** and **3b**) using Mo K α radiation. All hydrogen atoms were identified in difference Fourier maps. Secondary CH₂ (C–H = 0.99 Å) were positioned geometrically and refined using a riding model. Hydrogen atoms of NH groups as well as of the water molecules were refined with restrained distances of 0.88(1) Å (for N–H) and 0.86(1) Å (for O–H), respectively. Furthermore, an additional H···H restraint (1.35 Å) was introduced to obtain an H–O–H angle of about 104°. The isotropic displacement parameters of all H atoms were set at $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$. CCDC reference numbers: 950723–950725. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

3.1. Synthesis of 1,1'-Methylenebis(imidazolidine-2,4-dione) (**1**)

Aqueous formaldehyde (37%, 53.1 mL, 0.510 mol), hydantoin (101.6 g, 1.020 mol), H₂O (100 mL) and HCl (37%, 150 mL) were mixed and stirred for 72 h at room temperature. The resulting white precipitate was filtered off, washed with H₂O (200 mL), and dried in an oven at 115 °C for 24 h (yield 96.2 g, 89%). Single-crystals were grown by slow evaporation of a solution in H₂O/NH₃. Melting point (M.p.) 300 °C. ¹H NMR (DMSO-d₆, 300 MHz): δ 3.93 (s, 4H), 4.74 (s, 2H), 10.84 (s, 2H) ppm. ¹³C NMR (DMSO-d₆, 75 MHz): δ 48.5, 49.2, 157.4, 171.8 ppm. IR (neat): ν 3196 (m), 3074 (w), 1752 (m), 1609 (s), 1474 (m), 1454 (s), 1424 (m), 1376 (s), 1333 (m), 1263 (m), 1210 (s), 1171 (m), 1150 (s), 1098 (m), 984 (w), 961 (m), 896 (m), 843 (w), 760 (m), 714 (s), 696 (s), 639 (s), 599 (s), 572 (s), 444 (m) cm⁻¹.

3.2. Attempted Synthesis of 1,1'-Methylenebis(imidazolidine-2,4-dione), Monosodium Salt (**2a**)

1,1'-Methylenebis(imidazolidine-2,4-dione) (**1**) (2.0 g, 9.4 mmol, prepared as described above) was dissolved in a mixture of H₂O (5 mL) and ammonia (25% aqueous solution, 2.8 mL, 38 mmol). After addition of NaOH (0.38 g, 9.5 mmol) the solution was stirred for 10 min. Removal of the solvent by means of a rotary evaporator and vacuum-drying for 3 h at room temperature yielded a white paste (2.2 g). A sample of this paste (100 mg) was stirred in EtOH (3 mL) for 7 d at room temperature. The crystalline solid was filtered off and vacuum-dried to yield 81 mg (81%). Onset of decomposition: 193 °C. ¹H NMR (D₂O, 600 MHz): δ 4.08 (s, 4H), 4.94 (s, 2H) ppm. ¹³C NMR (D₂O, 150 MHz):

δ 51.9, 53.4, 167.0, 183.0 ppm. IR (neat): ν 3205 (w), 1753 (m), 1697 (m), 1572 (s), 1474 (m), 1455 (m), 1424 (m), 1400 (m), 1369 (m), 1332 (m), 1213 (s), 1172 (w), 1151 (m), 1099 (w), 996 (w), 962 (w), 897 (w), 857 (w), 793 (w), 764 (m), 697 (m), 672 (m), 641 (m), 626 (m), 600 (m), 575 (m), 445 (m) cm^{-1} .

3.3. Synthesis of 1,1'-Methylenebis(imidazolidine-2,4-dione), Disodium Salt, Tetrahydrate (**2b**)

1,1'-Methylenebis(imidazolidine-2,4-dione) (**1**) (95.6 g, 0.451 mol) was suspended in H_2O (250 mL), and NaOH (36.1 g, 0.903 mol) was added in portions. The mixture was stirred for 10 min, filtered, and the solvent was removed by means of a rotary evaporator. Vacuum-drying for 8 h at 50 $^\circ\text{C}$ yielded a clear paste which solidified after several days (124.0 g, 84%). Thermogravimetry indicated a tetrahydrate. Onset of decomposition: 189 $^\circ\text{C}$. ^1H NMR (D_2O , 300 MHz): δ 3.93 (s, 4H), 4.90 (s, 2H) ppm. ^{13}C NMR (D_2O , 75 MHz): δ 46.4, 49.2, 170.6, 187.0 ppm. IR (neat): ν 3355 (bm), 3010 (bm), 2737 (w), 1763 (w), 1685 (m), 1569 (s), 1460 (m), 1449 (m), 1406 (m), 1265 (m), 1347 (s), 1202 (s), 1154 (s), 1113 (m), 994 (w), 964 (m), 909 (w), 855 (w), 786 (s), 760 (m), 686 (m), 617 (m), 582 (m) cm^{-1} . Surprisingly, single-crystals of the mono-sodium salt 2.5-hydrate **2a** were obtained by slow evaporation of a solution in $\text{H}_2\text{O}/\text{MeOH}$.

3.4. Synthesis of 1,1'-Methylenebis(imidazolidine-2,4-dione), Monopotassium Salt (**3a**)

1,1'-Methylenebis(imidazolidine-2,4-dione) (**1**) (2.0 g, 9.4 mmol) was dissolved in a mixture of H_2O (5 mL) and ammonia (25% aqueous solution, 2.8 mL, 38 mmol). After addition of KOH (0.53 g, 9.4 mmol) the solution was stirred for 10 min. Removal of the solvent by means of a rotary evaporator and vacuum-drying for 3 h at room temperature yielded a white solid (2.35 g, 100%). H_2O : 0.42%. M.p. 257 $^\circ\text{C}$ (decomposition). ^1H NMR (D_2O , 300 MHz): δ 4.05 (s, 4H), 4.91 (s, 2H) ppm. ^{13}C NMR (D_2O , 75 MHz): δ 51.9, 53.9, 168.1, 184.1 ppm. IR (neat): ν 3208 (w), 1700 (s), 1599 (m), 1575 (m), 1474 (m), 1412 (m), 1349 (m), 1331 (m), 1283 (m), 1210 (s), 1191 (s), 1162 (m), 1117 (m), 948 (m), 902 (w), 857 (w), 790 (m), 766 (s), 717 (m), 681 (m), 648 (m), 610 (s), 589 (m), 573 (m), 440 (m) cm^{-1} .

3.5. Synthesis of 1,1'-Methylenebis(imidazolidine-2,4-dione), Dipotassium Salt, Tetrahydrate (**3b**)

1,1'-Methylenebis(imidazolidine-2,4-dione) (**1**) (1.0 g, 0.005 mol) was suspended in H_2O (5 mL), and KOH (0.5 g, 0.010 mol) was added to give a clear solution which was stirred for 10 min. The solvent was removed by means of a rotary evaporator. Vacuum-drying for 3 h at room temperature yielded a clear paste which crystallized overnight (yield 1.6 g, 93%). M.p. 65 $^\circ\text{C}$ (dec.). ^1H NMR (D_2O , 300 MHz): δ 3.95 (s, 4H), 4.91 (s, 2H) ppm. ^{13}C NMR (D_2O , 75 MHz): δ 43.8, 46.4, 166.1, 182.4 ppm. IR (neat): ν 3443 (m), 3256 (bm), 3122 (bm), 1796 (m), 1674 (m), 1598 (s), 1570 (s), 1469 (m), 1444 (s), 1423 (w), 1399 (m), 1368 (s), 1331 (s), 1267 (m), 1202 (s), 1160 (s), 996 (w), 960 (m), 896 (w), 865 (m), 792 (s), 765 (m), 700 (s), 681 (m), 616 (s), 571 (s), 494 (m), 432 (s) cm^{-1} .

4. Conclusions and Outlook

Crystallography is an indispensable tool for characterization of new materials. The alkali metal salts of 1,1'-methylenebis(imidazolidine-2,4-dione) were found to be coordination polymers. Preliminary

tests have shown that the disodium and dipotassium salts possess promising intumescent properties. We plan to develop these compounds as constituents of intumescent paints [7].

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Conflicts of Interest

The authors declare no conflict of interest.

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