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Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structure of seven organic acid–base adducts formed between acids, 2-aminophenol, and 2-amino-4-chlorophenol

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HIGHLIGHTS

- ► Seven organic acid-base adducts have been prepared and structurally characterized.
- ▶ The hydrogen bond interaction modes in all of the adducts have been ascertained.
- ▶ The classical hydrogen bonds are the major forces in all of the structures.
- ▶ The secondary interactions also play important roles in the packing of the adducts.

ARTICLE INFO

Article history: Received 19 March 2012 Received in revised form 4 January 2013 Accepted 4 January 2013 Available online 16 January 2013

Keywords: Crystal structure 3D framework Hydrogen bonds Acidic compounds 2-Aminophenols derivatives

ABSTRACT

Studies concentrating on hydrogen bonding between the base of 2-aminophenol, 2-amino-4-chlorophenol, and acidic compounds have led to an increased understanding of the role 2-aminophenol, and 2amino-4-chlorophenol have in binding with acidic compounds. Here anhydrous and hydrated multicomponent crystals of 2-aminophenol, and 2-amino-4-chlorophenol have been prepared with 2,4,6-trinitrophenol, p-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid, and fumaric acid. The crystals and complexes of the seven organic acid-base adducts were characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. The seven crystalline forms reported are organic salts except **2**. All of the adducts were formed in solution and obtained by the slow evaporation technique. All supramolecular architectures involve extensive $N-H\cdots O$, $O-H\cdots O$, and $CH\cdots O$ hydrogen bonds as well as other nonbonding interactions. The role of weak and strong hydrogen bonding in the crystal packing is ascertained.

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1. Introduction

The design and construction of multicomponent supermolecules or supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. However, self-assembled supramolecular architectures are often stabilized as a result of the synergy of a variety of weak noncovalent interactions [1–3]. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of non-covalent interactions, in building supramolecular systems [4].

Carboxylic acids represent one of the most prevalent functional groups in crystal engineering because they possess a hydrogen bond donor and acceptor with a geometry that facilitates self-association through supramolecular homosynthons via centrosymmetric dimer or catemer [5–7]. Furthermore, it is now recognized that carboxylic acids are ideal candidates for multicomponent crystals

since they form persistent supramolecular heterosynthons with a number of different complementary functional groups such as amine, and aromatic nitrogen, etc. For instance, much has been said about the use of carboxyl and pyridinyl groups in the design of supramolecular systems [8–13]. Besides the COOH group, the functional groups such as amine, halogen, and phenol OH groups are all good groups in forming organic solid through non-covalent interactions [14]. Aminophenols containing equal stoichiometries of –OH, and –NH₂ groups have been widely studied to understand the supramolecular synthons existing in their assemblies [15]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of aminophenols derivatives and carboxylic acids [16].

In order to understand the interaction modes aminophenols derivatives have in binding with acidic derivatives, we began to study the aminophenols-acids system, also aiming to find the role the weak noncovalent interactions played in forming the final supramolecular frameworks. Thus, in the following, we report the preparation and crystal structures of seven supramolecular



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^{0022-2860/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molstruc.2013.01.012



Scheme 1. The building blocks discussed in this paper.

compounds assembled via nonbonding interactions between carboxylic acids and 2-aminophenol (L1), and 2-amino-4-chlorophenol (L2) (Scheme 1). In this study, we got seven organic compounds composed of acidic units and 2-aminophenol derivatives, namely (2-aminophenol): (2,4,6-trinitrophenol) [(HL1)⁺ \cdot (pic⁻), pic⁻ = picrate, L1 = 2-aminophenol] (1), (2-amino-4-chlorophenol): (p-nitrobenzoic acid): H₂O [(L2) \cdot (Hnba) \cdot H₂O, Hnba = p-nitrobenzoic acid] (2), (2-aminophenol): (3,5-dinitrobenzoic acid) [(HL1)⁺ \cdot (dnb⁻), dnb⁻ = 3,5-dinitrobenzoate] (3), (2-amino-4-chlorophenol): (3,5-dinitrobenzoic acid) [(HL2)⁺ \cdot (dnb⁻)] (4), (2-aminophenol): (5-nitrosalicylic acid) [(HL1)⁺ \cdot (5-nsa⁻), 5-nsa⁻ = 5-nitrosalicylate] (5), (2-amino-4-chlorophenol): (3,5-dinitrosalicylic acid) [(HL2)⁺ \cdot (3,5-dns⁻), 3,5-dns⁻ = 3,5-dinitrosalicylate] (c), and (2-amino-4-chlorophenol): (fumaric acid)_{0.5} : H₂O [(HL2)⁺ \cdot (fum²⁻)_{0.5} \cdot H₂O, fum²⁻ = fumarate] (7) (Scheme 2).

2. Experimental section

2.1. Materials and physical measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer with 4 cm⁻¹ resolution. Microanalytical (C, H, N) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of supramolecular compounds

2.2.1. (2-Aminophenol): (2,4,6-trinitrophenol) [(HL1)⁺ · (pic⁻), pic⁻ = picrate] (1)

2-Aminophenol (10.9 mg, 0.10 mmol) was dissolved in 3 mL methanol. To this solution was added 2,4,6-trinitrophenol (23 mg, 0.1 mmol) in 10 mL methanol. Brown block crystals were obtained after several days by slow evaporation of the solvent (yield: 26 mg, 76.87%). mp 147–148 °C. Elemental analysis: Calc. for C₁₂H₁₀N₄O₈ (338.24): C, 42.57; H, 2.96; N, 16.56. Found: C, 42.51; H, 2.89; N, 16.52. Infrared spectrum (KBr disc, cm⁻¹): 3589s(v(OH)), 3440s(v_{as}(NH)), 3306s(v_s(NH)), 3190s, 3100s, 2940m, 2880m, 2848m, 2820m, 2676w, 2568w, 2370m, 2330m, 1740m, 1645m, 1614s, 1600s, 1560s, 1525s(v_{as}(NO₂)), 1480m, 1440m, 1360s, 1324s(v_s(NO₂)), 1260s, 1240m, 1210m, 1160m, 1020m, 980m, 920m, 878m, 840m, 790m, 720m, 680m, 660m, 620m.

2.2.2. (2-Amino-4-chlorophenol): (p-nitrobenzoic acid): H_2O [(L2) · (Hnba) · H_2O , Hnba = p-nitrobenzoic acid] (2)

2-Amino-4-chlorophenol (14.3 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added p-nitrobenzoic acid (17 mg, 0.1 mmol) in 2 mL methanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 18 mg, 54.76%, based on L2). mp 213–214 °C. Elemental analysis: Calc. for $C_{13}H_{13}ClN_2O_6$ (328.70): C, 47.46; H, 3.95; N, 8.52. Found: C, 47.37; H, 3.89; N, 8.49. Infrared spectrum (KBr disc, cm⁻¹): 3596s(v(OH)), 3230s(v_{as}(NH)), 3176s(v_s(NH)), 3079 m, 2989s, 2926s, 2682w, 2567w, 1763w, 1648s(v(C=O)), 1620m,



Scheme 2. The seven organic acid-base adducts described in this paper, 1-7.

1572m, 1538s($v_{as}(NO_2)$), 1505m, 1486m, 1448m, 1418m, 1326s($v_s(NO_2)$), 1288s(v(C-O)), 1226m, 1162m, 1094m, 1006m, 952w, 839m, 797w, 724m, 654w, 618w.

2.2.3. (2-Aminophenol): (3,5-dinitrobenzoic acid) $[(HL1)^{+} \cdot (dnb^{-}), dnb^{-} = 3,5$ -dinitrobenzoate] (3)

2-Aminophenol (10.9 mg, 0.10 mmol) was dissolved in 3 mL methanol. To this solution was added 3,5-dinitrobenzoic acid (21.2 mg, 0.1 mmol) in 4 mL methanol. Brown block crystals were obtained after several days by slow evaporation of the solvent (yield: 25 mg, 77.82%). mp 183–185 °C. Elemental analysis: Calc. for C₁₃H₁₁N₃O₇ (321.25): C, 48.56; H, 3.42; N, 13.07. Found: C, 48.52; H, 3.37; N, 12.99. Infrared spectrum (KBr disc, cm⁻¹): 3579s(v(OH)), 3454s(multiple, v_{as}(NH)), 3346s(v_s(NH)), 3158m,

3072m, 2989m, 2658w, 2582w, 1979w, 1835w, 1782w, 1664w, 1602s($v_{as}(COO^{-})$), 1590m, 1522s($v_{as}(NO_{2})$), 1462w, 1384s($v_{s}(-COO^{-})$), 1323s($v_{s}(NO_{2})$), 1252m, 1194m, 1128m, 1064m, 1011m, 952m, 903m, 856m, 802m, 753m, 726m, 674m, 626m.

2.2.4. (2-Amino-4-chlorophenol): (3,5-dinitrobenzoic acid) $[(HL2)^+ \cdot (dnb^-), dnb^- = 3,5-dinitrobenzoate]$ (4)

2-Amino-4-chlorophenol (14.3 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added 3,5-dinitrobenzoic acid (21.2 mg, 0.1 mmol) in 4 mL methanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 28 mg, 78.72%, based on L2). mp 178–180 °C. Elemental analysis: Calc. for $C_{13}H_{10}ClN_3O_7$ (355.69): C, 43.86; H, 2.81; N, 11.81. Found: C, 43.82; H, 2.73; N, 11.75. Infrared spectrum (KBr

Table 1

Summary of X-ray crystallographic data for complexes 1-7.

	1	2	3	4
Formula	$C_{12}H_{10}N_4O_8$	C13H13CIN2O6	C ₁₃ H ₁₁ N ₃ O ₇	C13H10CIN3O7
Fw	338.24	328.70	321.25	355.69
Т, К	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P-1	P-1	P2(1)	P-1
a, Å	8.1626(6)	6.6040(5)	9.4853(8)	7.3617(5)
b, Å	8.4942(8)	7.4679(6)	6.0759(7)	7.4375(7)
<i>c</i> , A	10.3537(11)	15.1801(14)	12.0898(13)	13.6853(13)
α, °	79.7650(10)	77.3260(10)	90	103.183(2)
β, °	82.0190(10)	82.0680(10)	95.1980(10)	94.1080(10)
γ, °	88.947(2)	88.123(2)	90	94.8200(10)
V, A ³	699.59(11)	723.42(10)	693.89(12)	723.79(11)
$D_{\rm relat}$ Mg/m ³	1 606	1 509	2 1 538	1 632
Absorption coefficient, mm^{-1}	0.138	0.296	0.128	0.309
F(000)	348	340	332	364
Crystal size, mm ³	$0.42 \times 0.18 \times 0.14$	$0.44 \times 0.40 \times 0.18$	$0.42 \times 0.23 \times 0.11$	$0.38 \times 0.33 \times 0.12$
θ range. °	2.44–25.01	2.78-25.02	2.62–25.01	2.79-25.02
Limiting indices	$-9 \leqslant h \leqslant 9$	$-7 \leq h \leq 7$	$-7 \leq h \leq 11$	$-8 \le h \le 3$
0	$-6 \leqslant k \leqslant 10$	$-8 \leqslant k \leqslant 6$	$-7 \leqslant k \leqslant 7$	$-8 \leqslant k \leqslant 8$
	$-12 \leqslant l \leqslant 12$	$-18\leqslant l\leqslant 15$	$-13 \leqslant l \leqslant 14$	$-16 \leqslant l \leqslant 16$
Reflections collected	3531	3641	3506	3610
Reflections independent (R_{int})	2434 (0.0191)	2503 (0.0172)	2399 (0.0275)	2494 (0.0149)
Goodness-of-fit on F ²	1.040	1.009	1.006	1.011
R indices $[I > 2\sigma I]$	0.0517, 0.1277	0.0407, 0.0976	0.0429, 0.0889	0.0407, 0.0940
R indices (all data)	0.0759, 0.1501	0.0617, 0.1138	0.0639, 0.1013	0.0631, 0.1094
Largest diff. peak and hole, e Å $^{-3}$	0.690, -0.441	0.300, -0.252	0.253, -0.253	0.218, -0.238
	5		6	7
Formula	$C_{13}H_{12}N_2O_6$		C ₁₃ H ₁₂ ClN ₃ O ₉	C ₈ H ₁₀ ClNO ₄
Fw	292.25		389.71	219.62
Т, К	298(2)		298(2)	298(2)
Wavelength, A	0.71073		0.71073	0.71073
Crystal system	Triclinic		Monoclinic	Monoclinic
Space group	P-1		P2(1)/n	P2(1)/c
a, A	10.7020(10)		7.1541(6)	5.645(3)
D, A	10.7709(11)		/ 2988(7)	04 555(40)
с, А			20 200(2)	21.777(12)
	12.4031(13)		29.388(2)	21.777(12) 7.992(4)
	108.702(2)		29.388(2) 90 90 06 2860(10)	21.777(12) 7.992(4) 90
β, \circ	12.403(13) 108.702(2) 97.5900(10)		29.388(2) 90 96.3860(10)	21.777(12) 7.992(4) 90 90.579(6)
β, \circ γ, \circ V Å ³	108.702(2) 97.5900(10) 92.7600(10) 1336.1(2)		29.388(2) 90 96.3860(10) 90	21.777(12) 7.992(4) 90 90.579(6) 90 982.4(9)
α, ° β, ° γ, ° V, Å ³ Z	12.405 (15) 108.702(2) 97.5900(10) 92.7600(10) 1336.1(2) 4		29.388(2) 90 96.3860(10) 90 1525.0(2) 4	21.777(12) 7.992(4) 90 90.579(6) 90 982.4(9) 4
β, \circ β, \circ γ, \circ $V, Å^3$ Z $D \rightarrow Mg/m^3$	108.702(2) 97.5900(10) 92.7600(10) 1336.1(2) 4 1.453		29.388(2) 90 96.3860(10) 90 1525.0(2) 4 1 697	21.777(12) 7.992(4) 90 90.579(6) 90 982.4(9) 4 1.485
β , ° γ , ° V, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient mm ⁻¹	108.702(2) 97.5900(10) 92.7600(10) 1336.1(2) 4 1.453 0.117		29.388(2) 90 96.3860(10) 90 1525.0(2) 4 1.697 0.311	21.777(12) 7.992(4) 90 90.579(6) 90 982.4(9) 4 1.485 0.377
$\beta_{r} \circ \beta_{r} \circ \gamma_{r} \circ \gamma_{r$	108.702(2) 97.5900(10) 92.7600(10) 1336.1(2) 4 1.453 0.117 608		29.388(2) 90 96.3860(10) 90 1525.0(2) 4 1.697 0.311 800	21.777(12) 7.992(4) 90 90.579(6) 90 982.4(9) 4 1.485 0.377 456
β, ° β, ° V, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$		29.388(2) 90 96.3860(10) 90 1525.0(2) 4 1.697 0.311 800 0.48 × 0.37 × 0.08	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times 0.19\times 0.15 \end{array}$
β, ° β, ° Y, Å Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, °	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$		29.388(2) 90 96.3860(10) 90 1525.0(2) 4 1.697 0.311 800 0.48 × 0.37 × 0.08 2.79–25.02	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ \end{array}$
β, ° β, ° Y, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$		$\begin{array}{l} 29.388(2) \\ 90 \\ 96.3860(10) \\ 90 \\ 1525.0(2) \\ 4 \\ 1.697 \\ 0.311 \\ 800 \\ 0.48 \times 0.37 \times 0.08 \\ 2.79-25.02 \\ -8 \leqslant h \leqslant 8 \end{array}$	$\begin{array}{l} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\end{array}$
β, ° β, ° γ, ° V, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$		$\begin{array}{l} 29.388(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times 0.37\times 0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -8\leqslant k\leqslant 8\end{array}$	$\begin{array}{l} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12 \end{array}$
β, ° γ, ° Y, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices	$12.403(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant h \leqslant 12$		$\begin{array}{l} 29.388(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times0.37\times0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -8\leqslant k\leqslant 8\\ -21\leqslant l\leqslant 34\\ \end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ \end{array}$
β, ° β, ° γ, ° Y, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices Reflections collected	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633		$\begin{array}{l} 29.388(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times0.37\times0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -8\leqslant k\leqslant 8\\ -8\leqslant k\leqslant 8\\ -21\leqslant l\leqslant 34\\ 7123\end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant 1\leqslant 9\\ 5103\\ \end{array}$
β, \circ β, \circ γ, \circ $V, Å^3$ Z $D_{calcd}, Mg/m^3$ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, \circ Limiting indices Reflections collected Reflections independent (R_{int})	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633 $4601 (0.0826)$		$\begin{array}{l} 29.388(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times 0.37\times 0.08\\ 2.79\text{-}25.02\\ -8\leqslant h\leqslant 8\\ 2.79\text{-}25.02\\ -8\leqslant k\leqslant 8\\ -21\leqslant l\leqslant 34\\ 7123\\ 2685\ (0.0615)\end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ 5103\\ 1744\ (0.0622) \end{array}$
β , ° β , ° γ , ° γ , ° γ , ° Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices Reflections collected Reflections independent (R_{int}) Goodness-of-fit on F^2	$12.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633 $4601 (0.0826)$ 1.021		$\begin{array}{l} 29.388(2)\\ 90\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times0.37\times0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -8\leqslant k\leqslant 8\\ -21\leqslant l\leqslant 34\\ 7123\\ 2685\ (0.0615)\\ 0.949\\ \end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ 5103\\ 1744\ (0.0622)\\ 1.042\\ \end{array}$
β, ° β, ° V, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices Reflections collected Reflections independent (R_{int}) Goodness-of-fit on F^2 R indices [$I > 2σI$]	$10.4031(13)$ $108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633 $4601 (0.0826)$ 1.021 $0.1444, 0.3276$		$\begin{array}{l} 29.388(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times 0.37\times 0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -21\leqslant 1\leqslant 34\\ 7123\\ 2685\ (0.0615)\\ 0.949\\ 0.0443\ ,0.1011\end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ 5103\\ 1744\ (0.0622)\\ 1.042\\ 0.0459,\ 0.1289\\ \end{array}$
β , ° γ ,	$108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633 $4601 (0.0826)$ 1.021 $0.1444, 0.3276$ $0.2878, 0.4527$		$\begin{array}{l} 9.358(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times 0.37\times 0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -8\leqslant k\leqslant 8\\ -21\leqslant 1\leqslant 34\\ 7123\\ 2685\ (0.0615)\\ 0.949\\ 0.0443\ , 0.1011\\ 0.0751\ , 0.1133\\ \end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ 5103\\ 1744\ (0.0622)\\ 1.042\\ 0.0459,\ 0.1289\\ 0.0574,\ 0.1366\\ \end{array}$
β, ° β, ° Y, ° Y, Å ³ Z D_{calcd} , Mg/m ³ Absorption coefficient, mm ⁻¹ F(000) Crystal size, mm ³ θ range, ° Limiting indices Reflections collected Reflections collected Reflections independent (R_{int}) Goodness-of-fit on F^2 R indices [$I > 2\sigma I$] R indices (all data) Largest diff, peak and hole, e Å ⁻³	$108.702(2)$ $97.5900(10)$ $92.7600(10)$ $1336.1(2)$ 4 1.453 0.117 608 $0.27 \times 0.25 \times 0.10$ $2.40-25.02$ $-9 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 14$ 6633 $4601 (0.0826)$ 1.021 $0.1444, 0.3276$ $0.2878, 0.4527$ $0.481, -0.434$		$\begin{array}{l} 9.353(2)\\ 90\\ 96.3860(10)\\ 90\\ 1525.0(2)\\ 4\\ 1.697\\ 0.311\\ 800\\ 0.48\times 0.37\times 0.08\\ 2.79-25.02\\ -8\leqslant h\leqslant 8\\ -21\leqslant l\leqslant 34\\ 7123\\ 2685\ (0.0615)\\ 0.949\\ 0.0443,\ 0.1011\\ 0.0751,\ 0.1133\\ 0.222,\ -0.233\\ \end{array}$	$\begin{array}{c} 21.777(12)\\ 7.992(4)\\ 90\\ 90.579(6)\\ 90\\ 982.4(9)\\ 4\\ 1.485\\ 0.377\\ 456\\ 0.22\times0.19\times0.15\\ 2.71-25.01\\ -6\leqslant h\leqslant 6\\ -25\leqslant k\leqslant 12\\ -9\leqslant l\leqslant 9\\ 5103\\ 1744\ (0.0622)\\ 1.042\\ 0.0459,\ 0.1289\\ 0.0574,\ 0.1366\\ 0.405,\ -0.370\\ \end{array}$

disc, cm⁻¹): 3612s(v(OH)), 3488s(v_{as}(NH)), 3296s(v_s(NH)), 3174m, 3087m, 2984s, 2688w, 2559w, 1626m, 1598s(v_{as}(COO⁻)), 1536s(v_{as}(NO₂)), 1492m, 1464m, 1414m, 1382s(v_s(COO⁻)), 1320s(v_{as}(NO₂)), 1282m, 1246m, 1202m, 1162m, 1094m, 1006m, 952w, 861w, 811m, 757w, 714m, 665w, 613w.

2.2.5. (2-Aminophenol): (5-nitrosalicylic acid) [(HL1)⁺ · (5-nsa⁻), 5-nsa⁻ = 5-nitrosalicylate] (5)

2-Aminophenol (10.9 mg, 0.10 mmol) dissolved in 2 mL ethanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 4 mL ethanol. Yellow prisms were afforded after several days of slow evaporation of the solvent, yield: 29 mg, 78.52% (based on L1). mp 196–198 °C. Elemental analysis: Calc. for

2.2.6. (2-Amino-4-chlorophenol): (3,5-dinitrosalicylic acid)

 $[(HL2)^{+} \cdot (3,5-dns^{-}), 3,5-dns^{-} = 3,5-dinitrosalicylate]$ (6)

2-Amino-4-chlorophenol (14.3 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added was added 3,5-dinitro-salicylic acid (22.8 mg, 0.1 mmol) in 6 mL ethanol. Colorless block

crystals were afforded after several days by slow evaporation of the solvent (yield: 28 mg, 71.85%, based on L2). mp 158–160 °C. Elemental analysis: Calc. for $C_{13}H_{12}ClN_3O_9$ (389.71): C, 40.03; H, 3.08; N, 10.77. Found: C, 39.95; H, 3.04; N, 10.69. Infrared spectrum (KBr disc, cm⁻¹): 3602s (v(OH)), 3486s(multiple, v_{as}(NH)), 3308s(v_s(NH)), 3066m, 2968m, 2684w, 2579w, 1637m, 1605m, 1596s(v_{as}(COO⁻)), 1540s(v_{as}(NO₂)), 1486w, 1388s(v_s(COO⁻)), 1354m, 1312s(v_s(NO₂)), 1279m, 1202m, 1159m, 1022m, 952m, 846m, 759m, 648m, 604m.

2.2.7. (2-Amino-4-chlorophenol): $(fumaric acid)_{0.5}$: H₂O $[(HL2^+) \cdot (fum^{2-})_{0.5} \cdot H_2O, fum^{2-} = fumarate]$ (7)

2-Amino-4-chlorophenol (14.3 mg, 0.1 mmol) was dissolved in 2 mL methanol. To this solution was added fumaric acid (12 mg, 0.1 mmol) in 8 mL ethanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 18 mg, 81.96%, based on L2). mp 239–240 °C. Elemental analysis: Calc. for C₈H₁₀ClNO₄ (219.62): C, 43.71; H, 4.55; N, 6.37. Found: C, 43.67; H, 4.52; N, 6.31. Infrared spectrum (KBr disc, cm⁻¹): 3588s(v(OH)), 3427s(v_{as}(NH)), 3328s(v_s(NH)), 3131s, 2958m, 2689w, 2587w, 1642s, 1612s, 1591s(v_{as}(COO⁻)), 1562m, 1505m, 1455m, 1380s(v_s(COO⁻)), 1343s, 1306m, 1284m, 1219m, 1167m, 1009m, 938m, 842 m, 759 m, 648 m.

2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). Data collections and reductions were performed using the SMART and SAINT software [17,18]. 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 [19]. Hydrogen atom positions for the seven structures were generated geometrically. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for compounds **1–7** are listed in Table 2; the relevant hydrogen bond parameters are provided in Table 3. The IR bands which indicate chemical functionalities in the resulting compounds are given in Table 4.

3. Results and discussion

3.1. Syntheses and general characterization

2-Aminophenol, and 2-amino-4-chlorophenol both have good solubility in common organic solvents, such as CH_3OH , C_2H_5OH , CH_3CN , $CHCl_3$, and CH_2Cl_2 . For the preparation of **1–7**, the acidic components 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 molecular structures and their atom labeling schemes for the seven structures are shown in Figs. 1, 3, 5, 7, 9, 11 and 13, respectively. The elemental analyses for the seven compounds are in good agreement with their compositions. The infrared spectra of **1–7** are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis.

The very strong and broad features at $3612-3176 \text{ cm}^{-1}$ arise from O—H or N—H stretching frequencies. The wave numbers of protonated NH₂ group (in **1**, **3**, **4**, **5**, **6**, **7**) were larger than the wave numbers of the NH₂ group in the compound **2**. Aromatic ring stretching and bending are in the regions of $1500-1630 \text{ cm}^{-1}$ and $600-750 \text{ cm}^{-1}$, respectively. The salts **3–7** show the characteristic bands for COO⁻ groups. Compound **2** displays strong IR peaks

Table	2
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Selected bond lengths (Å) and angles (°) for 1-7.

1			
N(1) - C(2)	1 465(3)	N(2) = C(8)	1 461(3)
N(3) - C(10)	1.103(3) 1.447(4)	N(2) = C(0) N(4) = C(12)	1.460(3)
O(1) - C(1)	1.117(1)	O(2) - C(7)	1.100(3)
C(2) = N(1) = H(1A)	1.00 5	C(2) = C(7) C(2) = N(1) = H(1P)	1.202(3)
U(1A) = N(1) = H(1A)	109.5	C(2) = N(1) = H(1B)	109.5
H(IA) = N(I) = H(IC)	109.5	C(2) = N(1) = H(1C)	109.5
H(IA) - N(I) - H(IC)	109.5	H(IB) - N(I) - H(IC)	109.5
C(3) - C(2) - N(1)	120.3(2)	C(1) - C(2) - N(1)	118.2(2)
2			
Cl(1)-C(11)	1.743(2)	N(1)-O(3)	1.216(3)
N(1)-O(4)	1.217(3)	N(1) - C(5)	1.471(3)
N(2) - C(9)	1.396(3)	O(1) - C(1)	1.281(3)
O(2) - C(1)	1 247(3)	O(5) - C(8)	1 369(3)
O(3) - N(1) - O(4)	122 6(2)	O(2) - C(1) - O(1)	1234(2)
	122.0(2)	0(2) 0(1) 0(1)	123.1(2)
3			
N(1)-C(2)	1.464(4)	N(2)-C(10)	1.469(4)
N(3)-C(12)	1.470(4)	O(1)-C(1)	1.377(4)
O(2)-C(7)	1.240(4)	O(3)-C(7)	1.255(3)
O(2) - C(7) - O(3)	125.7(3)		
4			
\mathbf{H}	1 740(2)	N(1) = C(2)	1 462(2)
V(1) = C(4)	1.740(2) 1.472(2)	N(1) = C(2)	1.402(3)
N(2) = C(10)	1.473(3)	N(3) = C(12)	1.476(3)
O(1) - C(1)	1.350(3)	O(2) = C(7)	1.270(3)
U(7) - U(7)	1.241(3)	U(7) = U(7) = U(2)	126.2(2)
5			
N(1) - O(4)	1.221(13)	N(1)-O(5)	1.241(11)
N(1) - C(5)	1.457(13)	N(2) - O(10)	1.230(10)
N(2) - O(9)	1.247(11)	N(2) - C(12)	1.440(13)
N(3) - C(16)	1.456(12)	N(4) - C(22)	1.439(13)
O(1) - C(2)	1.340(12)	O(2) - C(1)	1.253(12)
O(3) - C(1)	1270(12)	O(6) - C(9)	1343(12)
O(7) - C(8)	1.290(12)	O(8) - C(8)	1217(14)
O(11) - C(15)	1.250(11) 1.364(12)	O(12) - C(21)	1.217(11) 1.344(13)
O(4) - N(1) - O(5)	1.304(12) 1223(10)	O(12) = O(21) O(10) = N(2) = O(9)	1.044(10) 1206(10)
O(2) - C(1) - O(2)	122.3(10) 124.1(0)	O(10) = N(2) = O(3)	120.0(10) 125.7(10)
0(2) - C(1) - O(3)	124.1(9)	0(8) - 0(8) - 0(7)	123.7(10)
6			
Cl(1)-C(4)	1.722(3)	N(1)-C(2)	1.468(3)
N(2)-C(10)	1.444(3)	N(3)-C(12)	1.462(3)
O(1) - C(1)	1.358(3)	O(2) - C(7)	1.212(3)
O(3)-C(7)	1.303(3)	O(4) - C(9)	1.301(3)
O(2) - C(7) - O(3)	121.5(2)		
-			
	1 7 4 6 (2)	N(4) ((2)	1 400(2)
CI(1) - C(4)	1./46(3)	N(1) - C(2)	1.469(3)
U(1) - C(1)	1.363(3)	U(2) - U(7)	1.255(3)
U(3) - U(7)	1.264(3)	U(2) - U(7) - O(3)	124.36(19)

for COOH groups. The bands at ca. 1530 and 1320 cm^{-1} were attributed to the $v_{as}(NO_2)$ and $v_s(NO_2)$, respectively [20].

3.2. Structural descriptions

3.2.1. X-ray structure of (2-aminophenol): (2,4,6-trinitrophenol) $[(HL1)^+ \cdot (pic^-), pic^- = picrate, L1 = 2-aminophenol], (1)$

Salt **1** was prepared by reacting of a methanol solution of 2-aminophenol and 2,4,6-trinitrophenol in 1:1 ratio, which crystallizes as triclinic pale yellow crystals in the space group P-1. The asymmetric unit of **1** consists of a monocation of 2-aminophenol, and one anion of picrate, as shown in Fig. 1.

This is a salt where the OH groups of 2,4,6-trinitrophenol are ionized by proton transfer to the nitrogen atom (N(1)) of the 2-aminophenol moieties, which is also confirmed by the bond distance of O(2)–C(7) (1.262(3) Å) for phenolate $(1.24 \pm 0.01 Å)$ [21]. In the compound, there is one ion pair without solvent molecules, which is well agreement with the micro-analysis results. The N(1)–C(2) bond length is 1.465(3) Å, and is approximately equal to a C–N single-bond length, indicating that atom N(1) of the amino group must be *sp3* hybridized. This is also supported by the angles around C(2) (C(3)–C(2)–N(1), 120.3(2)°; C(1)–C(2)–N(1),

Table 3

Hydrogen bond distances and angles in studied structures 1-7.

D—H···A	d(D—H) (Å)	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	<(DHA) (°)
1				
$O(1) - H(1) \cdots O(5) = 1$	0.82	2.03	2.837(3)	167.2
N(1) - H(1C) - O(7)	0.89	2.07	2.924(3)	161.2
N(1) - H(1B) - O(2) = 0	0.89	1.95	2.823(3)	167.6
N(1) - H(1A) - O(3) = 3	0.89	2.46	2.964(3)	116.5
N(1) - H(1A) - O(2) = 3	0.89	1.93	2.799(3)	166.5
Z O(C) U(CD) N(2)#1	0.85	2.02	2.965(2)	177 E
O(6) = H(6C) = O(4) # 2	0.85	2.02	2.005(5)	177.5
$O(6) = H(6C) \cdots O(4) \# 2$	0.83	2.20	3.043(3)	177.0
$O(5) - H(5) \cdots O(6) = 3$	0.82	1.87	2.671(2)	100.0
$O(1) - H(1) \cdots O(2) = 4$	0.82	1.80	2.018(2)	1/1.0
N(2) = H(2A) = O(3) # G	0.80	2.20	3.034(3)	140.0
$N(2) = H(2A) \cdots O(3) \# 6$	0.86	2.32	3.101(3)	150.5
3				
$N(1)-H(1C)\cdots O(2)#1$	0.89	1.89	2.768(3)	170.1
N(1) - H(1B) - O(1) = 2	0.89	2.04	2.873(3)	155.1
N(1) - H(1A) - O(3) = 3	0.89	1.89	2.769(3)	171.9
4				
$O(1) - H(1) \dots O(7) = 1$	0.82	1 78	2 526(2)	149.8
$N(1) - H(1C) \dots O(2) + 2$	0.89	1 93	2,793(3)	162.7
$N(1) - H(1B) \dots O(1) + 3$	0.89	2 50	2 987(2)	114.7
N(1) - H(1B) - O(3) = 3	0.89	2.30	3 (093(2))	148.0
$N(1) - H(1B) \cdots O(1)$	0.89	2.19	2,670(2)	113.3
N(1) - H(1A) - O(2) = 4	0.89	1.89	2.734(2)	158.4
-	0.00	100	2001(2)	10011
5				
O(12) - H(12) - O(7) = 1	0.82	1.88	2.672(10)	162.7
O(11) - H(11A) - O(2) = 0	0.82	1.81	2.624(9)	169.3
$O(6) - H(6) \cdots O(7)$	0.82	1.78	2.518(11)	148.9
$O(1) - H(1) \cdots O(2)$	0.82	1.81	2.539(11)	148.1
N(4) - H(4C) - O(10) = 3	0.89	2.21	3.005(11)	148.3
$N(4) - H(4B) \cdots O(3)$	0.89	2.30	3.170(11)	166.5
$N(4) - H(4A) \cdots O(3) \# 2$	0.89	1.90	2.768(11)	166.3
$N(3) - H(3C) \cdots O(4) \# 4$	0.89	2.43	3.092(11)	131.3
$N(3) - H(3C) \cdots O(5) \# 4$	0.89	2.38	3.146(12)	144.1
N(3) - H(3B) - O(11)	0.89	2.25	2.694(10)	110.5
N(3) - H(3B) - O(3)	0.89	2.19	3.026(11)	155.2
$N(3) - H(3A) \cdots O(8) \# I$	0.89	1.78	2.632(11)	158./
6				
O(9)—H(9D)···O(4)#1	0.85	1.94	2.724(2)	152.1
$O(9) - H(9C) \cdots O(5)$	0.85	2.11	2.894(3)	152.8
$O(3) - H(3) \cdot \cdot \cdot O(4)$	0.82	1.65	2.424(3)	155.2
O(1) - H(1) - O(2) = 2	0.82	1.81	2.609(3)	166.3
$N(1)-H(1C)\cdots O(5)$	0.89	2.56	3.289(3)	140.3
$N(1)-H(1C)\cdots O(4)$	0.89	2.49	3.069(3)	123.1
N(1) - H(1C) - O(3) = 1	0.89	2.32	2.989(3)	132.1
N(1)—H(1B)····O(9)#3	0.89	1.98	2.870(3)	178.5
N(1)-H(1A) - O(9)#4	0.89	1.93	2.818(3)	173.1
7				
O(4) - H(4D) - O(3) = 2	0.85	2.00	2.838(3)	170.2
O(4) - H(4C) - C(1)#3	0.85	2.96	3.414(2)	115.5
O(4) - H(4C) = O(2) # 4	0.85	2.07	2.908(3)	170.2
$O(1) - H(1) \cdots O(2) # 4$	0.82	1.85	2.668(2)	177.5
N(1) - H(1C) - O(3) = 5	0.89	1.00	2.828(3)	175.8
N(1) - H(1B) - O(3) = 6	0.89	1.51	2.812(3)	163.9
N(1) - H(1A) - O(4) #7	0.89	1.55	2.817(3)	178.6
	0.00	1.00	2.01.(3)	170.0

Symmetry transformations used to generate equivalent atoms for 1: #1 x + 1, y, z - 1; #2 -x + 1, -y + 1, -z + 1; #3 x, y - 1, z. Symmetry transformations used to generate equivalent atoms for 2: #1 x, y - 1, z; #2 -x + 1, -y + 1, -z; #3 x + 1, y + 1, z; #4 -x, -y, -z + 1; #5 -x + 1, -y + 2, -z; #6 x - 1, y, z. Symmetry transformations used to generate equivalent atoms for 3: #1 -x + 1, -y + 1, -z; #3 -x + 1, y + 1/2, -z; #3 -x + 1, -y + 2, -z + 1; #5 -x + 1, -y + 2, -z; #6 x - 1, y, z. Symmetry transformations used to generate equivalent atoms for 3: #1 -x + 1, y - 1/2, -z; #3 -x + 1, y + 1/2, -z. Symmetry transformations used to generate equivalent atoms for 5: #1 -x + 1, -y + 1, -z; #2 -x, y + 1/2, -z; #3 -x + 1, y + 1/2, -z; #3 -x + 1, -y + 1, -z. Symmetry transformations used to generate equivalent atoms for 5: #1 -x + 1, -y + 1, -z; #2 -x, -y + 1, -z + 1; #3 -x + 1, -y + 2, -z + 1; #4 -x, -y, -z. Symmetry transformations used to generate equivalent atoms for 6: #1 -x + 1/2, y - 1/2, -z + 1/2; #2 x + 1, y - 1, z; #3 -x + 3/2, y + 1/2, -z + 1/2; #4 x, y + 1, z. Symmetry transformations used to generate equivalent atoms for 7: #2 -x + 1, -y + 1, -z + 1/2; #4 x + 1, y - 1, z; #3 -x + 1, -y + 1, -z + 1/2; #4 x + 1, y - 1, z; #3 -x + 1, -y + 1, -z + 1/2; #4 x + 1, -y - 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2; #4 x + 1, -y + 1, -z + 1/2;

118.2(2)°), and the bond angles concerning N(1) (C(2)–N(1)–H(1A), C(2)–N(1)–H(1C), C(2)–N(1)–H(1B), H(1A)–N(1)–H(1B), H(1A)–N(1)–H(1C), and H(1B)–N(1)–H(1C) are all 109.5°, indicating very nearly perfect *sp*3 hybridization). The N(1)–C(2) bond (1.465(3) Å) is longer by 0.05 Å than that (1.416(2) Å) in neutral 2-aminophenol [22], yet it is similar to the corresponding value at the salt of 2-aminophenol-HClO₄ [23]. The C–OH and C–C bonds within the aromatic

ring of the cation are comparable to that found in the crystal of a neutral 2-aminophenol [22].

The rms deviation of the phenyl ring of the picrate is 0.0211 Å, the ortho-nitro groups (N2–O3–O4, and N4–O7–O8) deviate from the phenyl ring plane and have dihedral angles of 34.7°, and 19.3° respectively with the phenyl plane, whereas the *para*-ni-tro group lies almost in the phenyl plane [with a dihedral angle of

Table 4
Character IR bands of chemical functionalities of the four organic salts 1–7.

Compound	v(OH)	$v_{as}(NH)$	$\nu_{s}(NH)$	ν(C==0)	v _{as} (COO)	v _s (COO)	v(CO)	$v_{as}(NO_2)$	$v_s(NO_2)$
1	3589s	3440s	3306s					1525s	1324s
2	3596s	3230s	3176s	1648s			1288s	1538s	1326s
3	3579s	3454s	3346s		1602s	1384s		1522s	1323s
4	3612s	3488s	3296s		1598s	1382s		1536s	1320s
5	3585s	3472s	3362s		1586s	1394s		1526s	1321s
6	3602s	3486s	3308s		1596s	1388s		1540s	1312s
7	3588s	3427s	3328s		1591s	1380s			



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



Fig. 2. 2D sheet structure of 1 extending along the direction that made an angle of ca 45° with the *bc* plane.

4.9° between the N3–O5–O6 group and the phenyl ring]. The two ortho-nitro groups intersect at an angle of 25.7° with each other, while the *para*-nitro group made dihedral angles of 30.0° (with N2–O3–O4), and 17.7° (with N4–O7–O8) with the two ortho nitro groups respectively. These structural data are similar to those in other structurally described picrates [24].

One anion is bonded to one cation through the bifurcated N–H···O hydrogen bonds produced between the aminium cation and the phenolate and one ortho-nitro group with N–O distances of 2.799(3)–2.964(3) Å. In this case the NH unit and the two O atoms involved in the hydrogen bonds generated a $R_1^2(6)$ motif according to [25]. Herein the phenyl ring of the cation and the phenyl ring of the anion are almost perpendicular to each other with a dihedral angle of 80.2° between the two rings. Under the N–H···O

hydrogen bonds the cation and the anion formed a bicomponent adduct. Such kind of bicomponent adducts were joined together via O—H···O hydrogen bond between the phenol unit of the cation and the *para*-nitro group of the neighboring bicomponent heteroadduct with N—O distance of 2.837(3) Å to form a 1D chain running along the *c* axis direction. The adjacent chains were combined together through N—H···O hydrogen bond between the aminium cation and the ortho nitro group with N—O distance of 2.924(3) Å, and O—O contact between the ortho nitro groups of the adjacent chains with O—O separation of 2.864 Å to form 2D sheet extending along the direction that made an angle of ca. 45° with the *bc* plane (Fig. 2). Two neighboring sheets were held together by the CH—O association between the aromatic 3-CH of the cation of one sheet and the ortho nitro group of its neighboring



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 *ac* plane.

sheet with C—O distance of 3.365 Å to form double sheet structure. It is worthy to note that the corresponding cations and anions in the same sheet were parallelly arranged, respectively; while the corresponding cations and anions at different sheets in the double sheet were antiparallelly arranged, respectively. The double sheets were further stacked along the direction that is perpendicular with its extending direction via the intersheet N—H…O hydrogen bond between the aminium group and the phenolate with N—O distance of 2.823(3) Å to form 3D layer network structure. In this regard the neighboring double sheets were slipped some distance from each other along the *b*, and *c* axes directions, respectively.

3.2.2. X-ray structure of (2-amino-4-chlorophenol): (p-nitrobenzoic acid): H_2O [(L2) · (Hnba) · H_2O , Hnba = p-nitrobenzoic acid] (2)

The compound 2 of the composition $[(L2) \cdot (Hnba) \cdot H_2O]$ was prepared by reaction equal mol of 2-amino-4-chlorophenol and p-nitrobenzoic acid, which crystallizes as triclinic colorless block crystals in the space group P-1. The asymmetric unit of two consists of one L2 molecule, one p-nitrobenzoic acid molecule, and one water molecule, as shown in Fig. 3. This is a cocrystal where the COOH groups of the p-nitrobenzoic acids are not ionized by proton transfer to the N atoms of the 2-amino-4-chlorophenol moieties, which is also confirmed by the bond length of C9—N2 which has similar bond length with the corresponding value in the crystals of 2-amino-4-chlorophenol [26].

Here the difference between the pairs of C—O bond distances of O(1)—C(1) (1.281(3)Å), and O(2)—C(1) (1.247(3)Å) is relatively small, which may be explained by the fact the formation of single or multiple hydrogen bonds at one oxygen atom should cause the associated C—O bond to lengthen. Here the O(2) involves in the hydrogen bond, while the O1 does not.

The carboxyl and the nitro groups deviated by 4.3° , and 1.6° respectively from the benzene ring composed of C2–C7. The r.m.s deviations of the phenyl rings of the p-nitrobenzoic acid and L2 from the mean planes of the rings are 0.0033 Å, and 0.0058 Å, respectively, both rings made dihedral angle of 0.8° with each other. Different from **1**, here the aromatic rings of the acid, and the base components are almost in the same plane.

Two L2 form homodimers via a pair of N-H···O hydrogen bonds between the amino group and the phenolic group with N-O distance of 3.034(3) Å. Two Hnba molecules are also aggregated together by a pair of CH-O associations between the 3-CH of the phenyl unit and the p-nitro group with C-O distance of 3.550 Å to form a homodimer. Such two kinds of homodimers were linked together by the CH-O contact between the 5-CH of the 2amino-4-chlorophenol and the carbonyl group of the p-nitrobenzoic acid with C–O distance of 3.463 Å to form a 1D chain running along the *c* axis direction. The chains were combined together by the interchain N-H···O hydrogen bond between the amino group of the L2 and the p-nitro group of Hnba with N-O distance of 3.101(3) Å to form 2D sheet extending on the *ac* plane (Fig. 4). In the sheet the water molecules were stitched between the adjacent chains via the O–H···O hydrogen bonds (O(5)-H(5)...O(6)#3), and O(6)-H(6C)···O(4)#2), and CH-O association between the 2-CH of the p-nitrobenzoic acid and the water molecule with C–O distance of 3.460 Å. It is worthy to point out that the adjacent chains in the sheet were slipped the distance of ca. c axis length along the c axis direction. While the first chain has the same projection as the third chain when we viewed from the *a* axis direction, so does the second chain and the fourth chain. The sheets were further stacked along the *b* axis direction by the $O-H \cdots N$ hydrogen bond between the water molecule and the amino group of L2 with N-O distance of 2.865(3) Å to form 3D layer network structure. Herein the adjacent sheets were slipped some distance from each other along the a, and c axes directions, respectively.

3.2.3. X-ray structure of (2-aminophenol): (3,5-dinitrobenzoic acid) $[(HL1)^+ \cdot (dnb^-), dnb^- = 3,5-dinitrobenzoate], (3)$

Compound **3** was prepared by reacting of a methanol solution of 2-aminophenol and 3,5-dinitrobenzoic acid in 1:1 ratio, which crystallizes as monoclinic pale yellow crystals in the centrosymmetric space group P2(1). The asymmetric unit of **3** consists of a cation of L1, and one anion of 3,5-dinitrobenzoate, as shown in Fig. 5.

Compound **3** is a salt where the COOH groups of 3,5-dinitrobenzoic acids are ionized by proton transfer to the nitrogen atoms of the L1, which is also confirmed by the bond distances of O(2)-C(7)(1.240(4) Å) and O(3)-C(7)(1.255(3) Å) for the carboxylates. The difference (\varDelta is 0.015 Å) in bond distances between O(2)-C(7)(1.240(4) Å) and O(3)-C(7)(1.255(3) Å) in the carboxylate group in compound **3** is in the range for ionized COOH groups [27].

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



Fig. 5. The structure of 3, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.



Fig. 6. 2D corrugated sheet structure of 3 that is running parallel to the bc plane.

One cation and one anion generate a bicomponent adduct via the ionic $N^+-H\cdots O^-$ hydrogen bond between the aminium cation and the carboxylate with N–O distance of 2.768(3) Å. Such kind of bicomponent adducts were linked together by the CH-O interaction between the phenyl CH (3-CH) of the cation and the nitro group with C–O distance of 3.432 Å to form a 1D wave chain running along the *c* axis direction. Here the distance (ca. 3.627(3) Å) between the O1 and O2 is too great to imply O–H···O hydrogen bond. The 1D wave chains were connected together by the CH-O interaction between the phenyl CH (3-CH) of the cation and the carboxylate with C–O distance of 3.271 Å, N–H…O association between the aminium group and the same O atom of the same carboxylate group that is involved in CH-O interaction with N-O distance of 2.769(3) Å, and $O-\pi$ interaction between the nitro group and the phenyl ring of the anion with O-Cg distance of 3.060 Å at the neighboring chains to form a 2D corrugated sheet structure (Fig. 6). In this regard the O- π interaction is much stronger than the archived result (3.59 Å) [28]. The corresponding anions and cations in the sheet were parallel to each other respectively. Two neighboring 2D corrugated sheets were joined together via the same side of the sheet by the $O-\pi$ interaction between the nitro group and the phenyl ring of the anion with O-Cg distance of 3.080 Å to form 2D double sheet structure. The 2D double sheets were further stacked along the *a* axis direction through the intersheet N-H...O hydrogen bond between the aminium unit and the phenol group of the cation at adjacent double sheets with O–N distance of 2.873(3) Å, O–N association (with O–N distance of 2.885 Å), and O–O (with O–O distance of 2.965 Å) contact to form 3D network structure.



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

3.2.4. X-ray structure of (2-amino-4-chlorophenol): (3,5-

dinitrobenzoic acid) $[(HL2)^+ \cdot (dnb^-), dnb^- = 3,5-dinitrobenzoate]$ (4) Similar to compound **3**, in **4** the asymmetric unit is occupied by one anion of 3,5-dinitrobenzoic acid, and a cation of $(HL2)^+$ (Fig. 7). The proton of the COOH group has transferred to the N atom of the L2 moiety. The assignment of **4** as a salt is based on successful



Fig. 8. 2D sheet structure of 4 extending parallel to the ac plane.

refinement of the relevant H atoms using X-ray data also. One cation is bonded to one anion through the O–H \cdots O hydrogen bond between the phenol group (donor) and the carboxylate with O–O separation of 2.526(2) Å to form a heteroadduct. The parallel heteroadducts were linked together along the *a* axis direction by the CH-O interaction between the 3-CH of the cation and the nitro group of the anion with C–O distance of 3.388 Å to form a 1D chain running along the *a* axis direction. Two neighboring chains were combined together by the N–H \cdots O hydrogen bond between the aminium group and the nitro group with N-O distance of 3.093(2) Å to form 1D double chain. The cations in the two chains at the double chain were antiparallely arranged, so did the anions. The double chains were further joined together by the CH-O association (there are a pair of CH–O interactions with C–O distance of 3.592 Å between the anions to form a $R_2^2(10)$ ring, there is also a CH–O contact with C–O distance of 3.278 Å between the 6-CH of the cation and the other O atom of the nitro group that is involved in the CH–O interaction between the anions) to form 2D sheet structure extending along the ac plane (Fig. 8). The 2D sheets propagate along the *b* axis direction by the π - π interaction between the aromatic rings of the cation and the anion with Cg-Cg distance of 3.312 Å, N- π interaction between the nitro group of the anion and the phenyl ring of the cation with N-Cg distance of 3.194 Å, and $O-\pi$ association between the nitro unit and the phenyl ring of the cation with O–Cg distance of 3.180 Å to form 3D network structure. The N-Cg distance observed in this compound is somewhat shorter than the reported N-Cg distance [29]. Here the adjacent sheets were slipped some distance from each other along the a axis direction.

3.2.5. X-ray structure of (2-aminophenol): (5-nitrosalicylic acid) [(HL1)⁺ · (5-nsa⁻), 5-nsa⁻ = 5-nitrosalicylate] (5)

Salt **5** was prepared by reacting of an ethanol solution of 2-aminophenol and 5-nitrosalicylic acid in 1:1 ratio, which crystallizes as triclinic pale yellow crystals in the centrosymmetric space group P-1. The asymmetric unit of **5** consists of two halves of the cations of HL1, and two halves of 5-nitrosalicylate anions, as shown in Fig. 9. Compound **5** is also a salt where the COOH groups of 5-nitrosalicylic acids are deprotonated. The difference between the pairs of bond distances of O(2)—C(1) (1.253(12) Å) and O(3)—C(1) (1.270(12) Å); O(7)—C(8) (1.290(14) Å), and O(8)—C(8) (1.217(14) Å) for the carboxylate are 0.017 Å, and 0.073 Å, respectively. The relative large \varDelta value for O(7)—C(8) (1.290(14) Å), and O(8)—C(8) (1.217(14) Å) are due to the fact that the O(7) is involved in forming more hydrogen bonds that that of O(8). Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the

phenol group $(O(1)-H(1)\cdots O(2), 2.539(11) Å$; and $O(6)-H(6)\cdots O(7)$, 2.518(11) Å), it is generally expected and found that the carboxylate group is essentially coplanar with the phenyl ring [torsion angle C2–C3–C1–O3, 166.03°, and C9–C10–C8–O8, 175.59°]. This feature is similar to that found in salicylic acid [30], and in the previously reported structure based on 5-nsa⁻ [30]. As expected the O–O separation is essentially in the upper limit of the documented data [2.489–2.509 Å] [31], 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 C6–C5–N1–O4, 174.75°; and C13–C12–N2–O9, 179.64°] compared with the reported torsion angle (175.4–180°) within the 5-nsa⁻ anions [31].

In the solid state, there is consistently ionic hydrogen bond formed between the NH^{+} group, and the 5-nitrosalicylate ion, which is to be expected [32]. There also exist strong coulombic interactions between charged cation units and the 5-nitrosalicylate anions.

Two anions and two cations produced a tetracomponent adduct via the N–H···O hydrogen bonds with N–O distances of 2.632(11)–3.146(12) Å. In the tetracomponent adduct the cations were inversionally related, so did the anions. The tetracomponent adducts were linked together via the O–H···O hydrogen bond between the phenol group of the cation and the carboxylate with



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



Fig. 10. 2D sheet structure of 5 which is extending parallel to the bc plane.

O–O distance of 2.624(9) Å to form 1D chain running parallel to the *c* axis direction. The chains were further joined together by the CH–O association between the phenyl CH of the anion and the phenol group of the anion belonging to the neighboring chains with C–O distance of 3.466 Å to form 2D sheet extending parallel to the *bc* plane (Fig. 10), herein the cations bonded to the sheet were protruded from the sheet plane. Two adjacent sheets were joined together via the same face of the sheet by the N-H···O (between the aminium cation and the carboxylate with N-O distance of 3.026(11) Å, and between the NH⁺₃ and the phenol moiety with N–O distance of 2.954 Å), and O– π (between the nitro group and the phenyl ring of the anion with O-Cg distance of 3.105 Å) interactions to form 2D double sheet structure. The double sheets were further propagated along the *a* axis direction via the CH–O contact between the 5-, and 6-CH of the cation and the nitro group of the anion belonging to two different sheets of the double sheet with C-O distances of 3.243-3.419 Å to form 3D layer network structure. Herein the adjacent double sheets were slipped some distance from each other along their extending direction.

3.2.6. X-ray structure of (2-amino-4-chlorophenol): (3,5dinitrosalicylic acid) [(HL2)⁺ \cdot (3,5-dns⁻), 3,5-dns⁻ = 3,5dinitrosalicylate], (6)

Crystallization of 2-amino-4-chlorophenol 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 2-amino-4-chlorophenol and 3,5-dinitrosalicylic acid are present in a 1:1 ratio in the molecular complex **6**. The crystal structure of **6** consists of one cation of HL2, and one monoanion of 3,5-dinitrosalicylic acid in the asymmetric unit (Fig. 11). Similar to the published organic salt bearing 3,5-dns⁻ [16], in **6** only the phenol OH groups of 3,5-dinitrosalicylic acids are ionized by proton transfer to the L2, and the COOH group remains protonized.

The C–O distance (O(4)-C(9), 1.301(3) Å) concerning the phenolate is longer than the corresponding value in the proton transfer compound bearing the 3,5-dns⁻ in which only the phenol group has been deprotonated [33]. The reason may be attributed to the fact that the O4 moiety participates in forming more hydrogen bonds (Table 3). The C–O distances (O(2)-C(7), 1.212(3), O(3)-C(7), 1.303(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. The torsion angles O6–N2–C10–C9, and O7–N3–C12–C13 are –179.0(2)°, and 156.5(3)°, respectively. In this regard, both nitro groups are nearly in the same plane as the phenyl ring of the anion, yet the 3-nitro group (O6-N2-O5) deviates somewhat less from the plane than the 5-nitro group (O7-N3-O8), which is different from the published results [33].

The water molecule was bonded to the cation via one N—H···O hydrogen bond (between the water molecule (acceptor) and the aminium cation with N—O distance of 2.818(3) Å (N(1)—H(1A)···O(9)#4, 2.818(3) Å, 173.1°), and one CH—O contact (between the 3-CH of the cation and the Ow atom with C—O distance of 3.333 Å) to generated a hydrogen bonded ring with graph set descriptor of $R_2^1(6)$. There also exists intramolecular O—H···O hydrogen bond with graph set of $S_1^1(6)$ which is between the COOH unit and the phenolate in the anion with O—O separation of 2.424(3) Å. The cation attached with the water molecule was linked with the anion via the O—H···O hydrogen bond between the phenol group of the cation and the carbonyl unit of the anion



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



Fig. 12. 1D chain structure of 6 built from Cl–Cl bond, and O–H…O interactions which is running along the *b* axis direction.



Fig. 13. The structure of 7, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.



Fig. 14. 2D sheet structure of 7 that is extending on the *ab* plane.

with O–O separation of 2.609(3) Å, and CH–O association between the 6-CH of the cation and the same carbonyl group with C-O distance of 3.222 Å to form a tricomponent adduct. The tricomponent adducts were linked together via the CH-O interaction between the nitro group and the aromatic CH of the cation with C-O distances in the range of 3.282-3.437 Å to form a hexacomponent adduct. In the hexacomponent adduct there existed an inversion centre which is located at the middle point of the two 5-nitro groups in the hexacomponent adduct. The hexacomponent adducts were combined together via the Cl-Cl bond between the cations and $O-H \cdots O$ hydrogen bond between the water molecule and the nitro group with O–O separation of 2.894(3) Å $(O(9)-H(9C)\cdots$ O(5), 2.894(3) Å, 152.8°) to form a 1D chain running along the baxis direction (Fig. 12). Here the Cl-Cl separation is 3.380 Å, which is within the range of a Cl-Cl bond [34]. The 1D chains were further stacked along the *a* axis direction via the N-H \cdots O $(N(1)-H(1C)\cdots O(4), 3.069(3)$ Å, 123.1°) hydrogen bond between the aminium cation and the phenolate with N-O distance of 3.069 Å, and π – π association between the phenyl moieties of the cation and the anion with Cg–Cg distances of ca. 3.246–3.382 Å to form 2D sheet extending parallel to the *ab* plane. The sheets were further stacked along the *c* axis direction to form 3D ABAB layer network structure through the intersheet N–H···O (N(1)–H(1C)···O(3)#1, 2.989(3) Å, 132.1°) hydrogen bond between the aminium cation and the phenol group with N–O distance of 2.989(3) Å, and O–H···O (O(9)–H(9D)···O(4)#1, 2.724(2) Å, 152.1°) hydrogen bond between the water molecule and the phenolate with O–O distance of 2.724(2) Å. It is worthy to mention that the chains at adjacent sheets made an angle of ca 60° with each other. The first sheet layer was parallel to the third sheet layer, so did the second sheet layer and the fourth sheet layer.

3.2.7. X-ray structure of (2-amino-4-chlorophenol): (fumaric acid)_{0.5} $[(HL_2)^+ \cdot (fum^{2-})_{0.5}, fum^- = fumarate]$ (7)

Similar to the above compounds, compound **7** was prepared by reaction of fumaric acid and 2-amino-4-chlorophenol in 1:1 ratio,

which crystallizes as monoclinic colorless crystals in the centrosymmetric space group P2(1)/c. The asymmetric unit of **7** consists of one cation of HL2, and half a dianion of fumarate, as shown in Fig. 13. The C8–C8#1 bond distance (1.282(5)Å) is for a simple C=C double bond. The C-O distances (O(2)-C(7), 1.255(3) Å; and O(3)–C(7), 1.264(3)Å) clearly indicate that the acid moieties in the compound are dianions when it formed hydrogen bonds with the aminium moiety.

At each cation there was attached a water molecule through the N-H···O hydrogen bond between the aminium group and the Ow atom with N–O distance of 2.817(3) Å, and CH–O association produced by the 3-CH of the cation with C—O distance of 3.393 Å. Two cations attached with the water molecules were bonded to one anion via the $O-H \cdots O$ hydrogen bond between the phenol group and the carboxylate with O–O distance of 2.668(2) Å to form a pentacomponent adduct. In the pentacomponent heteroadduct there is an inversion centre located at the middle point of the olefinic group in the fumarate. There are two kinds of pentacomponent adduct, although the component is the same, the difference is that the two kinds of pentacomponent adduct made an angle of ca 60° with each other. The same kinds of adjacent parallel pentacomponent adducts were linked together by the water molecule through the O–H···O hydrogen bond between the water molecule and the carboxylate with O–O separation of 2.838(3) Å. And the two kinds of different pentacomponent adducts were linked together via the Cl–O contact with Cl–O distance of 3.118 Å to form 2D sheet extending on the *ab* plane (Fig. 14). The Cl–O separation is longer than that in 5-chloro-1,2-dimethyl-4-nitro-1H-imidazole (2.899(1) Å), yet it is shorter than the values (3.285, and 3.498 Å) in 2-chloro-1-methyl-4-nitro-1H-imidazole [35]. The 2D sheets were further stacked along the *c* axis direction via N–H···O (between the aminium cation and the carboxylate with N-O distances of 2.812(3)–2.828(3) Å), and O–H···O (between the water molecule and the carboxylate with O–O distance of 2.908(3) Å) interactions to form 3D network structure.

4. Conclusion

Seven hybrid organic acid-base crystals have been prepared and their crystal structures determined. The different hydrogen bond interaction modes of the acidic components and the 2-aminophenol derivatives lead to a wide range of different structures such as 3D network structure, 3D layer network structure, and 3D ABAB layer structure.

Of the seven organic acid–base adducts six examples (1, 3, 4, 5, **6**, and **7**) involve proton transfer from the acidic units to the amine group of the 2-aminophenol derivatives to form a monocation. Compound **2** is a cocrystal. Here this phenomenon may be explained by the rule "strongest donor to strongest acceptor", for the carboxylic acids present in 1–7, the p-nitrobenzoic acid in 2 has the relatively larger pK_a than other acidic components discussed in this manuscript.

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 ... 2-aminophenol synthons. Except the classical hydrogen bonding interactions, the secondary propagating interactions also made significant contribution to the structure extension. The seven salts/cocrystal all possess weak C-H--O associations. There are also π - π associations in compounds 4, and **6**. The O– π interactions were found in **3**, **4**, and **5**, while **4** possesses additional N– π interaction. Salt **6** bears the Cl–Cl bond.

In conclusion, we have shown that 3D structures can be constructed by the synergic interactions such as classical hydrogen bond (N–H···O/O–H···O), CH–O, π – π , O– π , N– π , Cl–Cl, and Cl–O interactions between discrete components.

Acknowledgements

We gratefully acknowledge the financial support of the Education Office Foundation of Zheijang Province (Project No. Y201017321) and the financial support of the Xinmiao project of the Education Office Foundation of Zhejiang Province (Project No. 2009FK63).

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 851937 for 1, 835102 for 2, 851605 for 3, 851594 for 4, 835068 for 5, 851605 for 6, and, 816393 for 7. 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.molstruc.2013.01.012.

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