Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Piperazinediium bis(3,4,5-trihydroxybenzoate) dihydrate

Kun-Mei Su* and Zhen-huan Li

College of Materials and Chemical Engineering, and Tianjin Key Laboratory of Fiber Modification & Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China
Correspondence e-mail: primer673@126.com

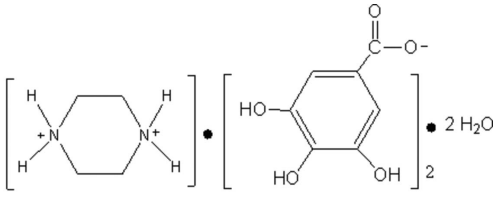
Received 30 July 2007; accepted 25 October 2007

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.107; data-to-parameter ratio = 11.9.

In the title compound, $C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_5^{-}\cdot 2H_2O$, the cation lies on a centre of symmetry. The crystal structure is stabilized by various intermolecular O—H···O and N—H···O hydrogen bonds, and by intermolecular aromatic π–π interactions, with a centroid-to-centroid distance of 3.348 (2) Å between the benzene rings of neighbouring anions.

Related literature

For related literature, see: Akao *et al.* (2001); Anand *et al.* (1997); Fukumoto & Mazza (2000); Harbowy & Ballentine (1997); Kawada *et al.* (1992); Li & Guo (2007); Saeki *et al.* (2000); Sartori *et al.* (2004); Stich & Rosin (1984).



Experimental

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_5^{-}\cdot 2H_2O$
M_r = 462.41
Monoclinic, $P2_1/n$
a = 8.197 (2) Å
b = 9.449 (2) Å
c = 12.655 (2) Å
β = 106.516 (3)°
V = 939.7 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 294 (2) K
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
5263 measured reflections
1922 independent reflections
1591 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.107
S = 1.10
1922 reflections
161 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O6^{i}	0.82	1.92	2.664 (2)	151
O4—H4···O1^{ii}	0.82	2.08	2.703 (2)	133
O5—H5···O1^{iii}	0.82	1.98	2.650 (2)	138
O6—H6A···O2	0.85 (3)	1.85 (3)	2.691 (2)	167 (3)
O6—H6B···O3^{iv}	0.83 (3)	2.31 (3)	2.829 (2)	121 (2)
O6—H6B···O4^{iv}	0.83 (3)	2.23 (3)	3.054 (2)	169 (3)
N—H1B···O2	0.92 (2)	1.90 (2)	2.787 (2)	161 (2)
N—H1A···O6^{i}	0.89 (2)	1.99 (2)	2.848 (2)	160.0 (17)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, -y+1, -z+2$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

The authors are grateful for the financial support of the Tianjin Polytechnic University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2020).

References

Akao, S., Takemura, G., Minatoguchi, S., Gotoh, K., Fujiwara, H. & Fukuda, K. (2001). *Anticancer Drugs*, **12**, 847–852.
Anand, K. K., Singh, B., Saxena, A. K., Chandan, B. K., Gupta, V. N. & Bhardwaj, V. (1997). *Pharm. Res.* **36**, 315–321.
Bruker (2000). *SMART* (Version 5.051) and *SAINT* (Version 5.A06). Bruker AXS Inc., Madison, Wisconsin, USA.
Fukumoto, L. R. & Mazza, G. J. (2000). *J. Agric. Food Chem.* **48**, 3597–3604.
Harbowy, M. E. & Ballentine, D. A. (1997). *Crit. Rev. Plant Sci.* **16**, 415–480.
Kawada, M., Ohno, Y., Ri, Y., Ikoma, T., Yuugetu, H., Asai, T., Watanabe, M., Yasuda, N., Kroes, B. H., van den Berg, A. J. J., Quarles van Ufford, H. C., Dijk, H. & Labadie, R. P. (1992). *Acid. Planta Med.* **58**, 499–504.
Li, Z.-H. & Guo, M.-L. (2007). *Acta Cryst.* E**63**, o1167–o1168.
Saeki, K., You, A., Isemura, M., Abe, I., Seki, T. & Noguchi, H. (2000). *Biol. Pharm. Bull.* **23**, 1391–1394.
Sartori, G., Ballini, R., Big, F., Bosia, G., Maggi, R. & Righi, P. (2004). *Chem. Rev.* **104**, 199–250.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Stich, H. F. & Rosin, M. P. (1984). *Adv. Exp. Med. Biol.* **177**, 1–29.

  doi:10.1107/S1600536807053020

supplementary materials

Acta Cryst. (2007). E**63**, o4512 [**doi:10.1107/S1600536807053020**]

Piperazinediium bis(3,4,5-trihydroxybenzoate) dihydrate

K.-M. Su and Z. Li

Comment

Gallic acid (3, 4, 5-trihydroxybenzoic acid) is one of the main endogenous phenolic acids found in plants as a free or esterified form, and a large amount of them is present in tea, being present at about 5% of the dry weight (Harbowy & Ballentine 1997). Significantly, it has been found that gallic acid and its derivatives are pharmacologically active, and possess antioxidative (Fukumoto & Mazza, 2000), antimutagenic, anticarcinogenic (Akao *et al.*, 2001; Saeki *et al.*, 2000; Stich & Rosin, 1984), antiinflammatory (Kawada *et al.*, 1992), and hepatoprotective activities (Anand *et al.*, 1997). In the earlier work, acetic anhydride had been used to protect hydroxyl group (Li & Guo, 2007). Herein we report the molecular and crystal structure of the title compound (Fig. 1)

The title compound (Fig. 1) was obtained from the solution of 3,4,5-trihydroxybenzoic acid monohydrate and piperazine. The bond distances and angles in the title compound are normal. The molecular packing (Fig. 2) is stabilized by hydrogen bonds of all H atoms in the O and N atoms (Table 1). The molecular packing (Fig. 2) is further stabilized by π—π stacking interactions between the benzene rings of adjacent molecules. The $Cg\cdots Cg^{v}$ distance is 3.348 (2) Å (*Cg* is the centroid of the C2—C7 ring; symmetry code as in Fig.2).

Experimental

Gallic acid monohydrate (3.76 g, 20 mmol) and piperazine (0.86 g, 10 mmol) were loaded into a 100 ml roundbottom flask, and then 50 ml H_2O were droped into above mixture. After reaction the solid gallic acid and piperazine dissolved into solution under heater. Crystals of the title compound were obtained by slow evaporation of deionic H_2O solution.

Refinement

The H atoms of the water molecule and the hydrogen atoms on the N atom were positioned in a different Fourier maps, there the parameters were freely refined. All other H atoms were positioned geometrically and refined using a riding model, with O—H = 0.82 Å for hydroxy H atoms, C—H = 0.93 Å for aromatic H atoms, and 0.97 Å for methylene H atoms, respectively, and with U_{iso}(H) = 1.5Ueq(O) for hydroxy, U_{iso}(H) = 1.2Ueq(C) for aromatic and methylene H atoms.

Figures

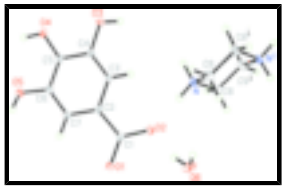


Fig. 1. The molecular structure of title compound, showing ???% probability displacement ellipsoids. H atoms are shown as small spheres of arbitary radii. [Symmetry code; (i) 1 − *x*, −*y*, 2 − *z*.]

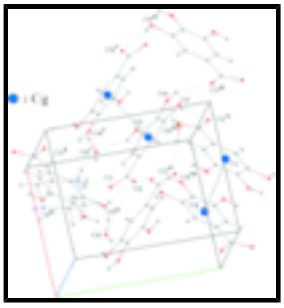


Fig. 2. π···π interactions, O—H···O and N—H···O hydrogen bonds (dotted lines) in the title compound. *Cg* denotes the ring centroid. [Symmetry codes: (i) 1/2 + *x*, 1/2 − *y*, *z* + 1/2; (ii) 3/2 − *x*, *y* − 1/2, 3/2 − *z*; (iii) 1/2 + *x*, 3/2 − *y*, *z* + 1/2; (iv) 1 − *x*, 1 − *y*, 2 − *z*; (v) 2 − *x*, 1 − *y*, 2 − *z*; (vi) 3/2 − *x*, *y* + 1/2, 3/2 − *z*; (vii) *x* − 1/2, 3/2 − *y*, *z* − 1/2.]

Piperazindiium bis(3,4,5-trihydroxybenzoate) dihydrate

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_5^{-}\cdot 2H_2O$	F_{000} = 488
M_r = 462.41	D_x = 1.634 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2556 reflections
a = 8.197 (2) Å	θ = 2.7–26.4º
b = 9.449 (2) Å	μ = 0.14 mm^{-1}
c = 12.655 (2) Å	T = 294 (2) K
β = 106.516 (3)º	Block, colorless
V = 939.7 (3) Å^3	0.20 × 0.16 × 0.12 mm
Z = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	1922 independent reflections
Radiation source: fine-focus sealed tube	1591 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.028
Detector resolution: 10.0 pixels mm^{-1}	θ_{max} = 26.4º
T = 294(2) K	θ_{min} = 2.7º
φ and ω scans	h = −10→9
Absorption correction: none	k = −11→11
5263 measured reflections	l = −11→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.039	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.107	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.3692P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.10	$(\Delta/\sigma)_{max} < 0.001$

1922 reflections	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
161 parameters	$\Delta\rho_{min}$ = −0.42 e Å^{-3}
4 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.58286 (17)	0.49827 (12)	0.69747 (9)	0.0276 (3)
O2	0.53936 (15)	0.33368 (12)	0.81110 (9)	0.0270 (3)
O3	0.83718 (16)	0.49981 (12)	1.19238 (9)	0.0279 (3)
H3	0.7719	0.4333	1.1896	0.042*
O4	1.02059 (15)	0.72094 (12)	1.17301 (9)	0.0277 (3)
H4	1.0744	0.7876	1.1583	0.042*
O5	1.02560 (14)	0.82015 (12)	0.96955 (9)	0.0249 (3)
H5	1.0160	0.8417	0.9053	0.037*
O6	0.2251 (2)	0.26564 (15)	0.68561 (10)	0.0325 (3)
H6A	0.325 (4)	0.295 (3)	0.717 (2)	0.067 (9)*
H6B	0.161 (3)	0.282 (3)	0.724 (2)	0.064 (8)*
N	0.58220 (17)	0.12224 (14)	0.97017 (12)	0.0215 (3)
H1A	0.651 (2)	0.151 (2)	1.0349 (18)	0.030 (5)*
H1B	0.592 (3)	0.186 (2)	0.9169 (19)	0.042 (6)*
C1	0.6055 (2)	0.44903 (16)	0.79314 (12)	0.0196 (3)
C2	0.71553 (19)	0.52807 (16)	0.89041 (12)	0.0179 (3)
C3	0.7195 (2)	0.48134 (16)	0.99537 (12)	0.0194 (3)
H3A	0.6495	0.4071	1.0033	0.023*
C4	0.8266 (2)	0.54420 (16)	1.08790 (12)	0.0187 (3)
C5	0.92582 (19)	0.65932 (16)	1.07747 (12)	0.0185 (3)
C6	0.92217 (19)	0.70748 (16)	0.97240 (13)	0.0179 (3)
C7	0.81769 (19)	0.64194 (16)	0.87896 (12)	0.0186 (3)
H7	0.8160	0.6739	0.8092	0.022*
C8	0.6298 (2)	−0.02284 (17)	0.94383 (14)	0.0257 (4)
H8A	0.7493	−0.0248	0.9467	0.031*
H8B	0.5638	−0.0484	0.8698	0.031*
C9	0.4030 (2)	0.12800 (18)	0.97492 (15)	0.0268 (4)

H9A	0.3271	0.1084	0.9023	0.032*
H9B	0.3784	0.2226	0.9959	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0437 (7)	0.0207 (6)	0.0155 (6)	−0.0033 (5)	0.0037 (5)	0.0001 (4)
O2	0.0343 (7)	0.0218 (6)	0.0215 (6)	−0.0079 (5)	0.0024 (5)	0.0016 (5)
O3	0.0448 (8)	0.0233 (6)	0.0148 (6)	−0.0069 (5)	0.0072 (5)	0.0005 (4)
O4	0.0376 (7)	0.0228 (6)	0.0180 (6)	−0.0087 (5)	0.0002 (5)	−0.0020 (5)
O5	0.0268 (6)	0.0243 (6)	0.0210 (6)	−0.0077 (5)	0.0026 (5)	0.0036 (5)
O6	0.0358 (8)	0.0343 (7)	0.0252 (7)	0.0079 (6)	0.0050 (6)	−0.0087 (5)
N	0.0236 (7)	0.0196 (7)	0.0214 (7)	−0.0013 (5)	0.0067 (6)	0.0028 (6)
C1	0.0221 (8)	0.0173 (7)	0.0191 (7)	0.0017 (6)	0.0053 (6)	0.0001 (6)
C2	0.0183 (7)	0.0171 (7)	0.0174 (7)	0.0020 (6)	0.0034 (6)	−0.0011 (6)
C3	0.0231 (8)	0.0155 (7)	0.0197 (8)	−0.0005 (6)	0.0065 (6)	0.0007 (6)
C4	0.0240 (8)	0.0171 (7)	0.0150 (7)	0.0043 (6)	0.0057 (6)	0.0012 (6)
C5	0.0198 (7)	0.0165 (7)	0.0167 (7)	0.0032 (6)	0.0011 (6)	−0.0028 (6)
C6	0.0158 (7)	0.0153 (7)	0.0224 (8)	0.0022 (6)	0.0052 (6)	0.0014 (6)
C7	0.0206 (7)	0.0200 (8)	0.0154 (7)	0.0029 (6)	0.0056 (6)	0.0025 (6)
C8	0.0250 (8)	0.0244 (8)	0.0311 (9)	0.0010 (7)	0.0135 (7)	−0.0023 (7)
C9	0.0234 (8)	0.0217 (8)	0.0351 (9)	0.0074 (7)	0.0082 (7)	0.0051 (7)

Geometric parameters (Å, °)

O1—C1	1.261 (2)	C2—C3	1.391 (2)
O2—C1	1.266 (2)	C2—C7	1.396 (2)
O3—C4	1.366 (2)	C3—C4	1.382 (2)
O3—H3	0.8200	C3—H3A	0.9300
O4—C5	1.368 (2)	C4—C5	1.387 (2)
O4—H4	0.8200	C5—C6	1.398 (2)
O5—C6	1.368 (2)	C6—C7	1.393 (2)
O5—H5	0.8200	C7—H7	0.9300
O6—H6A	0.85 (3)	C8—C9^{i}	1.508 (2)
O6—H6B	0.83 (3)	C8—H8A	0.9700
N—C9	1.488 (2)	C8—H8B	0.9700
N—C8	1.489 (2)	C9—C8^{i}	1.508 (2)
N—H1A	0.89 (2)	C9—H9A	0.9700
N—H1B	0.92 (2)	C9—H9B	0.9700
C1—C2	1.502 (2)		
C4—O3—H3	109.5	O4—C5—C4	116.8 (1)
C5—O4—H4	109.5	O4—C5—C6	123.8 (1)
C6—O5—H5	109.5	C4—C5—C6	119.4 (1)
H6A—O6—H6B	111 (3)	O5—C6—C7	124.1 (1)
C9—N—C8	111.6 (1)	O5—C6—C5	115.6 (1)
C9—N—H1A	109 (1)	C7—C6—C5	120.3 (1)
C8—N—H1A	110 (1)	C6—C7—C2	119.8 (1)
C9—N—H1B	107 (1)	C6—C7—H7	120.1

C8—N—H1B	111 (1)	C2—C7—H7	120.1
H1A—N—H1B	108 (2)	N—C8—C9^{i}	110.17 (13)
O1—C1—O2	122.4 (1)	N—C8—H8A	109.6
O1—C1—C2	119.6 (1)	C9^{i}—C8—H8A	109.6
O2—C1—C2	118.0 (1)	N—C8—H8B	109.6
C3—C2—C7	119.6 (1)	C9^{i}—C8—H8B	109.6
C3—C2—C1	118.1 (1)	H8A—C8—H8B	108.1
C7—C2—C1	122.5 (1)	N—C9—C8^{i}	111.90 (13)
C4—C3—C2	120.6 (2)	N—C9—H9A	109.2
C4—C3—H3A	119.7	C8^{i}—C9—H9A	109.2
C2—C3—H3A	119.7	N—C9—H9B	109.2
O3—C4—C3	122.6 (1)	C8^{i}—C9—H9B	109.2
O3—C4—C5	117.1 (1)	H9A—C9—H9B	107.9
C3—C4—C5	120.3 (1)		
O1—C1—C2—C3	171.50 (14)	C3—C4—C5—C6	−2.8 (2)
O2—C1—C2—C3	−8.9 (2)	O4—C5—C6—O5	2.1 (2)
O1—C1—C2—C7	−11.1 (2)	C4—C5—C6—O5	−179.08 (13)
O2—C1—C2—C7	168.51 (14)	O4—C5—C6—C7	−177.75 (14)
C7—C2—C3—C4	−1.7 (2)	C4—C5—C6—C7	1.1 (2)
C1—C2—C3—C4	175.86 (14)	O5—C6—C7—C2	−179.52 (13)
C2—C3—C4—O3	−178.62 (14)	C5—C6—C7—C2	0.3 (2)
C2—C3—C4—C5	3.1 (2)	C3—C2—C7—C6	0.0 (2)
O3—C4—C5—O4	−2.3 (2)	C1—C2—C7—C6	−177.44 (14)
C3—C4—C5—O4	176.13 (14)	C9—N—C8—C9^{i}	−55.1 (2)
O3—C4—C5—C6	178.85 (13)	C8—N—C9—C8^{i}	56.0 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O6^{ii}	0.82	1.92	2.664 (2)	151
O4—H4···O1^{iii}	0.82	2.08	2.703 (2)	133
O5—H5···O1^{iv}	0.82	1.98	2.650 (2)	138
O6—H6A···O2	0.85 (3)	1.85 (3)	2.691 (2)	167 (3)
O6—H6B···O3^{v}	0.83 (3)	2.31 (3)	2.829 (2)	121 (2)
O6—H6B···O4^{v}	0.83 (3)	2.23 (3)	3.054 (2)	169 (3)
N—H1B···O2	0.92 (2)	1.90 (2)	2.787 (2)	161 (2)
N—H1A···O6^{ii}	0.89 (2)	1.99 (2)	2.848 (2)	160.0 (17)

Symmetry codes: (ii) *x*+1/2, −*y*+1/2, *z*+1/2; (iii) *x*+1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+3/2, *y*+1/2, −*z*+3/2; (v) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

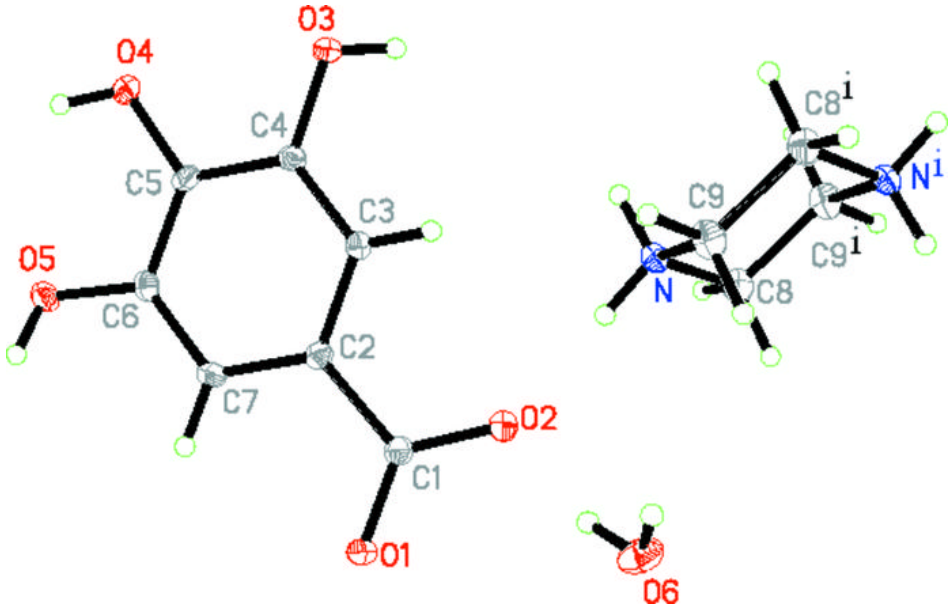
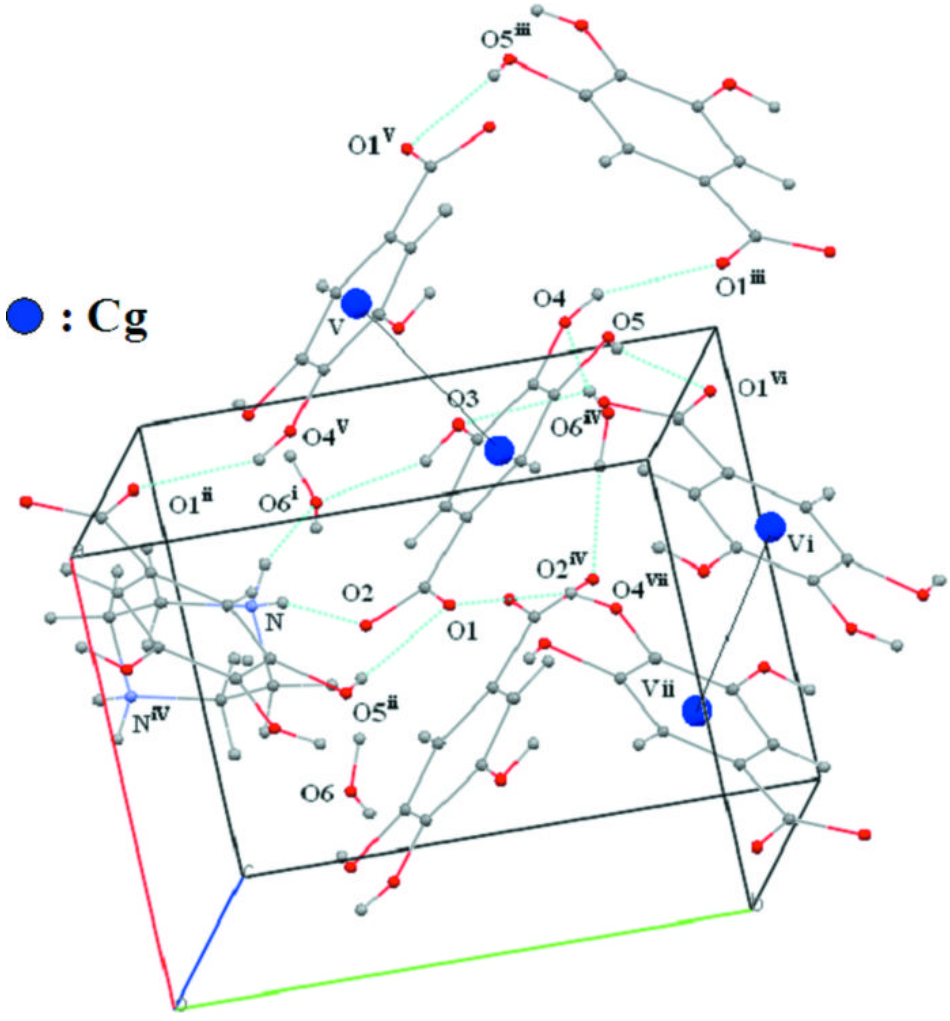


Fig. 2


: Cg
O5iii
O1V
V
O4
O5
O1iii
O1vi
O3
O6iv
O4V
O1ii
O6i
Vi
O2iv
O4vii
O2
N
O1
Vii
O5ii
NiV
O6