

A two-dimensional yttrium phthalate coordination polymer, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_\infty$, exhibiting different coordination geometries[†]

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Abstract. A hydrothermal reaction of a mixture of $\text{Y}(\text{NO}_3)_3$, 1,2-benzenedicarboxylic acid (1,2-BDC) and NaOH gives rise to a new yttrium phthalate coordination polymer, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_\infty$, **I**. The Y ions in **I** are present in four different coordination environments with respect to the oxygen atoms (CN6 = octahedral, CN7 = pentagonal bipyramid, CN8 = dodecahedron and CN9 = capped square antiprism). The oxygen atoms of the 1,2-BDC are fully deprotonated, and show variations in their connectivity with Y atoms. The Y atoms themselves are connected through their vertices forming infinite Y–O–Y one-dimensional chains. The Y–O–Y chains are cross-linked by the 1,2-BDC anions forming a corrugated layer structure. The layers are supported by favourable $p\cdots p$ interactions between the benzene rings of the 1,2-BDC anions. The variations in the coordination environment of the Y atoms and the presence of Y–O–Y interactions along with the favourable $p\cdots p$ interactions between the benzene rings from different layers are noteworthy structural features. Crystal data: triclinic, space group = $P\bar{1}$ (no. 2), $a = 12.6669$ (2), $b = 13.8538$ (2), $c = 16.0289$ Å, $\alpha = 75.20$ (1), $\beta = 69.012$ (1), $\gamma = 65.529$ (1)°, $V = 2371.28$ (7) Å³, $D_{\text{calc}} = 1.922$ g cm⁻³, $m_{\text{MoK}\alpha} = 4.943$ mm⁻¹. A total of 9745 reflections collected and merged to give 6566 unique reflections ($R_{\text{int}} = 0.0292$) of which 5252 with $I > 2\sigma(I)$ were considered to be observed. Final $R_2 = 0.0339$, $wR_2 = 0.0724$ and $S = 1.036$ were obtained for 704 parameters.

Keywords. Yttrium; phthalic acid; coordination polymer; layered structure.

1. Introduction

The synthesis and structure of metal coordination polymers based on benzene carboxylic acids are of topical interest.¹ The past few years have witnessed impressive developments in the use of multiple carboxylates as anions in the design of new metal-organic frameworks (MOFs). Many of the MOF compounds exhibit good adsorption behaviour besides being thermally stable up to 400–500°C. Though the major portion of the work on metal–carboxylate networks has concentrated on the *d*-block elements such as Zn, Cu, Co etc., the analogous lanthanide ions are also being investigated.^{2–10} The coordination sites of the *d*-block elements are, in general, completely occupied by the bridging carboxylates, whereas the higher coordination numbers of the lanthanide ions may afford

[†]Dedicated to Professor C N R Rao on his 70th birthday

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accessible coordination sites. The high coordination numbers of the lanthanide ions may cause difficulty in controlling the synthetic reactions and thereby the structures of the products. However, the fascinating coordination geometry and the possibility of incorporation of ancillary ligands (such as water or solvent molecules) can be attractive for synthetic chemists. In addition, the ancillary ligands may be removed without collapse of the MOF, thereby generating porous solids with coordinatively unsaturated and Lewis-acid lanthanide ions, which could have potential catalytic activity.^{11,12} This rationale has prompted us to investigate the formation of new frameworks using yttrium and other lanthanide ions with benzene-1,2-dicarboxylic acid (1,2-BDC), employing hydrothermal methods. In addition, the choice of 1,2-BDC is also based on the fact that the acid subtends an angle of 60° between the two carboxylate groups. Such a disposition of the acid functionality can give rise to many interesting compounds with a variety of binding modes. A few of the select binding modes of 1,2-BDC are given in figure 1. It also gives a unique opportunity to investigate the role of *p*..*p* interactions on the structure and its stability. During the course of this study, we have now isolated a new yttrium benzene dicarboxylate of the composition, $[Y_4(H_2O)_2(C_8H_4O_4)_6]_{\infty}$, **I**. Compound **I** possesses a two-dimensional layered structure with the Y^{III} ions exhibiting a variety of different coordination geometries. Both intra- and inter-layer *p*..*p* interactions involving the 1,2-

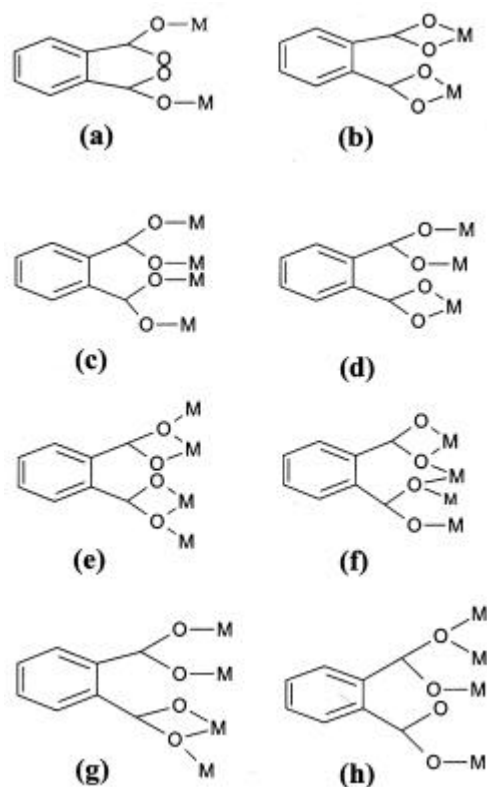


Figure 1. Some of the common binding modes observed in 1,2-benzenedicarboxylic acid (1,2-BDC).

BDC anions have been observed. The inter-layer *p*...*p* interactions appear to be reasonably strong and appears to contribute to the structural stability. In this paper, we describe the synthesis and structure of this unusual solid.

2. Experimental

The title compound $[Y_4(H_2O)_2(C_8H_4O_4)_6]_{\infty}$, **I**, was synthesised under hydrothermal conditions. In a typical synthesis, 0.275 g of $Y(NO_3)_3$ was dissolved in 5 ml of water. To this, 0.339 g of 1,2-BDC, and 1.2 ml of NaOH (5 M solution) were added under continuous stirring and the mixture was homogenised at room temperature. The final mixture with the composition, $Y(NO_3)_3 : 2(1,2-BDC) : 6NaOH : 278H_2O$, was sealed in a 23 ml PTFE-lined acid digestion bomb and heated at 180°C for 72 h under autogeneous pressure. The resulting product contained large quantity of rod-like crystals, which were filtered under vacuum and dried at ambient temperature. The initial and final pH of the mixture was ~5 and ~4, respectively. The yield of **I** was about ~75% based on Y. The product was characterised by powder XRD, IR and TGA, in addition to single crystal X-ray diffraction.

The powder XRD pattern indicated that the product is a new material; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction. The experimental powder XRD pattern along with the simulated one is given in figure 2. Infrared (IR) spectra was recorded in the range 400–4000 cm^{-1} using the KBr pellet

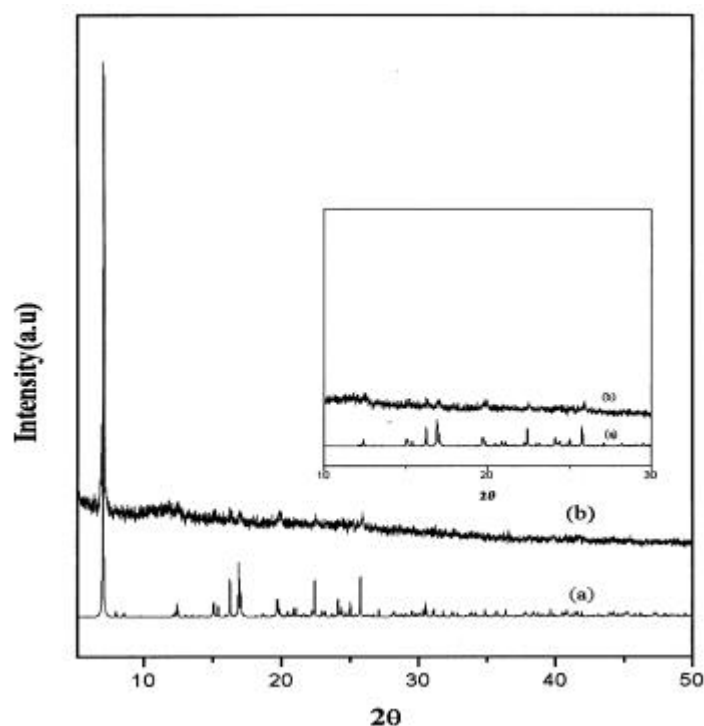


Figure 2. Powder XRD pattern (CuK α) of **I**, $[Y_4(H_2O)_2(C_8H_4O_4)_6]_{\infty}$ (a) experimental and (b) simulated.

method (figure 3). The IR spectra showed typical peaks. IR bands for **I** bonded water, $\nu(\text{OH}) = 3300(\text{s}), 3480(\text{s}) \text{ cm}^{-1}$, $\delta(\text{OH}) = 1446 \text{ cm}^{-1}(\text{s})$, $\nu(\text{CH}_{\text{aromatic}}) = 3080(\text{s}), 1612 \text{ cm}^{-1}(\text{s})$, $\nu(\text{CO}) = 1285(\text{w}) \text{ cm}^{-1}$, $\nu(\text{CH}_{\text{aromatic-in-plane}}) = 1152(\text{s}), 1088(\text{s})^{-1}$, $\nu(\text{CH}_{\text{aromatic-out-of-plane}}) = 855(\text{s}), 755(\text{s}) \text{ cm}^{-1}$. Thermogravimetric analysis (TGA) was carried out in oxygen atmosphere (flow rate = 50 ml min^{-1}) in the range between 25 and 900°C (heating rate = 5°C min^{-1}) (figure 4). The compound showed two distinct weight losses. The first weight loss of 3.06% at $275\text{--}325^\circ\text{C}$ agrees well with the some surface adsorbed water along with the loss of two molecules of bound water to **Y** (calc. 2.62%). The loss of the bound water molecules appears to be irreversible and the structure loses its crystalline nature with the loss of water molecules, as indicated by powder XRD. The second weight loss of 65% was noticeably sharp around 425°C and corresponds to the loss of the benzene carboxylate (calc. 71.5%). The observed lower weight loss probably due to some of the sample being thrown out of the crucible due to the exothermicity of the decomposition reaction. The calcined product was crystalline, as indicated by powder XRD lines, and corresponds to the crystalline phase Y_2O_3 (JCPDS: 43-1036).

3. Single crystal structure determination

A suitable single crystal of compound **I** ($0.32 \times 0.24 \times 0.42 \text{ mm}$) was carefully selected under a polarising microscope and glued to a thin glass fibre. Crystal structure determination by X-ray diffraction was performed on a Siemen's Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK α radiation,

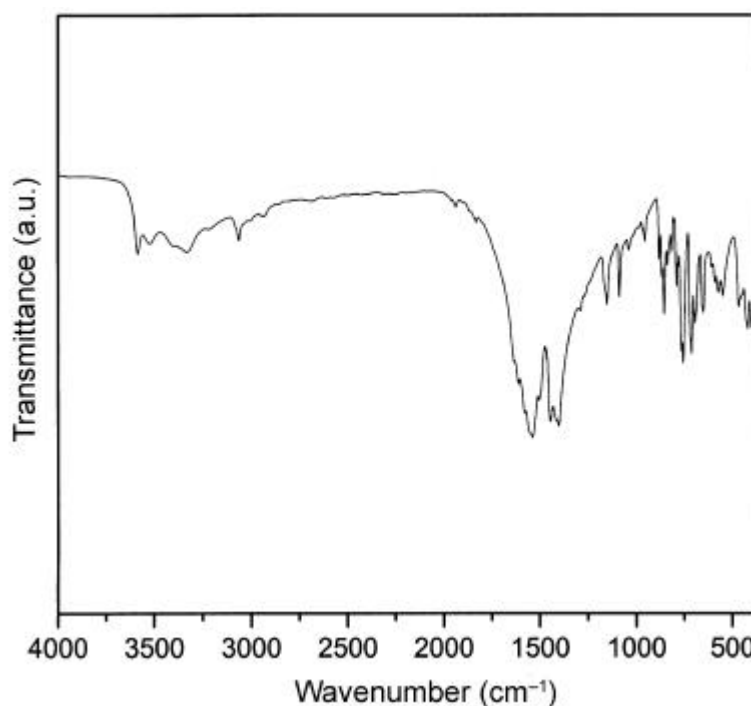


Figure 3. FT-IR spectra of **I**, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_\infty$ showing the typical bands.

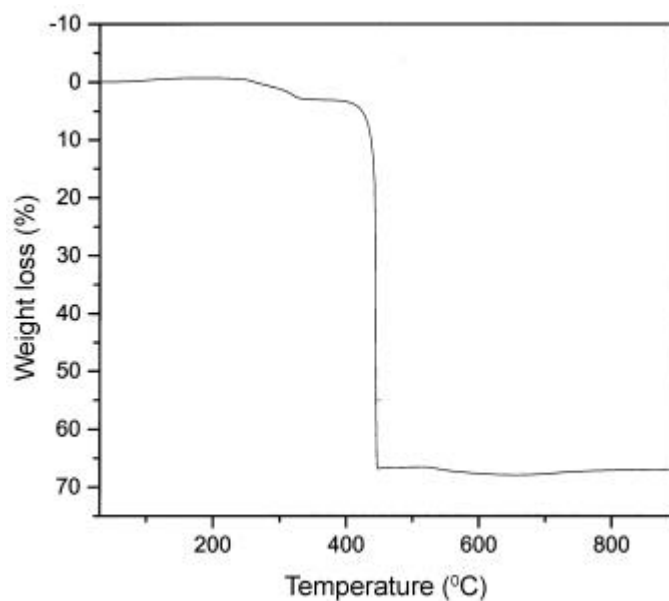


Figure 4. TGA studies of **I**, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_\infty$. Note the sharp mass loss at $\sim 450^\circ\text{C}$.

Table 1. Crystal data and structure refinement parameters for **I**, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_\infty$.

Empirical formula	$\text{C}_{48}\text{H}_{28}\text{O}_{26}\text{Y}_4$
Formula weight	1376.31
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	12.6669 (2)
b (Å)	13.8538 (2)
c (Å)	16.0289 (3)
α (°)	75.201 (1)
β (°)	69.012 (1)
γ (°)	65.529 (1)
V (Å ³)	2371.28 (7)
Z	2
D (calc) (g cm ⁻³)	1.922
m (mm ⁻¹)	4.943
I (MoK α) (Å)	0.71073
F (000)	1352
2θ range (°)	1.37–23.26
Total data collected	9745
Unique data	6566
Observed data [$I > 2s(I)$]	5252
R_{merge}	0.0292
R indexes [$I > 2s(I)$]	$R_1 = 0.0339^a$; $wR_2 = 0.0724^b$
R indexes [all data]	$R_1 = 0.0506^a$; $wR_2 = 0.0805^b$
Largest difference map peak and hole (eÅ ⁻³)	0.608 and -0.507

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; ^b $wR_2 = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$. $w = 1 / [s^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max.(F_0^2, 0) + 2(F_c^2)^2] / 3$, where $a = 0.0232$ and $b = 0.8469$

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**, $[\text{Y}_4(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_6]_{\infty}$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Y(1)	4990(1)	40(1)	2412(1)	20(1)
Y(2)	1818(1)	1210(1)	4636(1)	19(1)
Y(3)	146(1)	487(1)	7417(1)	19(1)
Y(4)	-1922(1)	-1122(1)	10026(1)	19(1)
O(1)	4673(3)	-875(3)	1623(2)	30(1)
O(2)	6528(3)	-1483(3)	2659(2)	31(1)
O(3)	5308(3)	753(3)	3381(2)	29(1)
O(4)	3518(3)	1599(2)	2110(2)	29(1)
O(5)	6452(3)	436(2)	1209(2)	28(1)
O(6)	3531(3)	-417(2)	3585(2)	27(1)
O(7)	2791(3)	38(3)	5593(2)	35(1)
O(8)	3448(3)	1686(3)	4126(3)	40(1)
O(9)	1770(3)	1945(3)	3209(2)	31(1)
O(10)	1199(3)	2573(2)	5483(2)	27(1)
O(11)	1676(3)	-314(2)	4390(2)	26(1)
O(12)	-283(3)	1928(2)	4671(2)	27(1)
O(13)	4(3)	1023(2)	5964(2)	23(1)
O(14)	-1878(3)	1205(3)	7886(2)	33(1)
O(15)	2059(3)	-663(3)	6988(2)	40(1)
O(16)	1025(3)	1782(3)	6898(2)	31(1)
O(17)	-265(3)	1442(3)	8590(2)	37(1)
O(18)	-237(3)	-913(3)	7101(2)	37(1)
O(19)	-3693(3)	-1348(3)	10459(3)	39(1)
O(20)	-2721(3)	296(2)	9120(2)	29(1)
O(21)	-1816(3)	-1882(2)	11485(2)	28(1)
O(22)	154(3)	-1902(2)	9902(2)	26(1)
O(23)	-1468(3)	-1893(2)	8691(2)	29(1)
O(24)	-1694(3)	367(2)	10410(2)	28(1)
O(25)	-1363(3)	-3021(2)	9926(2)	32(1)
O(26)	128(3)	-726(2)	8694(2)	27(1)
C(1)	-701(4)	1689(4)	5500(3)	21(1)
C(2)	-2003(4)	2307(4)	5968(3)	21(1)
C(3)	-2955(4)	1924(4)	6246(3)	21(1)
C(4)	-4121(4)	2579(4)	6657(3)	29(1)
C(5)	-4341(5)	3582(4)	6820(4)	36(1)
C(6)	-3387(5)	3949(4)	6573(4)	40(2)
C(7)	-2230(5)	3322(4)	6140(4)	32(1)
C(11)	-2709(4)	1140(4)	8599(3)	23(1)
C(12)	-3730(4)	2158(3)	8876(3)	20(1)
C(13)	-4944(4)	2260(4)	9139(3)	21(1)
C(14)	-5832(4)	3200(4)	9446(3)	30(1)
C(15)	-5524(5)	4020(4)	9503(4)	41(2)
C(16)	-4333(5)	3917(4)	9245(4)	40(2)
C(17)	-3437(5)	2993(4)	8932(4)	32(1)
C(21)	4569(5)	1458(4)	3891(3)	24(1)
C(22)	5056(4)	2104(4)	4162(3)	23(1)
C(23)	4263(5)	3070(4)	4500(4)	37(1)
C(24)	4713(6)	3732(4)	4673(4)	48(2)
C(25)	5931(6)	3466(4)	4484(4)	46(2)
C(26)	6729(5)	2513(4)	4157(4)	35(1)
C(27)	6300(4)	1815(4)	4013(3)	21(1)

Contd...

Table 2. (Contd...)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
C(31)	-1427(4)	-2812(4)	9135(3)	24(1)
C(32)	-1494(4)	-3624(4)	8707(3)	23(1)
C(33)	-1980(4)	-3336(4)	7980(3)	23(1)
C(34)	-2023(5)	-4125(4)	7622(4)	33(1)
C(35)	-1620(5)	-5181(4)	7979(4)	43(2)
C(36)	-1148(5)	-5471(4)	8703(4)	40(2)
C(37)	-1100(5)	-4702(4)	9066(4)	34(1)
C(41)	706(4)	-1539(4)	9151(3)	22(1)
C(42)	2030(4)	-2156(3)	8777(3)	20(1)
C(43)	2964(4)	-1851(4)	8753(3)	20(1)
C(44)	4163(4)	-2536(4)	8428(3)	31(1)
C(45)	4419(5)	-3450(4)	8100(4)	38(1)
C(46)	3491(5)	-3730(4)	8102(4)	44(2)
C(47)	2304(5)	-3097(4)	8450(4)	35(1)
C(51)	1221(4)	2511(4)	6278(3)	21(1)
C(52)	1446(4)	3369(3)	6509(3)	21(1)
C(53)	1943(4)	3188(4)	7218(3)	23(1)
C(54)	2028(5)	4032(4)	7467(4)	35(1)
C(55)	1669(5)	5048(4)	7006(4)	43(2)
C(56)	1205(5)	5235(4)	6298(4)	42(2)
C(57)	1115(5)	4400(4)	6052(3)	32(1)
C(71)	2462(4)	2194(4)	2461(3)	23(1)
C(81)	-2437(5)	-2086(4)	12274(3)	23(1)
C(91)	2792(4)	-731(4)	6224(4)	26(1)
C(92)	5331(5)	-1422(4)	972(3)	24(1)
C(101)	7293(5)	824(4)	935(3)	22(1)
C(111)	2710(4)	-825(4)	3913(3)	21(1)

^a*U*(eq) is defined as one-third of the orthogonalized *U*_{ij} tensor

I = 0.71073 Å) operating at 40 kV and 40 mA. Pertinent details for the structure determinations are presented in table 1. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.¹³ The structure was solved and refined using SHELXTL-PLUS suite of program.¹⁴ All the hydrogen atoms were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. Final *R* values of *R*₁ = 0.0339 and *wR*₂ = 0.0724 were obtained for refinements varying atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against |*F*²| was carried out using the SHELXTL-PLUS¹⁴ suite of programs. Details of the final refinements are given in table 1. The final atomic coordinates, selected bond distances and angles for **I** is listed in tables 2 and 3.

4. Results and discussion

The asymmetric unit of **I** contains 78 non-hydrogen atoms, of which four Y atoms are crystallographically independent. All the four Y atoms have different coordination environment with respect to its nearest neighbour oxygen atoms. Thus, the Y(1) binds to six oxygen atoms belonging to the carboxylate groups of six 1,2-BDC atoms, Y(2) binds

Table 3. Selected bond distances and angles in **I** [Y₄(H₂O)₂(C₈H₄O₄)₆]_∞.

Bond	Distance (Å)	Bond	Distance (Å)
Y(1)–O(1)	2.229(3)	Y(3)–O(15)	2.247(3)
Y(1)–O(3)	2.262(3)	Y(3)–O(26)	2.292(3)
Y(1)–O(2)	2.263(3)	Y(3)–O(13)	2.305(3)
Y(1)–O(4)	2.270(3)	Y(3)–O(16)	2.319(3)
Y(1)–O(5)	2.279(3)	Y(3)–O(17)	2.357(3)
Y(1)–O(6)	2.286(3)	Y(3)–O(18)	2.390(3)
Y(2)–O(7)	2.221(3)	Y(4)–O(20)	2.222(3)
Y(2)–O(8)	2.239(3)	Y(4)–O(19)	2.229(3)
Y(2)–O(9)	2.266(3)	Y(4)–O(21)	2.335(3)
Y(2)–O(10)	2.313(3)	Y(4)–O(22)	2.346(3)
Y(2)–O(11)	2.331(3)	Y(4)–O(23)	2.414(3)
Y(2)–O(12)	2.409(3)	Y(4)–O(24)	2.446(3)
Y(2)–O(13)	2.566(3)	Y(4)–O(25)	2.458(3)
Y(2)–O(6)	2.810(3)	Y(4)–O(5) ^{#1}	2.847(3)
Y(3)–O(14)	2.239(3)	Y(4)–O(26)	2.866(3)
Angle	Amplitude (°)	Angle	Amplitude (°)
O(1)–Y(1)–O(3)	171.16(12)	O(19)–Y(4)–O(21)	85.67(13)
O(1)–Y(1)–O(2)	86.23(12)	O(20)–Y(4)–O(22)	123.73(12)
O(3)–Y(1)–O(2)	88.11(12)	O(19)–Y(4)–O(22)	147.26(12)
O(1)–Y(1)–O(4)	94.38(11)	O(21)–Y(4)–O(22)	74.94(11)
O(3)–Y(1)–O(4)	91.61(11)	O(20)–Y(4)–O(23)	77.61(12)
O(1)–Y(1)–O(5)	92.04(12)	O(21)–Y(4)–O(23)	132.39(11)
O(3)–Y(1)–O(5)	94.14(12)	O(22)–Y(4)–O(23)	87.38(11)
O(2)–Y(1)–O(5)	84.19(12)	O(20)–Y(4)–O(24)	74.98(11)
O(4)–Y(1)–O(5)	92.95(12)	O(19)–Y(4)–O(24)	122.45(12)
O(1)–Y(1)–O(6)	85.47(12)	O(21)–Y(4)–O(24)	83.60(11)
O(3)–Y(1)–O(6)	88.25(12)	O(22)–Y(4)–O(24)	81.87(11)
O(2)–Y(1)–O(6)	94.90(12)	O(23)–Y(4)–O(24)	137.87(11)
O(4)–Y(1)–O(6)	87.98(12)	O(20)–Y(4)–O(25)	128.37(11)
O(5)–Y(1)–O(6)	177.41(11)	O(19)–Y(4)–O(25)	75.98(12)
O(7)–Y(2)–O(8)	83.75(13)	O(21)–Y(4)–O(25)	79.03(11)
O(7)–Y(2)–O(9)	150.34(13)	O(22)–Y(4)–O(25)	74.60(11)
O(8)–Y(2)–O(9)	78.67(13)	O(23)–Y(4)–O(25)	53.54(11)
O(7)–Y(2)–O(10)	91.25(11)	O(24)–Y(4)–O(25)	153.66(11)
O(8)–Y(2)–O(10)	78.99(12)	O(20)–Y(4)–O(5) ^{#1}	76.03(11)
O(9)–Y(2)–O(10)	108.39(12)	O(19)–Y(4)–O(5) ^{#1}	74.30(11)
O(7)–Y(2)–O(11)	82.12(12)	O(21)–Y(4)–O(5) ^{#1}	72.04(10)
O(8)–Y(2)–O(11)	127.29(12)	O(22)–Y(4)–O(5) ^{#1}	122.12(10)
O(9)–Y(2)–O(11)	89.72(12)	O(23)–Y(4)–O(5) ^{#1}	148.33(10)
O(10)–Y(2)–O(11)	151.46(12)	O(24)–Y(4)–O(5) ^{#1}	48.62(10)
O(7)–Y(2)–O(12)	132.06(12)	O(25)–Y(4)–O(5) ^{#1}	139.59(11)
O(8)–Y(2)–O(12)	140.11(12)	O(20)–Y(4)–O(26)	75.60(11)
O(9)–Y(2)–O(12)	73.90(11)	O(19)–Y(4)–O(26)	153.12(12)
O(10)–Y(2)–O(12)	82.80(11)	O(21)–Y(4)–O(26)	120.04(10)
O(11)–Y(2)–O(12)	81.32(11)	O(22)–Y(4)–O(26)	48.44(10)
O(7)–Y(2)–O(13)	80.31(12)	O(23)–Y(4)–O(26)	70.48(10)
O(8)–Y(2)–O(13)	147.46(11)	O(24)–Y(4)–O(26)	72.02(10)
O(9)–Y(2)–O(13)	125.97(11)	O(25)–Y(4)–O(26)	99.89(10)
O(10)–Y(2)–O(13)	73.22(10)	O(5) ^{#1} –Y(4)–O(26)	118.79(9)
O(11)–Y(2)–O(13)	78.30(10)	C(92)–O(1)–Y(1)	134.6(3)

Contd...

Table 3. (Contd...)

Angle	Amplitude (°)	Angle	Amplitude (°)
O(12)–Y(2)–O(13)	52.36(10)	C(81)#2–O(2)–Y(1)	142.6(3)
O(7)–Y(2)–O(6)	76.98(11)	C(21)–O(3)–Y(1)	129.7(3)
O(8)–Y(2)–O(6)	77.68(11)	C(71)–O(4)–Y(1)	141.8(3)
O(9)–Y(2)–O(6)	76.04(11)	C(101)–O(5)–Y(1)	146.0(3)
O(10)–Y(2)–O(6)	154.84(10)	C(101)–O(5)–Y(4) ^{#2}	85.2(3)
O(11)–Y(2)–O(6)	49.68(10)	Y(1)–O(5)–Y(4) ^{#2}	119.69(12)
O(12)–Y(2)–O(6)	121.60(10)	C(111)–O(6)–Y(1)	151.9(3)
O(13)–Y(2)–O(6)	125.15(9)	C(111)–O(6)–Y(2)	83.1(3)
O(14)–Y(3)–O(15)	163.24(13)	Y(1)–O(6)–Y(2)	116.14(12)
O(14)–Y(3)–O(26)	89.84(12)	C(91)–O(7)–Y(2)	146.5(3)
O(15)–Y(3)–O(26)	81.21(12)	C(21)–O(8)–Y(2)	151.4(3)
O(14)–Y(3)–O(13)	87.50(12)	C(71)–O(9)–Y(2)	139.7(3)
O(15)–Y(3)–O(13)	93.44(12)	C(51)–O(10)–Y(2)	128.9(3)
O(26)–Y(3)–O(13)	150.91(10)	C(111)–O(11)–Y(2)	106.2(3)
O(14)–Y(3)–O(16)	112.00(12)	C(1)–O(12)–Y(2)	96.7(3)
O(15)–Y(3)–O(16)	84.46(12)	C(1)–O(13)–Y(3)	142.2(3)
O(26)–Y(3)–O(16)	129.98(11)	C(1)–O(13)–Y(2)	88.8(3)
O(13)–Y(3)–O(16)	77.27(11)	Y(3)–O(13)–Y(2)	121.48(12)
O(14)–Y(3)–O(17)	75.62(12)	C(11)–O(14)–Y(3)	137.3(3)
O(15)–Y(3)–O(17)	114.91(13)	C(91)–O(15)–Y(3)	129.0(3)
O(26)–Y(3)–O(17)	74.17(12)	C(51)–O(16)–Y(3)	146.1(3)
O(13)–Y(3)–O(17)	132.61(11)	C(92) ^{#1} –O(19)–Y(4)	158.5(3)
O(16)–Y(3)–O(17)	69.22(12)	C(11)–O(20)–Y(4)	152.0(3)
O(14)–Y(3)–O(18)	83.28(12)	C(81)–O(21)–Y(4)	143.7(3)
O(15)–Y(3)–O(18)	80.72(13)	C(41)–O(22)–Y(4)	107.7(3)
O(26)–Y(3)–O(18)	74.75(11)	C(31)–O(23)–Y(4)	92.7(3)
O(13)–Y(3)–O(18)	76.17(11)	C(101) ^{#1} –O(24)–Y(4)	104.7(3)
O(16)–Y(3)–O(18)	148.60(12)	C(31)–O(25)–Y(4)	91.5(3)
O(17)–Y(3)–O(18)	142.17(13)	C(41)–O(26)–Y(3)	149.1(3)
O(20)–Y(4)–O(19)	86.19(13)	C(41)–O(26)–Y(4)	82.3(3)
O(20)–Y(4)–O(21)	148.07(12)	Y(3)–O(26)–Y(4)	127.96(12)

Symmetry transformations used to generate equivalent atoms: ^{#1} $x-1, y, z+1$; ^{#2} $x+1, y, z-1$

eight oxygen atoms from the carboxylate groups of five 1,2-BDC anions, Y(3) bind with seven oxygen atoms, five of which are from the carboxylate groups of five 1,2-BDC and the other two are terminal ones (two coordinated water molecules) and Y(4) is coordinated to nine oxygen atoms of the carboxylate groups of six 1,2-BDC anions. It is rare that the same metal ion has four different coordination environments within the same compound. The geometry of each of the Y atoms can be described as octahedron (Y(1), CN = 6), pentagonal bipyramid (Y(3), CN = 7), dodecahedron (U(2), CN = 8) and capped square antiprism (Y(4), CN = 9). The coordination geometry of each of the Y atoms is shown in figure 5(a–d). Similar coordination arrangements have been observed recently in a yttrium 1,2-BDC coordination polymer.¹⁵

The Y atoms have a varying distances depending on the coordination arrangement with oxygen atoms. The Y–O distances are in the range 2.221(3)–2.886(3) Å [(Y(1)–O)_{av} = 2.265, (Y(2)–O)_{av} = 2.103, (Y(3)–O)_{av} = 2.307 and (Y(4)–O)_{av} = 2.463 Å]. The longer Y–O distances (>2.5 Å) appear to be associated with the oxygen atoms that are three-coordinated (links two Y atoms and also a carbon atom of the carboxylate). The O–Y–O

bond angles also reflect the differences in the coordination geometries around the Y atoms. Thus, O–Y–O bond angles are in the range $48.44(10)$ – $177.41(11)^\circ$ [$(\text{O–Y}(1)\text{–O})_{\text{av}} = 107.1$, $(\text{O–Y}(2)\text{–O})_{\text{av}} = 99.7$, $(\text{O–Y}(3)\text{–O})_{\text{av}} = 102$ and $(\text{O–Y}(4)\text{–O})_{\text{av}} = 102.55^\circ$] have been observed in **I**. As mentioned earlier, the Y atoms are bonded together through their oxygen vertices with an average Y–O–Y bond angle of 121.3° . The Y atoms are connected with carbon atoms through the O atoms with a variety of bond angles. The Y–O–C bond angles are in the range $83.1(3)$ – $158.5(3)^\circ$ with an average value of 146.3° . There are six carboxylate anions have been grouped individually as C2–C7 with C1 and C111 as carboxylates (acid-1), C12–C17 with C11 and C61 as carboxylates (acid-2), C22–C27 with C21 and C91 as carboxylates (acid-3), C32–C37 with C31 and C71 as carboxylates, C42–C47 with C41 and C101 as carboxylates and C52–C57 with C51 and C81 as carboxylates. The C–O distances of the carboxylate anion are in the $1.242(6)$ – $1.281(5)$ Å (av. 1.262 Å). The O–C–O bond angles are as expected for this type of bonding. The torsion angles, in general, represent the degree of distortion of the carboxylate units from the plane of the benzene ring due to the bonding with the metal atoms. In **I**, the torsion angles suspended between the two carboxylate groups from the benzene ring are as follows: acid-1 = 0.32 , acid-2 = -9.79 , acid-3 = -14.5 , acid-4 = 1.23 , acid-5 = -3.18 and acid-6 = 7.98° . This clearly indicates that the carboxylate groups of the acids -2, -3 and -6 are more distorted compared to -1, -4 and -5. The various bond distances and angles, observed in **I**, are comparable with those reported for similar compounds in the literature.^{2–10}

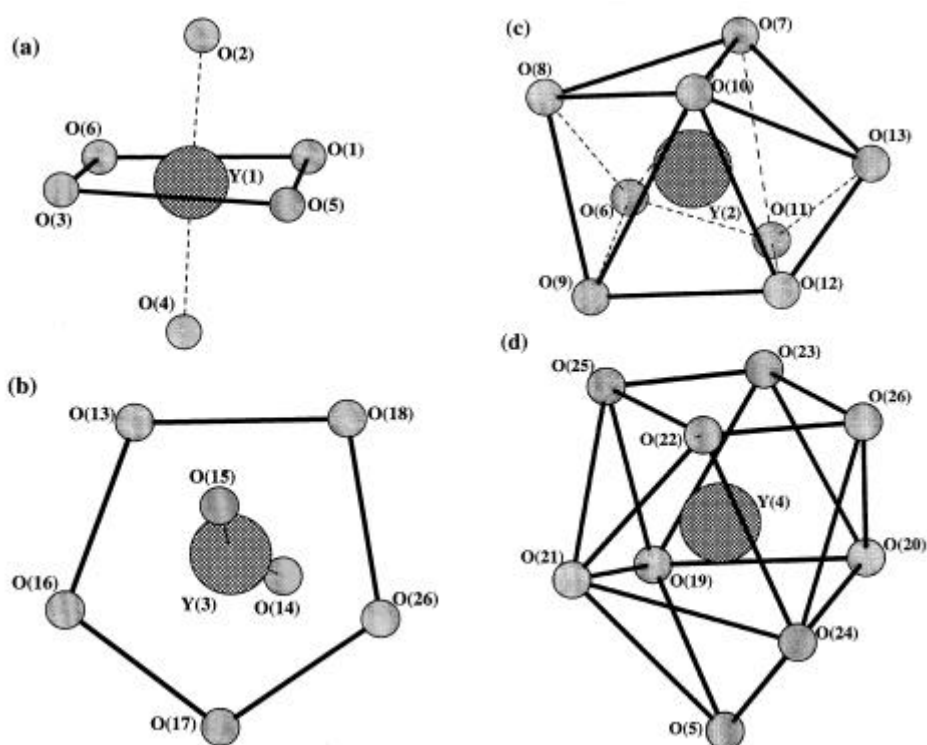


Figure 5. The coordination environment around the central Y atom (a) Y(1), (b) Y(3), (c) Y(2) and (d) Y(4).

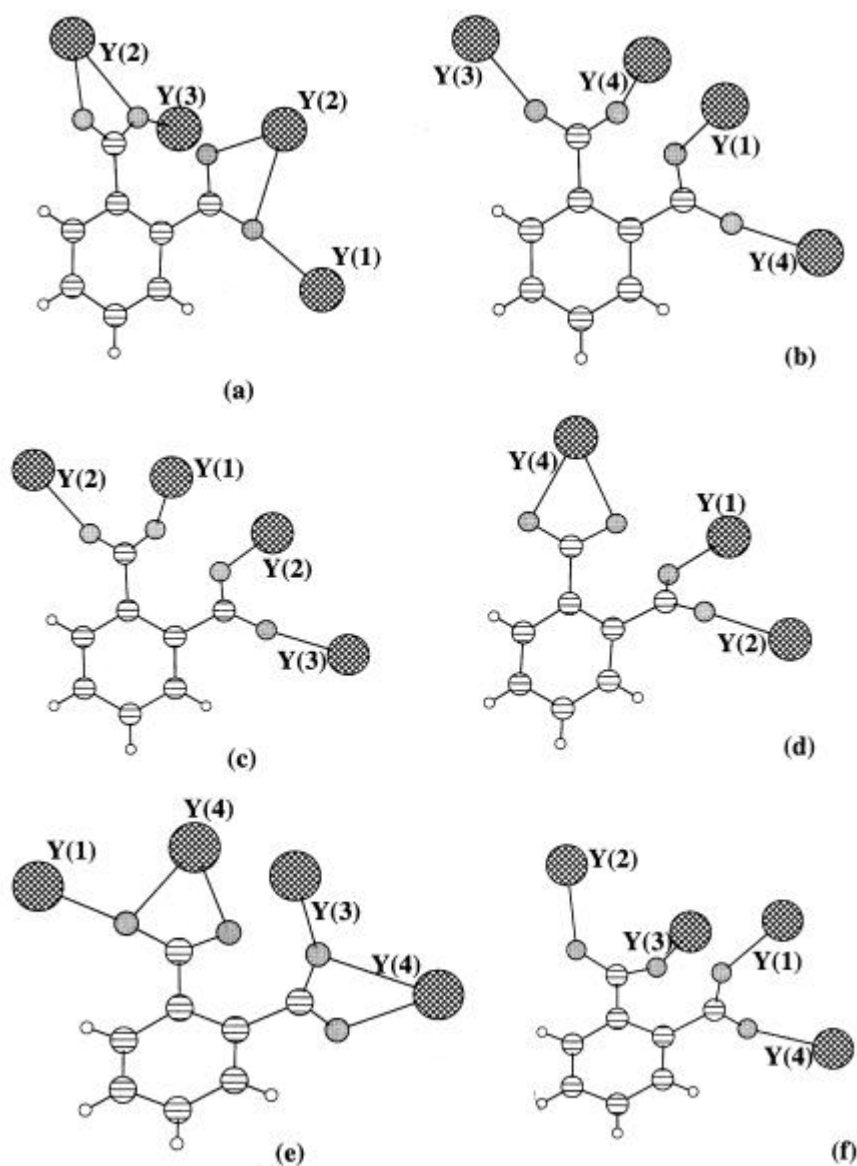


Figure 6. Figure shows the connectivity between the 1,2-BDC anions and the Y atoms: (a) acid-1, (b) acid-2, (c) acid-3, (d) acid-4, (e) acid-5 and (f) acid-6. (See text for the description of the acids.)

The six 1,2-BDC anions also show distinct differences in their connection modes with the Y atoms. The connectivity involving each of the six 1,2-BDC anions are shown figure 6(a–f). The six 1,2-BDC anions can be organised in to three types based on their bonding with Y atoms. Thus, three 1,2-BDC anions have monodendate connectivity through all the carboxylate oxygen atoms (figure 6b, c and f), two 1,2-BDC anions show *bis*-bidendate bonding by both the carboxylate groups (figure 6a and e), and one 1,2-BDC

anion show bi-dendate connectivity with respect to one of the carboxylate and the other is mono-dendate (figure 6d). This is indeed an unique arrangement. As shown in figure 1, the following binding modes of 1,2-BDC, in h, e and d correspond to the bonding found in the present structure.

The two-dimensional structure of **I** consists of a network of Y polyhedra connected together through their corners to give rise to an infinite one-dimensional Y–O–Y chains (figure 7a). The one-dimensional Y–O–Y chains are connected through the 1,2-BDC anions to form the layer structure as shown in figure 7b. Within the layer, the large number of *p...p* interactions creates a corrugated nature to the sheets. The connectivity between the Y atoms within the layer is shown in figure 8. As can be seen, the Y–Y distances have different values ranging from 4.251–7.742 Å. The Y distances within the chain are the following: Y(1)...Y(2) = 4.33, Y(2)...Y(3) = 4.251, Y(3)...Y(4) = 4.642 and Y(4)...Y(1) = 4.441 Å. The distances between the chains have generally higher values (figure 8).

The 1,2-BDC, in general, suspends an angle of 60° between the carboxylate groups. This would presumably give rise to interesting *p...p* interactions with in a solid. The role

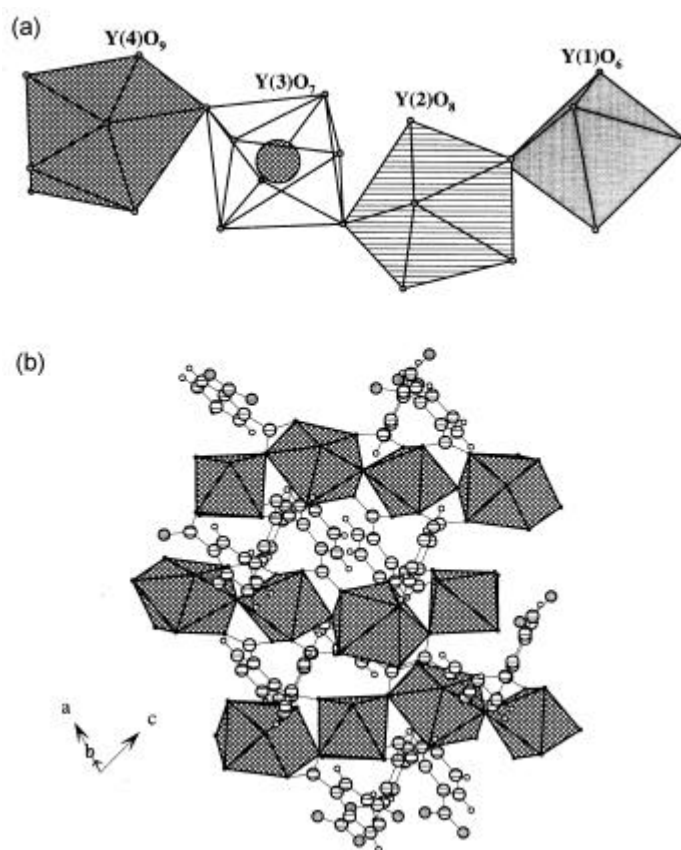


Figure 7. (a) Figure shows the connectivity between the differently coordinated Y atoms. Note that the Y polyhedra are connected through their corners. (b) Structure of **I** showing the connectivity between the Y polyhedra and the 1,2-BDC anions.

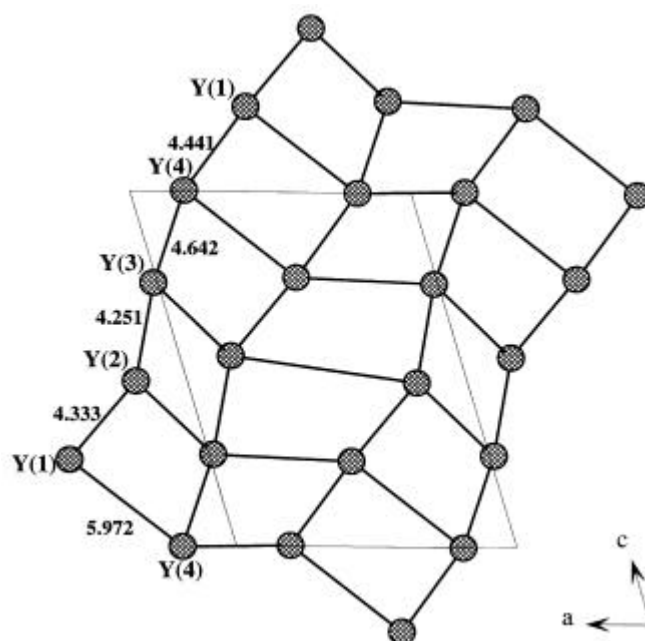


Figure 8. Figure shows the Y atom connectivity within the layer. Note the formation of a corrugated sheet-like structure (see text).

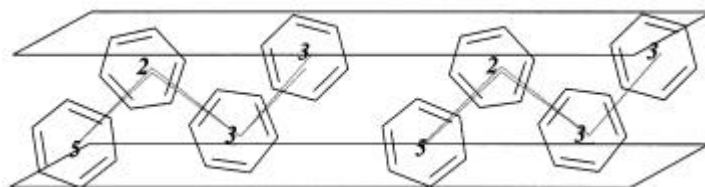


Figure 9. A schematic representation of position of benzene rings within a layer and their possible interactions with the neighbouring layer (see text).

of *p*..*p* interactions for the stability of organic compounds have been discussed recently, with particular emphasis on the centroid-centroid distances (d) and the angle (θ) suspended between the benzene rings.¹⁶ A correlation between the two (d and θ), has been discussed in terms of a phase-diagram with the distances and angles having a unique relationship. From this, the following interactions appear to be important for different values of the centroid-centroid distance (d) and angles (θ): (i) $d = 0-3 \text{ \AA}$ and $\theta = 50-90^\circ$, (ii) $d = 3-7 \text{ \AA}$ and $\theta = 0-50^\circ$, (iii) $d = 4-7.5 \text{ \AA}$, $\theta = 140-180^\circ$ and (iv) $d = 6-7 \text{ \AA}$ and $\theta = 0-145^\circ$. In the present structure, though covalent linkages exist between the Y atoms, and 1,2-BDC and Y, the close proximity between the benzene rings gives rise to interesting *p*..*p* interactions. Two distinct *p*..*p* interactions have been observed in **I**: one is the intra-layer and the other is the inter-layer. The interactions between the acids 1 and 2 within the layer (intra) with $d = 4.205 \text{ \AA}$ and $\theta = 8.19^\circ$ can be classified as strong, while

that between acids 3 and 6 with $d = 5.027 \text{ \AA}$ and $q = 118.43^\circ$ is moderate. Compared to the intra-layer, the inter-layer interactions appear to be more and in number. Thus the interactions between the acids 1 and 3' ($d = 5.458 \text{ \AA}$, $q = 16.28^\circ$), 1 and 5' ($d = 6.568 \text{ \AA}$, $q = 92.98^\circ$), 3 and 2' ($d = 6.012 \text{ \AA}$, $q = 11.33^\circ$), 3 and 3' ($d = 5.022 \text{ \AA}$, $q = 0^\circ$), 3 and 6' ($d = 4.66 \text{ \AA}$, $q = 3.85^\circ$) and 5 and 2' ($d = 5.217 \text{ \AA}$, $q = 8.43^\circ$) appear to be strong and the interactions involving the acids 4 and 6' ($d = 8.250 \text{ \AA}$, $q = 118.44^\circ$) are moderate. A schematic representation of the inter-layer **p...p** interactions observed in **I** is presented in figure 9. Since there are no other interactions between the layers, the **p...p** interactions appear to be the dominant interactions responsible for holding the layers apart and intact.

5. Conclusions

The hydrothermal synthesis and structure of a new yttrium 1,2-benzenedicarboxylate has been accomplished. The compound has a layered structure formed by the connectivity involving the Y and 1,2-BDC anions. The Y atoms are present in four different coordination geometries, which is noteworthy. In addition, the Y atoms are connected through their corners forming an infinite Y–O–Y one-dimensional chain. The layers are held together by the **p...p** interactions between the benzene rings between the two layers. The present study offers further scope for investigating the role of **p...p** interactions in the structural stability of coordination polymers. We are presently pursuing this theme.

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