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# Structure of six anhydrous molecular salts assembled from noncovalent associations between carboxylic acids and bis-N-imidazoles

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#### HIGHLIGHTS

▶ Six organic salts with 3D structure have been prepared and characterized.

▶ The classical hydrogen bond between bis-imidazoles and acids have been discussed.

▶ Other noncovalent associations are also discussed.

▶ The classical hydrogen bond is the primary interaction in the structures built from OH···Im synthon.

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## ABSTRACT

Six crystalline organic acid–base adducts derived from bis(N-imidazolyl) and carboxylic acids (3,5-dinitrobenzoic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid, and phthalic acid) were prepared and characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. The six compounds are all organic salts. In salts **1**, **2**, **4**, **5**, and **6** the corresponding bis(imidazole) derivatives are diprotonated, while in **3**, the corresponding bis(imidazole) derivative is only monoprotonated.

All supramolecular architectures of the salts **1–6** involve extensive N–H···O, O–H···O, CH···O, and CH<sub>2</sub>···O hydrogen bonds as well as other noncovalent interactions. The role of weak and strong noncovalent interactions in the crystal packing is ascertained. All the salts displayed 3D framework structures under the cooperation of these weak interactions.

The results presented herein indicate that the strength and directionality of the N<sup>+</sup>-H···O<sup>-</sup>, O-H···O, and N-H···N hydrogen bonds between carboxylic acids and ditopic imidazoles are sufficient to bring about the formation of binary organic salts.

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#### 1. Introduction

Multicomponent crystals and organic acid–base complexes have received considerable attention over the past few years [1,2] not only because of their intriguing structural motifs [3,4] but also for their useful properties and promising applications as functional materials [5,6]. The design and construction of multicomponent supermolecules or supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of noncovalent interactions, in building supramolecular systems [7]. Of these interactions hydrogen bond interactions are the most powerful organizing force for the formation of supramolecules [8–11].

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Because of the predictable supramolecular properties and the ability to form strong and directional hydrogen bonds, carboxylic acids were frequently chosen as building blocks for crystal engineering [12–14]. Numerous organic acid–base compounds from carboxylic acids and a variety of N-containing basic building blocks have been documented recently [15–19].

Imidazole and its derivatives are ubiquitous in biological and biochemical structure and function, which attracted special attention in the construction of some interesting metal-organic frameworks in recent years [20–25]. And also, great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [26–28]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of imidazoles [29– 33] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [29,33], (bis(1methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methyl)amine [31], etc.).





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Following our previous works of acid–base adducts based on bis(imidazole) and dicarboxylic acid [34,35], herein we report the synthesis and crystal structure of six supramolecular compounds assembled *via* hydrogen bonding interactions between carboxylic acids and bis(imidazole). In this study, we got six organic compounds composed of carboxylic acids and symmetric ditopic bis-imidazol-1-yl compounds (Scheme 1), namely  $[(H_2L1^{2+}) \cdot (dna^{-})_2]$  (1) where L1 = 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole, dna<sup>-</sup> = 3,5-dinitrobenzoate,  $[(H_2L2)^{2+} \cdot (5-nsa^{-})_2]$  (2) where L2 = bis(N-imidazolyl)methane, 5-nsa<sup>-</sup> = 5-nitrosalicylate,  $[(HL3)^+ \cdot (3,5-dns^{-})_2]$  (3) where L3 = 1,5-bis(1-benzimidazolyl)-3-oxapentane, 3,5-dns<sup>-</sup> = 3,5-dinitrosalicylate,  $[(H_2L2)^{2+} \cdot (3,5-dns^{-})_2]$  (4),  $[(H_2L4)^{2+} \cdot (3,5-dns^{-})_2]$  (5) where L4 = 1,4-bis(*N*-imidazolyl)butane, and  $[(H_2L2)^{2+} \cdot (Hpta^{-})_2]$  (6) where Hpta<sup>-</sup> = hydrogen phthalate.

#### 2. Experimental section

#### 2.1. Materials and methods

L1–L4 were prepared as described previously [36]. All other reagents were commercially available and used as received. The C, H, and N micro-analysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

#### 2.2. Preparation of the salts

#### 2.2.1. $[(H_2L1^{2+})\cdot(dna^{-})_2]$ (1)

1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazoleL1(27.6 mg, 0.1 mmol) was dissolved in 4 mL of methanol. To this solution was added 3,5-dinitrobenzoic acid (21.2 mg, 0.1 mmol) in 4 mL methanol. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, light yellow block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the title compound  $[(H_2L1^{2+})\cdot(dna^{-})_2]$  (1), yield 36 mg, 51.38% (Based on L1). m. p. 186-187 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C<sub>31</sub>H<sub>24</sub>N<sub>8</sub>O<sub>12</sub> (700.58): C, 53.10; H, 3.42; N, 15.98. Found: C, 53.02; H, 3.36; N, 15.89. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3465s(multiple, v<sub>as</sub>(NH)), 3336s(v<sub>s</sub>(NH)), 3072 m, 2989 m, 1979w, 1835w, 1782w, 1664w, 1602s(v<sub>as</sub>(COO<sup>-</sup>)), 1590 m, 1522s  $(v_{as}(NO_2))$ , 1462w, 1384s $(v_s(COO^-))$ , 1323s $(vs(NO_2))$ , 1252 m, 1194 m, 1128 m, 1064 m, 1011 m, 952 m, 903 m, 856 m, 802 m, 753 m, 726 m, 674 m, 626 m.

### 2.2.2. $[(H_2L2)^{2+} \cdot (5-nsa^{-})_2]$ (2)

Bis(N-imidazolyl)methane (15.0 mg, 0.1 mmol) was dissolved in 1 mL methanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 3 mL methanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 27.0 mg, 52.5%, based on L2). mp 194–195 °C. Elemental analysis: Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>6</sub>O<sub>10</sub> (514.41): C, 48.99; H, 3.50; N, 16.33. Found: C, 48.95; H, 3.47; N, 16.26. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3684s(v(OH)), 3496s(multiple, v<sub>as</sub>(NH)), 3374s(v<sub>s</sub>(NH)), 3046 m, 2960 m, 1982w, 1836w, 1764w, 1598s(v<sub>as</sub>(COO<sup>-</sup>)), 1556 m, 1524s (v<sub>as</sub>(NO<sub>2</sub>)), 1484w, 1392s(v<sub>s</sub>(COO<sup>-</sup>)), 1352 m, 1319s(v<sub>s</sub>(NO<sub>2</sub>)), 1246 m, 1193 m, 1135 m, 1084 m, 1028 m, 946 m, 852 m, 768 m, 708 m, 672 m, 637 m, 604 m.

#### 2.2.3. [(HL3) <sup>+</sup>·(3,5-dns<sup>-</sup>)] (**3**)

1,5-Bis(1-benzimidazolyl)-3-oxapentane L3 (29 mg, 0.10 mmol) dissolved in 3 mL ethanol. To this solution was added 3,5-dinitrosal-

icylic acid (22.8 mg, 0.1 mmol) in 6 mL methanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 35 mg, 65.48% based on L3. mp 191–192 °C. Elemental analysis: Calc. for  $C_{25}H_{22}N_6O_8(534.49)$ : C, 56.13; H, 4.11; N, 15.71. Found: C, 56.06; H, 4.04; N, 15.63. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3574s (v(OH)), 3486s(multiple,  $v_{as}(NH)$ ), 3338s( $v_s(NH)$ ), 3054 m, 2972 m, 1996w, 1868w, 1783w, 1614 m, 1592s( $v_{as}(COO^{-})$ ), 1530s( $v_{as}(NO_2)$ ), 1474w, 1406s( $v_s(COO^{-})$ ), 1358 m, 1314s( $v_s(NO_2)$ ), 1240 m, 1120 m, 1013 m, 946 m, 868 m, 806 m, 757 m, 680 m, 638 m.

## 2.2.4. $[(H_2L2)^{2+} \cdot (3,5-dns^{-})_2]$ (4)

Bis(N-imidazolyl)methane (15.0 mg, 0.1 mmol) was dissolved in 1 mL ethanol. To this solution was added 3,5-dinitrosalicylic acid (22.8 mg, 0.1 mmol) in 6 mL methanol. Yellow prisms were afforded after several days of slow evaporation of the solvent, yield: 35 mg, 57.91% (based on L2). mp 91–92 °C. Elemental analysis: Calc. for  $C_{21}H_{16}N_8O_{14}(604.42)$ : C, 41.69; H, 2.65; N, 18.53. Found: C, 41.62; H, 2.58; N, 18.48. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3612s (v(OH)), 3479s(multiple,  $v_{as}(NH)$ ), 3356s( $v_s(NH)$ ), 3048 m, 2972 m, 1982w, 1884w, 1768w, 1697s( $v_{as}(C=O)$ ), 1624 m, 1525s ( $v_{as}(NO_2)$ ), 1486w, 1412 m, 1362 m, 1316s( $v_s(NO_2)$ ), 1286s( $v_s(C=O)$ ), 1235 m, 1178 m, 1126 m, 1066 m, 992 m, 856 m, 802 m, 754 m, 688 m, 634 m, 605 m.

#### 2.2.5. $[(H_2L4)^{2+} \cdot (3,5-dns^{-})_2]$ (5)

1,4-Bis(*N*-imidazolyl)butane L4 (19.9 mg, 0.1 mmol) dissolved in 2 mL of ethanol. To this solution was added 3,5-dinitrosalicylic acid (22.8 mg, 0.1 mmol) in 6 mL methanol. Light yellow prisms were afforded after several days of slow evaporation of the solvent, yield: 36 mg, 55.68% (based on L4). mp 121–122 °C. Elemental analysis: Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>8</sub>O<sub>14</sub> (646.50): C, 44.55; H, 3.40; N, 17.32. Found: C, 44.52; H, 3.32; N, 17.24. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3654s (v(OH)), 3446s(multiple, v<sub>as</sub>(NH)), 3329s(v<sub>s</sub>(NH)), 3054 m, 2972 m, 1828w, 1714s(v<sub>as</sub>(C=O)), 1618 m, 1528s(v<sub>as</sub> (NO<sub>2</sub>)), 1478w, 1365 m, 1317s(v<sub>s</sub>(NO<sub>2</sub>)), 1284s(v<sub>s</sub>(C=O)), 1248 m, 1192 m, 1016 m, 964 m, 916 m, 862 m, 796 m, 755 m, 684 m, 638 m, 602 m.

#### 2.2.6. $[(H_2L2)^{2+} \cdot (Hpta^{-})_2]$ (6)

Bis(N-imidazolyl)methane (15.0 mg, 0.1 mmol) was dissolved in 1 mL methanol. To this solution was added phthalic acid (17 mg, 0.1 mmol) in 5 mL ethanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 26.0 mg, 54.1%, based on L2). mp 132–133 °C. Elemental analysis: Calc. for  $C_{23}H_{20}N_4O_8$  (480.43): C, 57.45; H, 4.16; N, 11.66. Found: C, 57.37; H, 4.11; N, 11.62. Infrared spectrum (KBr disc, cm<sup>-1</sup>): 3665s(v(OH)), 3462s(multiple, v<sub>as</sub>(NH)), 3376s(v<sub>s</sub>(NH)), 3032 m, 2979 m, 2926 m, 1821w, 1771w, 1712s(v<sub>as</sub>(C=O)), 1642 m, 1592 m, 1566s(v<sub>as</sub>(COO<sup>-</sup>)), 1482 m, 1422 m, 1378s(v<sub>s</sub>(COO<sup>-</sup>)), 1310 m, 1288s(v<sub>s</sub>(C=O)), 1239 m, 1189 m, 1128 m, 1072 m, 1028 m, 936 m, 884 m, 818 m, 725 m, 662 m, 614 m.

#### 2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collections and reductions were performed using the SMART and SAINT software [37,38]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on  $F^2$  using SHELXTL package [39]. Hydrogen atom positions for the six structures were generated geometrically. Further details of the structural analysis are summarized in Tables 1 and 2.



Scheme 1. The building blocks discussed in this paper.

#### 3. Results and discussion

#### 3.1. Syntheses and general characterization

1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole, 1,5-bis (1-benzimidazolyl)-3-oxapentane, bis(N-imidazolyl)methane, and bis(N-imidazolyl)butane all have good solubility in common organic solvents, such as CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CN, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. For the preparation of **1–6**, the acids were mixed directly with the base in methanol and/or ethanol solvents in 1:1 ratio, which was allowed to evaporate at ambient conditions to give the final crystalline products. The elemental analyses for the six compounds are in good agreement with their compositions. The infrared spectra of **1–6** are consistent with their confirmed by X-ray diffraction analysis. The very strong and broad features at 3700–3300 cm<sup>-1</sup> arise from O–H or N–H stretching frequencies. Aromatic and imidazol ring stretching and bending are in the regions of  $1500-1630 \text{ cm}^{-1}$  and  $600-750 \text{ cm}^{-1}$ , respectively. The compounds **1**, **2**, **3**, and **6** show the characteristic bands for COO<sup>-</sup> group. Compounds **4**, **5**, and **6** display strong IR peaks for COOH groups. The bands at *ca*. 1530 and 1320 cm<sup>-1</sup> were attributed to the v<sub>as</sub>(NO<sub>2</sub>) and v<sub>s</sub>(NO<sub>2</sub>), respectively [40].

#### 3.1.1. X-ray structure of $[(H_2L1^{2+})\cdot(dna^{-})_2]$ (1)

Salt **1** crystallizes as monoclinic pale yellow crystals in the centrosymmetric space group C2/c. The asymmetric unit of **1** consists of half a dication of 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole, and one anion of 3,5-dinitrobenzoate, as shown in Fig. 1.

This is a salt where the COOH groups of 3,5-dinitrobenzoic acids are ionized by proton transfer to the nitrogen atoms of the 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole moieties, which

#### Table 1

Summary of X-ray crystallographic data for complexes 1-3.

	1	2	3
Formula	$C_{31}H_{24}N_8O_{12}$	$C_{21}H_{18}N_6O_{10}$	C <sub>25</sub> H <sub>22</sub> N <sub>6</sub> O <sub>8</sub>
Fw	700.58	514.41	534.49
Т, К	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	C2/c	P2/c	P-1
<i>a</i> , Å	9.9370(10)	8.6670(8)	13.5757(12)
b, Å	10.9609(12)	11.0959(12)	13.6543(13)
c, Å	28.540(3)	23.328(2)	13.7485(14)
α, deg.	90	90	97.9990(10)
$\beta$ , deg.	93.6900(10)	98.4150(10)	106.217(2)
γ, deg.	90	90	91.0000(10)
V, Å <sup>3</sup>	3102.1(5)	2219.3(4)	2419.0(4)
Z	4	4	4
$D_{\text{calcd}}$ , Mg/m <sup>3</sup>	1.500	1.540	1.468
Absorption coefficient, mm <sup>-1</sup>	0.118	0.125	0.112
F(0 0 0)	1448	1064	1112
Crystal size, mm <sup>3</sup>	$0.46 \times 0.33 \times 0.12$	$0.40 \times 0.33 \times 0.32$	$0.48 \times 0.43 \times 0.32$
$\theta$ range, deg	2.77-25.01	2.55-25.02	2.33-25.02
Limiting indices	$-11 \leqslant h \leqslant 11$	$-8 \leqslant h \leqslant 10$	$-8 \leqslant h \leqslant 16$
	$-12 \leqslant k \leqslant 12$	$-11 \leq k \leq 13$	$-16 \leqslant k \leqslant 15$
	$-33 \leqslant l \leqslant 20$	$-25 \leqslant l \leqslant 27$	$-16 \leqslant l \leqslant 16$
Reflections collected	7147	10923	12219
Reflections independent $(R_{int})$	2622 (0.0890)	3915 (0.0463)	8412 (0.0299)
Goodness-of-fit on F <sup>2</sup>	1.219	1.025	1.039
R indices $[I > 2\sigma I]$	0.1519, 0.3651	0.0523, 0.1303	0.0713, 0.1961
R indices (all data)	0.2123, 0.3974	0.1486, 0.1711	0.1613, 0.2615
Largest diff. peak and hole, e $Å^{-3}$	0.611, -0.582	0.221, -0.154	1.059, -0.482

#### Table 2

Summary of X-ray crystallographic data for complexes 4-6.

	4	5	6
Formula	$C_{21}H_{16}N_8O_{14}$	$C_{24}H_{22}N_8O_{14}$	C <sub>23</sub> H <sub>20</sub> N <sub>4</sub> O <sub>8</sub>
Fw	604.42	646.50	480.43
Т, К	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	C2/m
a, Å	9.554(3)	4.6129(4)	15.0468(12)
b, Å	11.113(3)	12.9249(13)	18.6291(16)
c, Å	12.707(4)	12.9980(13)	8.116(10)
α, deg.	81.436(4)	115.592(2)	90
$\beta$ , deg.	74.756(4)	96.4670(10)	105.6730(10)
γ, deg.	67.871(4)	95.0350(10)	90
<i>V</i> , Å <sup>3</sup>	1203.9(6)	686.39(11)	2190(3)
Z	2	1	4
$D_{\text{calcd}}$ , Mg/m <sup>3</sup>	1.667	1.564	1.457
Absorption coefficient, mm <sup>-1</sup>	0.143	0.131	0.112
F(0 0 0)	620	334	1000
Crystal size, mm <sup>3</sup>	$0.48 \times 0.40 \times 0.32$	$0.28\times0.21\times0.12$	$0.47 \times 0.38 \times 0.36$
$\theta$ range, deg	2.49-28.25	3.00-25.01	2.61-25.02
Limiting indices	$-12 \leqslant h \leqslant 11$	$-5 \leqslant h \leqslant 5$	$-13 \leqslant h \leqslant 17$
	$-14 \leqslant k \leqslant 9$	$-15 \leqslant k \leqslant 12$	$-22\leqslant k\leqslant 22$
	$-16 \leqslant l \leqslant 15$	$-14 \leqslant l \leqslant 15$	$-9 \leqslant l \leqslant 9$
Reflections collected	7625	3507	5478
Reflections independent $(R_{int})$	5647 (0.0200)	2396 (0.0297)	2003 (0.0253)
Goodness-of-fit on F <sup>2</sup>	1.035	0.996	1.037
R indices $[I > 2\sigma I]$	0.0503, 0.1405	0.1364, 0.3267	0.0434, 0.0990
R indices (all data)	0.0848, 0.1638	0.2048, 0.3626	0.0811, 0.1243
Largest diff. peak and hole, e Å $^{-3}$	0.336, -0.307	0.763, -0.363	0.262, -0.234

is also confirmed by the bond distances of O(1)–C(10) (1.221(8) Å) and O(2)–C(10) (1.277(9) Å) for the carboxylates (Table 3). The difference ( $\Delta$  is 0.056 Å) in bond distances between O(1)–C(10) (1.221(8) Å) and O(2)–C(10) (1.277(9) Å) in the carboxylate group in compound **1** is caused by the fact that O(2) is involved in forming more hydrogen bonds than that of O(1) (Table 4). L1 is doubly protonated and the cation with the NH<sup>+</sup> groups on the imidazole rings in **1** resembles 4,4'–H<sub>2</sub>bipy cations [41]. The protonated L1 cations display trans conformation in which the inversion center is located at C(9).

In the compound, there is one ion pair without solvent molecules, which is well agreement with the micro-analysis results. In compound **1**, there exist strong electrostatic interactions between charged cation units of  $NH^+$  and the anion of 3,5-dinitrobenzoate.

One cation and two anions generate a tricomponent adduct *via* the ionic  $N^+$ — $H^{...}O^-$  hydrogen bond between the NH<sup>+</sup> cation and



Fig. 1. The structure of 1, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

the carboxylate with N–O distance of 2.541(8) Å. Such kind of tricomponent adducts were linked together by the CH---O interaction between the benzene CH of the cation and the nitro group with C···O distance of 3.404 Å, and  $CH_2$ ···O association between the propyl linker and the other O atom of the same nitro group that is involved in  $CH \cdots O$  interaction with  $C \cdots O$  distance of 3.544 Å to form a 1D chain running along the *a* axis direction. Two neighboring chains were linked together by the CH--O interaction to form a double chain, in this case, the two chains are parallel to each other, however the corresponding cations and anions in the two chains were antiparallelly arranged. The double chains were stacked along the *b* axis direction *via* the  $\pi$ - $\pi$  interaction between the aromatic ring of the cation and the benzene ring of the anion with Cg-Cg distance of 3.388 Å. and CH…O interactions (between the N–CH–N of the cation at one chain and the O atom of the carboxylate at the neighboring chain with C···O distance of 3.137 Å, and between the benzene CH of the cation and the nitro group with  $C \cdots O$  distance of 3.335 Å) to form a 2D sheet parallel to the *ab* plane (Fig. 2). Such kind of sheets were further stacked along the *c* axis direction via the CH...O association between the benzene CH of the cation and the nitro group with C···O distances of 3.335-3.448 Å to form 3D network structure.

#### 3.1.2. X-ray structure of $[(H_2L2)^{2+} (5-nsa^{-})_2]$ (2)

Salt **2** crystallizes as monoclinic pale yellow crystals in the centrosymmetric space group P2/c. The asymmetric unit of **2** consists of two halves of the dications of H<sub>2</sub>L2, and two 5-nitrosalicylate anions, as shown in Fig. 3. The C18–C21, and O8 atoms were all disordered over two positions with occupancy factor of 0.5 respectively. The atoms C11–C14, and O3 were all disordered over two positions with occupancy factor of 0.5 respectively, also. Compound **2** is also a salt where the COOH groups of 5-nitrosalicylic acids are deprotonated, which is also confirmed by the pairs of bond distances of O(1)–C(9) (1.260(9) Å) and O(2)–C(9) (1.249(9) Å); O(6)–C(16) (1.252(9) Å), and O(7)–C(16) (1.255(8) Å) for the carboxylate (Table 3). The protonated L2 cations display *trans* configuration in which the inversion centers are located at C(4), and C(8), respectively.

In the solid state, there is consistently hydrogen bond formed between the  $NH^+$  group, and the 5-nitrosalicylate ion, which is to be expected [42]. There also exist strong coulombic interactions between charged cation units of  $NH^+$  and the 5-nitrosalicylate anions.

Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group  $(O(3)-H(3)\cdots$ O(2), 2.436(17) Å, and O(8)—H(8)···O(7), 2.466(13) Å) (Table 4), it is generally expected and found that the carboxylate group is nearly coplanar with the benzene ring [torsion angle C18-C17-C16-O6, 163°, C11–C10–C9–O1, 164.79°]. There exists a hydrogen bonded  $S_1^{(6)}$  ring in the anion. This feature is similar to that found in salicylic acid [43], and in the previously reported structure of proton-transfer compound based on 5-nsa<sup>-</sup> [44]. As expected the O-O separation is in the lower limit of the documented data [2.489–2.509 Å] [44], but it is slightly contracted compared with the nonproton transfer examples (2.547-2.604 Å, mean: 2.588 Å), as a result of deprotonation. The 5-nitro group also varies little conformationally [torsion angle C20–C21–N6–O10, 160.93°; C13-C14-N5-O5, 172.91°] compared with the reported torsion angle (175.4–180°) within this set of compounds [44].

Two anions were bonded to the cation through the  $N-H\cdots O$ hydrogen bond between the NH<sup>+</sup> cation and the carboxylate group with N–O distances of 2.682(7)–3.053(9) Å, and CH···O interaction between 4-CH of the imidazole moiety and the carboxylate with  $C \cdots O$  distance of 3.054 Å to form a tricomponent heteroadduct. Here every NH<sup>+</sup> formed two N–H···O hydrogen bonds with the COO<sup>-</sup> group in bifurcate mode. Such heteroadducts were connected together via the CH...O interactions (between the 5-CH of one imidazole and one O atom of the nitro group with C···O distance of 3.257 Å, and between N–CH–N of another imidazole in the same cation and the other O atom of the same nitro group with C···O distance of 3.110 Å to form a 1D chain running along the aaxis direction. Such adjacent parallel chains were joined together by  $\pi$ - $\pi$  interaction (between the anion benzene rings and the imidazole rings with Cg–Cg distance of 3.275 Å), CH<sub>2</sub>…O interaction (between the methylene spacer of the cation and the carboxylate group with C···O distance of 3.221 Å), and CH···O interaction (between the N–CH–N of the cation and the carboxylate with  $C \cdots O$ distance of 3.210 Å) to form a 2D sheet extending along the *ab* plane (Fig. 4). In the sheet there existed CH...O interactions between 5-CH of the imidazole at the fourth chain and the nitro group at the first chain with  $C \cdots O$  distance of 3.230 Å, and between the other O atom of the 5-nitro unit at the first chain and the N-CH-N of the cation at the fourth chain with C···O distance of 3.116 Å. Such kind of sheets were further stacked along the *c* axis direction *via* the intersheet CH···O interaction between the phenol group of the anion and 4-CH of the imidazole of the cation with C···O distances of 3.239–3.243 Å to form 3D network structure.

Table 3
Selected bond lengths (Å) and angles (°) for $1-6$ .

1			
N(1)-C(1)	1.337(10)	N(1)-C(3)	1.375(9)
N(1)-C(8)	1.471(9)	N(2)-C(1)	1.288(10)
N(2)-C(2)	1.354(10)	N(3)-C(13)	1.457(10)
N(4)-C(15)	1.446(11)	O(1) - C(10)	1.221(8)
O(2)-C(10)	1.277(9)	C(1) - N(1) - C(3)	105.4(6)
C(1) - N(1) - C(8)	127.7(7)	C(3)-N(1)-C(8)	126.2(7)
C(1) - N(2) - C(2)	106.3(7)	N(2) - C(1) - N(1)	113.6(8)
O(1)-C(10)-O(2)	124.5(7)		
2			
$\frac{2}{N(1)-C(1)}$	1 344(8)	N(1) - C(2)	1 366(10)
N(1) - C(4)	1.544(0) 1.456(7)	N(2) - C(1)	1 298(9)
N(2) - C(3)	1360(9)	N(2) = C(5)	1 335(8)
N(3) - C(7)	1.300(3) 1.370(10)	N(3) - C(8)	1.555(8)
N(4) - C(5)	1 305(9)	N(4) - C(6)	1 346(9)
N(5) = O(5)	1.303(3) 1.214(10)	N(4) = C(0) N(5) = O(4)	1 225(8)
N(5) - C(14)	1.214(10) 1 4(2)	N(5) - C(14')	1.223(0) 1.5(3)
N(6) - O(10)	1 213(10)	N(6) = O(9)	1 228(9)
N(6) - C(21)	14(3)	N(6) - C(21')	1.5(3)
O(1) - C(9)	1 260(9)	O(2) - C(9)	1 249(9)
O(3) - C(11)	1 36(8)	O(6) - C(16)	1 252(9)
O(7) - C(16)	1 255(8)	O(8) - C(18)	1.36(2)
O(3') - C(11')	1 33(10)	O(8') - C(18')	131(2)
C(1) - N(1) - C(2)	107.5(7)	C(1) - N(1) - C(4)	126.4(6)
C(2) - N(1) - C(4)	125.7(6)	C(1) - N(2) - C(3)	110.0(7)
C(5) - N(3) - C(7)	107.7(6)	C(5) - N(3) - C(8)	126.5(6)
C(7) - N(3) - C(8)	125.5(6)	C(5) - N(4) - C(6)	108.7(7)
N(2) - C(1) - N(1)	108.0(8)	N(1)#1-C(4)-N(1)	112.4(8)
N(4) - C(5) - N(3)	108.8(8)	N(3) - C(8) - N(3) + 2	112.8(9)
O(2) - C(9) - O(1)	124.6(8)	O(6) - C(16) - O(7)	124.0(8)
3			
<b>3</b>	1 241(5)	N(1) C(2)	1 202(5)
N(1) - C(1) N(1) - C(15)	1.541(5)	N(1) - C(3) N(2) - C(1)	1.395(5)
N(1) - C(13) N(2) - C(2)	1.470(5)	N(2) = C(1) N(2) = C(8)	1.295(5)
N(2) - C(2) N(2) - C(10)	1.365(3)	N(3) = C(6) N(2) = C(19)	1.541(5)
N(3) = C(10) N(4) = C(8)	1.377(3)	N(3) - C(18)	1.404(3) 1.201(5)
N(4) - C(3) N(5) - C(19)	1.327(3)	N(4) = C(3) N(5) = C(21)	1.391(5)
N(5) - C(13) N(5) - C(33)	1.555(5) 1.457(5)	N(5) = C(21) N(6) = C(19)	1.391(5)
N(6) - C(20)	1 384(6)	N(0) = C(15) N(7) = C(26)	1 348(6)
N(7) - C(28)	1.364(0) 1.361(7)	N(7) = C(20) N(7) = C(36)	1.348(0)
N(8) - C(26)	1.309(6)	N(8) - C(27)	1.405(0)
N(9) - C(40)	1.565(6)	N(10) - C(42)	1.373(0) 1.454(6)
N(11) - C(47)	1.130(0) 1.502(7)	O(1) - C(16)	1.402(5)
O(1) - C(17)	1.416(5)	O(2) - C(35)	1.402(6)
O(2) - C(34)	1.417(6)	O(3) - C(37)	1.234(6)
O(4) - C(37)	1.276(6)	O(5) - C(39)	1.267(5)
O(10) - C(44)	1.243(8)	O(11) - C(44)	1.243(7)
O(12)-C(46)	1.263(7)	C(1) - N(1) - C(3)	106.8(3)
C(1) - N(1) - C(15)	125.7(4)	C(3) - N(1) - C(15)	127.5(3)
C(1) - N(2) - C(2)	106.9(4)	C(8)-N(3)-C(10)	107.1(3)
C(8)-N(3)-C(18)	127.5(4)	C(10)-N(3)-C(18)	125.4(3)
C(8) - N(4) - C(9)	104.9(4)	C(19)-N(5)-C(21)	107.6(4)
C(19)-N(5)-C(33)	124.6(4)	C(21)-N(5)-C(33)	127.7(4)
C(19)-N(6)-C(20)	107.4(4)	C(26)—N(7)—C(28)	105.8(4)
C(26)—N(7)—C(36)	127.6(5)	C(28)—N(7)—C(36)	126.6(4)
C(26)—N(8)—C(27)	105.4(4)	N(2)-C(1)-N(1)	112.5(4)
N(4) - C(8) - N(3)	112.9(4)	N(6)-C(19)-N(5)	111.6(4)
N(8)—C(26)—N(7)	113.8(5)	O(3) - C(37) - O(4)	123.1(5)
O(5)-C(39)-C(40)	124.2(4)	O(11)-C(44)-O(10)	120.7(7)
4			
N(1) - C(1)	1.327(3)	N(1)-C(3)	1.372(3)
N(1)-C(7)	1.464(3)	N(2)-C(1)	1.309(3)
N(2) - C(2)	1.352(4)	N(3)-C(4)	1.327(3)
N(3)-C(6)	1.376(3)	N(3)-C(7)	1.451(3)
N(4) - C(4)	1.307(3)	N(4)-C(5)	1.363(3)
N(5)-C(13)	1.441(3)	N(6)-C(11)	1.452(3)
N(7)-C(18)	1.456(3)	N(8)-C(20)	1.448(3)
O(1)-C(8)	1.236(3)	O(2)-C(8)	1.291(3)
O(3)-C(10)	1.279(3)	O(8)-C(15)	1.233(3)
O(9)-C(15)	1.299(3)	O(10)-C(17)	1.277(2)
C(1) - N(1) - C(3)	108.1(2)	C(1)-N(1)-C(7)	125.5(2)
C(3) - N(1) - C(7)	126.43(19)	C(1) - N(2) - C(2)	108.8(2)
C(4) - N(3) - C(6)	108.3(2)	C(4) - N(3) - C(7)	125.3(2)
C(6) - N(3) - C(7)	126.15(19)	C(4) - N(4) - C(5)	109.2(2)
N(2) - C(1) - N(1)	109.0(2)	N(4) - C(4) - N(3)	108.7(2)

Table 3 (continued)			
N(3)—C(7)—N(1) O(8)—C(15)—O(9)	109.68(17) 121.5(2)	O(1)—C(8)—O(2)	121.8(2)
$5 \\ N(1)-C(1) \\ N(1)-C(4) \\ N(2)-C(2) \\ N(4)-C(11) \\ O(2)-C(6) \\ C(1)-N(1)-C(3) \\ C(3)-N(1)-C(4) \\ N(2)-C(1)-N(1) \\ \end{array}$	1.333(8) 1.475(8) 1.364(8) 1.459(8) 1.320(8) 108.0(5) 125.0(5) 109.1(6)	N(1)-C(3) N(2)-C(1) N(3)-C(9) O(1)-C(6) O(3)-C(8) C(1)-N(1)-C(4) C(1)-N(2)-C(2) O(1)-C(6)-O(2)	1.389(8) 1.305(8) 1.456(8) 1.214(9) 1.296(8) 126.9(6) 109.4(5) 120.8(7)
	1.329(3) 1.455(3) 1.365(3) 1.239(3) 1.271(3) 125.78(19) 109.2(2) 111.2(2) 120.4(2)	$\begin{array}{l} N(1)-C(3) \\ N(2)-C(1) \\ O(1)-C(5) \\ O(3)-C(9) \\ C(1)-N(1)-C(3) \\ C(3)-N(1)-C(4) \\ N(2)-C(1)-N(1) \\ O(2)-C(5)-O(1) \end{array}$	1.360(3) 1.303(3) 1.267(3) 1.227(3) 108.2(2) 125.99(17) 108.4(2) 119.7(2)

Symmetry transformations used to generate equivalent atoms for **2**: #1 - x + 1, *y*, -z + 1/2; #2 - x, *y*, -z + 1/2.

Symmetry transformations used to generate equivalent atoms for **6**: #1 -x, y, -z+2.

#### 3.1.3. X-ray structure of [(HL3)<sup>+</sup>·(3,5-dns<sup>-</sup>)] (**3**)

Crystallization of 1,5-bis(1-benzimidazolyl)-3-oxapentane and 3,5-dinitrosalicylic acid in a 1:1 ratio from the mixed solvent of methanol and ethanol gave single crystals suitable for X-ray diffraction. Structure determination (Table 1) revealed that 1,5bis(1-benzimidazolyl)-3-oxapentane and 3,5-dinitrosalicylic acid are present in a 1:1 ratio in the molecular complex **3**. The crystal structure of **3** consists of two halves of monoprotonated L3, and two halves of monoanion of 3,5-dinitrosalicylic acid in the asymmetric unit (Fig. 5). Different from the salts 1-2, here the bis-N-imidazole is monoprotonated. The reason may be that this molecule(L3) may be too flexible introducing factors that result more important than the small difference between the donors to decide the preferred molecular interactions. In 3 the COOH groups of 3,5-dinitrosalicylic acids are ionized by proton transfer to the nitrogen atoms of the benzimidazole moieties, and the phenol OH group remains protonized.

The C–O distances in the carboxylate O(10)–C(44)–O(10) are almost equal with each other within the experimental error, indicating that the negative charge was distributed equally on both O atoms. While for the COO<sup>-</sup> group O(3)–C(37)–O(4), two C–O bond lengths (The C–O distances of COO<sup>-</sup> of the 3,5-dinitrosalicylate are ranging from 1.234(6) (O(3)–C(37)) to 1.276(6) Å (O(4)–C(37) with  $\Delta$  = 0.042 Å) are basically not equal with an average value of 1.255(6) Å (Table 3). The significantly difference between the two bonds is attributed to the fact that O4 atom is involved in forming more hydrogen bonds than that of O3 (Table 4).

All the benzimidazole rings are essentially planar with the largest deviation from the mean plane of 0.0199 Å. The HL3 adopts *cis* configuration with the planes of the two benzimidazole rings in the same cation inclined by  $6.4^{\circ}$  (for the cation bearing N3, and N4 atoms), and  $15.7^{\circ}$  (for the cation bearing N7, and N8 atoms) for the two independent cations, respectively. The benzimidazole rings formed dihedral angles of  $65^{\circ}$  (for the ring bearing N1, and N2 atoms),  $71.1^{\circ}$  (for the ring bearing N3, and N4 atoms),  $64.6^{\circ}$  (for the ring bearing N5, and N6 atoms), and  $72.1^{\circ}$  (for the ring bearing N7, and N8 atoms) with the plane defined by the oxapentane spacer.

The torsion angles O8–N10–C42–C43, and O6–N9–C40–C41 are 178.14°, and 178.63°, respectively. In this regard, both nitro

#### Table 4

Hydrogen bond distances and angles in studied structures 1-6.

D—H···A	d(D—H) (Å)	d(H···A) (Å)	$d(D \cdot \cdot \cdot A)$ (Å)	<(DHA) (°)
1		( )	( )	()
N(2)—H(2)···O(2)#2	0.86	1.74	2.541(8)	154.0
2				
N(2)−H(2)···O(6)#3	0.86	1.83	2.684(7)	169.5
N(2)−H(2)···O(7)#3	0.86	2.56	3.053(9)	117.3
N(4) - H(4) - O(1) = 1	0.86	1.83	2.682(7)	171.8
N(4) - H(4) - O(2) = 1	0.86	2.53	3.027(9)	117.3
O(3) - H(3) - O(2)	0.82	1.71	2.436(17)	146.1
O(8) - H(8) - O(7)	0.82	1.72	2.466(13)	149.9
O(3') - H(3') - O(2)	0.82	1.79	2.521(15)	146.9
O(8') - H(8') - O(7)	0.82	1.73	2.450(15)	144.8
3				
$D(12) = H(12) \dots D(11)$	0.82	1 77	2 512(9)	149.8
O(4) - H(4A) O(5)	0.82	1.68	2.312(5) 2.436(5)	151.9
N(6) - H(6) - N(8) = 1	0.86	1.80	2.665(5)	176.7
N(2) - H(2) - N(4) = 2	0.86	1.81	2.671(5)	175.6
	0.00	1101	2107 1(0)	17010
4	0.00	2.64	0.007(0)	
O(9) - H(9) - O(6) = 1	0.82	2.64	3.037(3)	111.5
$O(9) - H(9) \cdots O(10)$	0.82	1.72	2.477(2)	153.7
O(2) - H(2A) O(13) #2	0.82	2.64	3.072(3)	114.8
$O(2) - H(2A) \cdots O(3)$	0.82	1./1	2.469(2)	154.2
$N(4) - H(4) \cdots O(8)$	0.86	1.91	2.723(3)	157.4
$N(2) - H(2) \cdot \cdot \cdot O(1) = 3$	0.86	1.88	2.718(3)	165.1
5				
O(2) - H(2A) - O(3)	0.82	1.76	2.523(6)	153.1
N(2)−H(2)···O(4)#2	0.86	2.29	2.890(8)	126.7
N(2)−H(2)···O(3)#2	0.86	1.92	2.715(7)	154.1
6				
$0(4) - H(4) \cdots O(4) = 3$	0.82	1 54	2.362(4)	175.2
O(1) - H(1) - O(1) = 2	0.82	1 55	2.302(1) 2.371(3)	177.1
N(2) - H(2) - O(1) # 4	0.86	2.50	3 093(3)	127.1
N(2) - H(2) - O(2) #4	0.86	1.84	2 695(4)	174 9
(2) (2) (2) (2) (4	0.00	1.0 1	2.000(4)	17 1.5

Symmetry transformations used to generate equivalent atoms for **1**: #2 x + 1, *y*, *z*. Symmetry transformations used to generate equivalent atoms for **2**: #1 - x + 1, *y*, -z + 1/2; #3 x - 1, y + 1, *z*.

Symmetry transformations used to generate equivalent atoms for **3**: #1 - x + 2, -y + 1, -z; #2 - x + 2, -y + 2, -z.

Symmetry transformations used to generate equivalent atoms for **4**: #1 - x + 1, -y + 2, -z + 1; #2 - x + 2, -y + 2, -z + 2; #3 x - 1, y, z - 1.

Symmetry transformations used to generate equivalent atoms for **5**: #2 - x, -y + 1, -z + 2.

Symmetry transformations used to generate equivalent atoms for **6**: #2 x, -y + 2, z; #3 x, -y + 1, z; #4 x, y - 1, z + 1.

groups are nearly in the same plane as the benzene ring of the anion, yet the 3-nitro (O6–N9–O7) deviates somewhat less from the plane than the 5-nitro (O8–N10–O9) group, which is different from the published results [45]. While the nitro groups in the other anion deviate 178.37° (for the O13–N11–O14 group), and 166.79°

(for the O15–N12–O16 group) respectively from the phenyl ring plane of the anion. Herein the 3-nitro unit (the O13–N11–O14 group) is essentially coplanar with the phenyl ring of the anion, while the 5-nitro group (O15–N12–O16 group) is rotated out of the plane.

Since the potentially hydrogen bonding hydroxyl group is present in the *ortho* position to the carboxyl group in the anion, it forms the more facile intramolecular hydrogen bonding. Thus the usual intramolecular hydrogen bond is found between the phenol OH group and a carboxylate O atom (O(5)—H(5A)···O(4), 2.436(5) Å, 151.9° O(12)—H(12)···O(11), 2.512(9) Å, 149.8°) which is similar to the corresponding value (2.409 Å) in proton-transfer compound of [(hmt)<sup>+</sup> [(dnsa)<sup>-</sup>] [46,47]. Yet the value is as expected generally smaller than the distance found for the parent dnsa acid monohydrate [2.566(3) Å] [48], and in the neutral species found in the adduct compound. For the presence of the intramolecular hydrogen bond, there also exists hydrogen bonded motif with graphical descriptor of S<sub>1</sub><sup>1</sup>(6).

Two monoprotonated cations were linked together in head to tail fashion *via* the N—H···N hydrogen bond with N—N separation of 2.671 Å to form a dimer. In the dimer the two cations were inversionally related and formed a 24-membered ring. The cation dimers were connected together by a pair of antiparallelly arranged anions through the CH. O associations to form a 1D chain running along the *c* axis direction. In this regard one kind of CH···O interaction is produced between the benzene CH of the cation and the 5-nitro group of the anion with C···O distance of 3.502 Å, the other kind of CH···O interaction is made between the phenol group of the anion and the benzene CH of the cation with C···O distance of 3.445 Å. Such kind of 1D parallel chains were joined together by CH<sub>2</sub>···O interaction between the CH<sub>2</sub> unit of the oxapentane spacer and the 5-nitro group with C···O distance of 3.586 Å,  $CH_2-\pi$  interaction between the CH<sub>2</sub> of the oxapentane spacer and the aromatic ring of the cation with C–Cg distance of 3.549 Å, and  $\pi$ - $\pi$  interactions between the benzimidazole rings of the cation with Cg-Cg distance of 3.313 Å to form 2D sheet structure extending in the direction that made an angle of  $ca 45^{\circ}$  with the *bc* plane (Fig. 6). Such kind of sheets were further stacked along the direction that is perpendicular with its extending direction via the CH<sub>2</sub>...O association (between the CH<sub>2</sub> of the oxapentane spacer and the carboxylate with  $C \cdots O$  distance of 3.362 Å, and between the  $CH_2$  of the oxapentane spacer and the 5-nitro group with C···O distance of 3.502 Å), and CH···O interactions (between the benzene CH of the cation and the 5-nitro group of the anion with C···O distance of 3.437 Å, and between the N–CH–N of the imidazole moiety and the nitro and the carboxylate units belonging to two different anions respectively with  $C \cdots O$  distances of 3.231–3.121 Å) to form 3D layer network structure.



Fig. 2. 2D sheet structure of 1 running parallel to the ab plane.



Fig. 3. The structure of 2, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.



Fig. 4. 2D sheet structure of 2 extending along the *ab* plane.

#### 3.1.4. X-ray structure of $[(H_2L2)^{2+} (3,5-dns^{-})_2]$ (4)

The compound **4** crystallizes as Triclinic block crystals in the space group P-1. The asymmetric unit of **4** consists of one cation of bis(N-imidazolylium)methane, and two independent monoanions of 3,5-dinitrosalicylate, as shown in Fig. 7. Similar to **3**, compound **4** is also an organic salt. However in this case it is the phenol H that has been deprotonated which is different from **3**. The C–O distances 1.279(3) Å (O(3)–C(10)), and 1.277(2) Å (O(10)–C(17)) concerning the phenolate are similar to the proton transfer compound bearing the 3,5-dns<sup>-</sup> in which only the phenol group has been deprotonated [49]. The C–O distances O(1)–C(8), 1.236(3), O(2)–C(8), 1.291(3); O(8)–C(15), 1.233(3) Å, O(9)–C(15), 1.299(3) Å in the COOH show characteristic C=O, and C–O distances which are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms as mentioned above (Table 3).

The anions were linked together *via* the O—H···O hydrogen bond between the COOH moiety and the 5-nitro group with O—O distances of 3.037(3)–3.072(3) Å to form a 1D chain running along the *c* axis direction. Herein the adjacent anions are in the same plane and rotate about 45° from each other, while the third anion is parallel to the first anion in the chain, so does the second anion and the fourth anion. Two neighboring chains were combined together by the cations *via* the N—H···O association between the NH<sup>+</sup> cation and the carbonyl group of the anion with N—O distance of 2.723(3) Å and CH···O association between the N–CH–N of the cation and the 3-nitro group with C···O distances of 3.118-3.204 Å to form a double chain. Such kind of double chains were further stacked along the a axis direction by the  $\pi$ - $\pi$  interactions between the benzene ring of the anion with Cg—Cg distance of 3.388 Å and CH…O interaction between 4-CH of the imidazole of one double chain and the carbonyl of its adjacent double chain with C···O distance of 3.300 Å to form a sheet extending parallel to the ac plane (Fig. 8). The thickness of the sheet is ca. 15.638 Å. Such kind of sheets were stacked along the b axis direction by the intersheet  $CH \cdots O$  (between 4-CH of the cation at one sheet and the carbonyl unit of its neighboring sheet with C···O distance of 3.480 Å), and  $CH_2$ ···O interactions to form 3D ABAB layer network structure. Herein every H of the CH<sub>2</sub> spacer in the cation made a bifurcate  $CH_2 \cdots O$  association with the phenolate and the 3-nitro groups in the same anion to generate a  $R_1^2(6)$  ring in which the C···O distances are ranged from 3.226 Å to 3214 Å. There also found intersheet O- $\pi$  interaction between the O atom of the 5-nitro group and the imidazole ring with O–Cg distance of 2.931 Å. The O–Cg distance in **4** is significantly shorter than that found in the archived data (3.12 Å) [50]. In this regard the corresponding anions and the cations between two adjacent layers were antiparallelly arranged. The anions at the first layer were parallel to the anions at the third layer, and the cations at the first layer were also parallel to the cations at the third layer, so did the corresponding anions and cations at the second layer and the fourth layer.



**Fig. 5.** The structure of **3**, showing the component of the title compound (for the crowdedness of the structure the atom-numbering was not labeled). Displacement ellipsoids were drawn at the 30% probability level.

#### 3.1.5. X-ray structure of $[(H_2L4)^{2+} (3,5-dns^{-})_2]$ (5)

Similar to the salt **4**, the asymmetric unit of **5** consists of half a dication of N,N'-butylenebis(imidazole), and one monoanion of 3,5-dns<sup>-</sup>, as shown in Fig. 9. Here it is also the phenol group that

has ionized, while the COOH remains protonized. The C-O distances of the COOH of 3,5-dinitrosalicylate are ranging from 1.214(9) Å (O(1)–C(6)) to 1.320(8) Å (O(2)–C(6)) with the  $\triangle$  value of 0.106 Å, which suggests that the carboxyl group is protonated. In the cation, protonation at atom N2 leads to an increase in the C(1)-N(2)-C(2) [109.4(5)°] angle compared to that observed in the neutral L4  $(104.15(4)^\circ)$ , and this angle is almost equal to the corresponding angle on its hydrochloride salt (109.08(3)°) [51]. It was found that protonation of the imidazole ring nitrogen atoms causes no significant change in conformation of the (H<sub>2</sub>L4)<sup>2+</sup> dication in 5 in comparison to the corresponding neutral molecule 1-(4-(1H-imidazol-1-yl)butyl)-1H-imidazole (L4) [51]. The imidazole rings in 5 have trans-(ap) position in respect to C4-C5 bond (angle C4–C5–C4A–C5A, 180°), which is different from the corresponding 1,1'-(1,4-butanediyl)bis(imidazolium) dihydrochloride [51]. The two imidazole rings in the same cation were antiparallellv arranged.

The nitro groups N3–O4–O5, and N4–O6–O7 deviate by  $6^{\circ}$ , and  $6.3^{\circ}$  from the mean plane of the phenyl ring of the anion. The carboxyl group deviated by only  $3^{\circ}$  from the phenyl ring plane of the 3,5-dinitrosalicylate.

At each cation there are bonded two anions via the bifurcated N–H···O association between the NH<sup>+</sup> cation and the phenolate and the 3-nitro group respectively with N–O distances of 2.715(7)–2.890(8) Å to generate a bicomponent adduct. For the presence of these two hydrogen bonds, there are hydrogen bonded  $R_1^2(6)$  ring in the bicomponent heteroadduct. There also exists intramolecular O–H···O hydrogen bond with graph set of  $S_1^{-1}(6)$  between the COOH unit and the phenolate with O–O separation of 2.523 Å. Such kind of bicomponent heteroadducts were linked together *via* the CH<sub>2</sub>···O association between the CH<sub>2</sub> group of the butane spacer and the 5-nitro unit with C···O distance of 3.117 Å to form a 1D chain running along the *c* axis direction (Fig. 10). Such kind of chains were combined together *via* the



Fig. 6. 2D sheet structure of **3** which is extending in the direction that made an angle of *ca* 45° with the *bc* plane.



Fig. 7. The structure of 4, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.



Fig. 8. 2D sheet structure of 4 built from double chains via  $\pi$ - $\pi$ , and CH–O interactions, which is extending parallel to the *ac* plane.



Fig. 9. The structure of 5, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

CH···O interactions (between 4-CH of the anion and 5-nitro of the anion belonging to different chains with C···O distance of 3.424 Å, between N–CH–N of the cation and the carbonyl group of the anion with C···O distance of 3.202 Å, and between 5-CH of the imidazole and 3-nitro group of the anion with C···O distance of 3.211 Å) to form 3D network structure.

#### 3.1.6. X-ray structure of $[(H_2L2)^{2+}(Hpta^{-})_2]$ (6)

The asymmetric unit of **6** consists of half a dication of bis(Nimidazolyl)methane, and two halves of monoanion of phthalic acid, which is shown in Fig. 11. Here the acidic Hs at the hydrogen phthalate were disordered over the COO<sup>-</sup> and COOH groups each with occupancy factor of 0.5, respectively. The cation also displays *trans* conformation. Similar with the reported adduct of phthalate [52], the carboxylates in the anion are almost in the same plane as the phenyl ring.

The anions formed a 1D chain along the *c* axis direction *via* the CH···O interactions between the benzene CH of one anion and the carboxylate group of its neighboring anion with C···O distances of 3.369-3.410 Å. In the chain the anions were arranged in head to tail fashion. Such parallel anionic chains were packed along the *a* 



**Fig. 11.** The structure of **6**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

axis direction, yet there are not any interactions between such neighboring chains. In this case the anions at two adjacent chains were antiparallelly arranged and slipped some distance from each other along the *c* axis direction. The third anion chain has the same projection on the bc plane as the first anion chain, so does the second anion chain and the fourth anion chain. Such discrete anion chains also extend parallelly in the bc plane, the anions at the third chain in the *bc* plane were parallel to the anions at the first chain, but the anions at the neighboring chains were antiparallel to each other. Two adjacent anionic chains were combined together along the *a* axis direction by the cations *via* the N–H $\cdots$ O, and CH $\cdots$ O associations to form 1D flat pipelike structure in which the width of the flat pipe is *ca*. half the length of the *b* axis. Here the  $NH^+$ group functioned as bifurcate donor forming two N-H...O hydrogen bonds with the same carboxylate group with N-O distances in the range of 2.696–3.093 Å. The CH...O interactions are found between N-CH-N of the cation and the carboxylate with C···O distance of 3.242 Å. There are also anion chains that are not bonded with the cations through the N–H $\cdots$ O hydrogen bonds. The flat pipelike structure and the anion chains not bonded with the cations are arranged alternatively on the *bc* plane, and they are joined



Fig. 10. 1D chain structure of 5 which is running along the c axis direction.



Fig. 12. 2D sheet structure of 6 when viewed from the *a* axis direction.

together *via* the CH<sub>2</sub>···O interaction (between the methylene bridge of the cation and one O atom of the carboxylate with C···O distance of 3.138 Å), CH···O interaction (between the N–CH–N of the imidazole and the other O of the same carboxylate with C···O distance of 3.107 Å), and CH– $\pi$  interaction (between the benzene CH of the anion and the imidazole ring of the cation with C–Cg distance of 3.652 Å) to form 2D sheet structure (Fig. 12). Such kind of 2D sheets were further stacked along the *a* axis direction *via* the intersheet CH···O interactions between 4-CH of the imidazole moiety and the carboxylate with C···O distance of 3.165 Å to form 3D ABAB layer network structure. In this regard the second sheet was slipped about half the *b* axis length along the *b* axis direction, while the third sheet has the same projection on the *bc* plane as the first sheet, so does the fourth sheet and the second sheet.

#### 4. Conclusion

Six organic acid-base salts with 3D frameworks have been prepared and structurally characterized. The different hydrogen bond interaction modes of the carboxylic acid and the bis(imidazole) lead to a wide range of different structures such as 3D network structure, 3D layer network structure, and 3D ABAB layer structure.

Of the six salts five examples (**1**, **2**, **4**, **5**, and **6**) involve proton transfer from the carboxylic acids to both N atoms of the bis(imidazole) molecules to form a dication, while in salt **3**, the bis(imidazole) molecule of L3 is only monoprotonated to exhibit a valence number of + 1.

This study has demonstrated that the N–H···O/O–H···O hydrogen bonds are the primary intermolecular force in a family of structures containing the OH···im synthons. Except the classical hydrogen bonding interactions, the secondary propagating interactions also made significant contribution to the structure extension. All salts possess weak C–H···O/CH<sub>2</sub>···O associations. Two types of secondary C–H···O/CH<sub>2</sub>···O interactions were observed based upon their geometric preferences, intra- and interchain interactions. Based upon an analysis of the metrics displayed by each set of interactions, it seems that intra- and interchain C–H···O/CH<sub>2</sub>···O CH<sub>2</sub>···O interactions are of equal structural importance. There are

also  $\pi$ - $\pi$  associations in compounds **1**-**4**. The CH- $\pi$  interactions were found in **6**, while **3** possesses CH<sub>2</sub>- $\pi$  interaction. Salt **4** bears the O- $\pi$  interaction.

In conclusion, we have shown that 3D structures can be constructed by synergistic effect of the various noncovalent interactions such as strong directional hydrogen bond (N<sup>+</sup>–H···O<sup>-</sup>, O–H···O, and N–H···N), CH–O/CH<sub>2</sub>–O,  $\pi$ – $\pi$ , CH– $\pi$ , CH<sub>2</sub>– $\pi$ , and O– $\pi$  interactions between discrete components.

#### Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 851526 for **1**, 858644 for **2**, 858645 for **3**, 851525 for **4**, 851524 for **5**, and 835839 for **6**. Copies of this information may be obtained free of charge from the +44 (1223)336 033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc. 2012.04.082.

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