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Crystal structure and Hirshfeld surface analysis of 1-carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium chloride 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate: a new polymorph of L-dopa HCl and isotypic with its bromide counterpart

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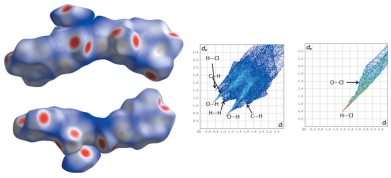
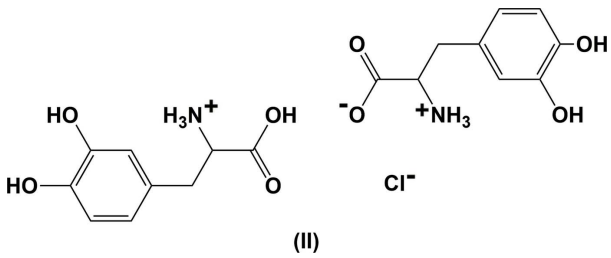
The title molecular salt, $C_9H_{12}NO_4^+\cdot Cl^-\cdot C_9H_{11}NO_4$, is isotypic with that of the bromide counterpart [Kathiravan *et al.* (2016). *Acta Cryst.* E**72**, 1544–1548]. The title salt is a second monoclinic polymorph of the L-dopa HCl structure reported earlier in the monoclinic space group $P2_1$ [Jandacek & Earle (1971). *Acta Cryst.* B**27**, 841–845; Mostad & Rømming (1974). *Acta Chemica Scand.* B**28**, 1161–1168]. In the title compound, monoclinic space group $I2$, one of the dopa molecules has a positive charge with a protonated α-amino group and the α-carboxylic acid group uncharged, while the second dopa molecule has a neutral charge, the α-amino group is protonated and the α-carboxylic acid is deprotonated. In the previously reported form, a single dopa molecule is observed in which the α-amino group is protonated and the α-carboxylic acid group is uncharged. The invariant and variations of various types of intermolecular interactions present in these two forms of dopa HCl structures are discussed with the aid of two-dimensional fingerprint plots.

1. Chemical context

The aromatic amino acid enzyme, tyrosine-3-hydroxylase, catalyses the conversion of the amino acid L-tyrosine to L-dopa (L-3,4-dihydroxyphenylalanine). After successful conversion, the L-dopa molecule acts as a precursor for neurotransmitter molecules, such as dopamine, norepinephrine and epinephrine. The L-dopa molecule is found to be an effective drug in the symptomatic treatment of Parkinson's disease (Chan *et al.*, 2012). Polymorphism is very common amongst pharamaceutically important molecules and is responsible for differences in many properties (Bernstein, 2002, 2011; Nangia, 2008; Guranda & Deeva, 2010). The first monoclinic form (I) [space group $P2_1$ and $z' = 1$] of L-dopa HCl was reported in the 1970s (Jandacek & Earle, 1971; Mostad & Rømming, 1974). Herein, we report on the crystal and molecular structure of a second monoclinic polymorph, form (II) (space group $I2$) of L-dopa HCl. The hydrogen-bonding patterns and the relative contributions of various intermolecular interactions present in forms (I) and (II) are compared.





(II)

2. Structural commentary

The asymmetric unit of the title compound, (II), is illustrated in Fig. 1. It consists of two dopa molecules, and a Cl^- anion located on a twofold rotation axis. As observed in the isotypic L-dopa HBr molecular salt (III) (Kathiravan *et al.*, 2016), one of the dopa molecules is in the zwitterionic form and the other in the cationic form. In the cationic dopa molecule, the α-amino group is protonated and carries a positive charge and the hydrogen atom (H4*O*) of the α-carboxylic acid group is located in a general position and was refined with 50% occupancy.

The crystal structures of L-dopa (Mostad *et al.*, 1971), its hydrochloride form (I) (Jandacek & Earle, 1971; Mostad & Rømming, 1974), the hydrobromide form (III) (Kathiravan *et al.*, 2016) and the dihydrate form (André & Duarte, 2014), have been reported. The dihydrate form of dopa crystallizes in the orthorhombic space group $P2_12_12_1$ with a single dopa molecule in its zwitterionic form. The free dopa molecule and its hydrochloride form (I) crystallized in the monoclinic space group $P2_1$. In the L-dopa structure, the dopa molecule is in the zwitterionic form, while in the latter the α-amino group is protonated and the α-carboxylic acid is neutral. As mentioned earlier (Kathiravan *et al.*, 2016), the deposited coordinates of the L-dopa HCl structure belong to the *R* configuration. Therefore, the L-dopa HCl structure was inverted and the inverted model used for superposition. As shown in Fig. 2, one of the dopa molecules of the title molecular salt (II) is superimposed with the inverted model of L-dopa HCl (I) and one of the dopa molecules of the isotypic Br compound (III). The r.m.s. deviation of the former pair is 0.105 Å while for the latter pair it is calculated to be 0.094 Å.

3. Supramolecular features

The crystal structure of the title molecular salt (II) displays a network of intermolecular N—H···Cl, N—H···O and O—H···O hydrogen bonds (Table 1), producing a three-dimensional framework (Fig. 3). It is of interest to note that the N—H···O and O—H···O hydrogen-bonding geometries in the title compound are slightly different when compared to its isotypic bromide counterpart (III) (Kathiravan *et al.*, 2016). A short intermolecular O—H···O hydrogen bond links the

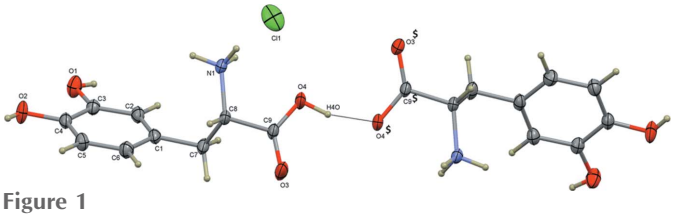


Figure 1
The molecular structure of the title molecular salt, (II), showing the atom labelling scheme [symmetry code: (\$) $-x+3, y, -z+1$]. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3^{i}	0.82	1.98	2.746 (2)	155
O2—H2*O*···O1^{ii}	0.82	2.33	2.999 (2)	140
O2—H2*O*···O2^{ii}	0.82	2.16	2.8730 (8)	146
O4—H4*O*···O4^{iii}	0.90 (3)	1.50 (3)	2.373 (2)	161 (8)
N1—H1*A*···Cl1^{iv}	0.91 (3)	2.35 (4)	3.249 (2)	167 (3)
N1—H1*B*···Cl1	0.89 (3)	2.31 (3)	3.178 (2)	166 (2)
N1—H1*C*···O3^{v}	0.90 (3)	1.93 (3)	2.7901 (19)	160 (3)

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

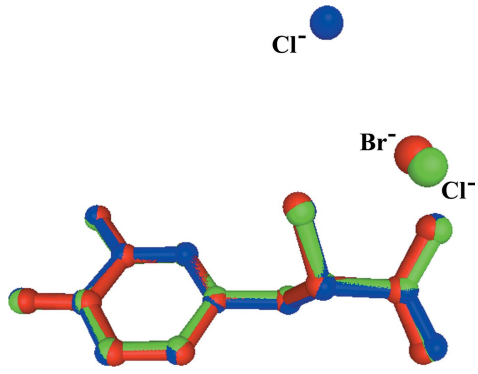


Figure 2
Structural superimposition of cationic dopa molecules in (II) (red), bromide counterpart (green) and form (I) L-dopa HCl (blue).

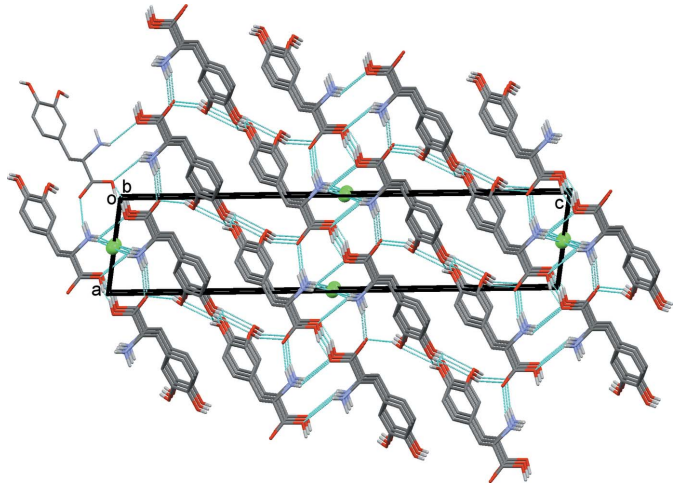


Figure 3
Crystal packing of the title molecular salt, (II), viewed along the *b* axis. The hydrogen bonds are shown as dashed lines (see Table 1), and C-bound H atoms have been omitted for clarity.

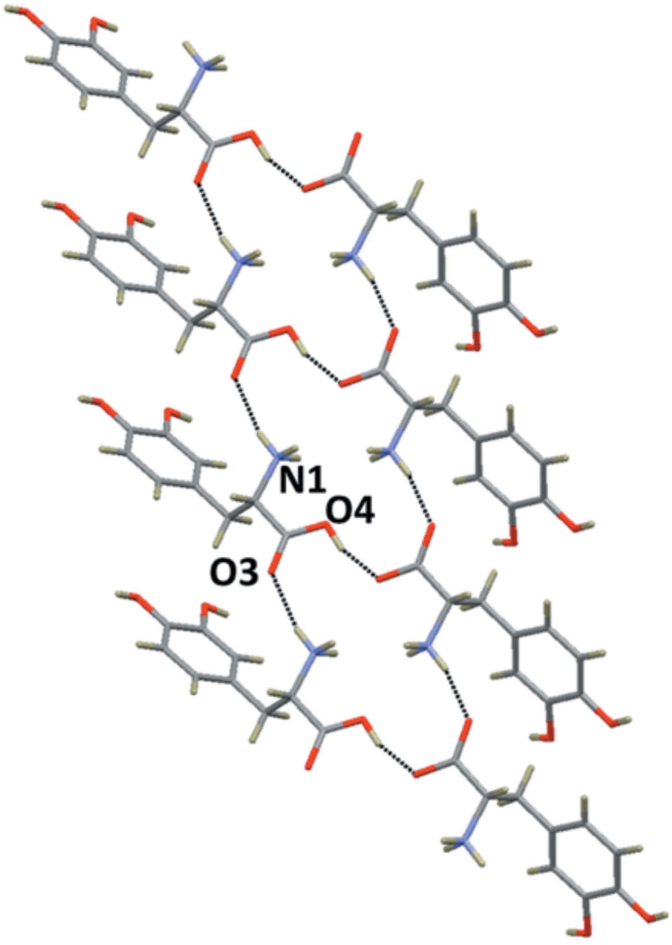


Figure 4
Part of the crystal structure of (II) showing the $R_4^4(18)$ motifs formed through N—H···O and O—H···O hydrogen bonds (see Table 1).

carboxylic acid group of a dopa molecule with the carboxylate group of an adjacent dopa molecule. This interaction produces dopa dimers that are arranged as ribbons propagating along the *b* axis (Fig. 3). As observed in the bromide counterpart (III), the protonated amino group acts as a threefold donor for three intermolecular hydrogen bonds, two of them with Cl^- anions and one with the carbonyl oxygen atom, O3, of the dopa acid group. One of the characteristic features observed

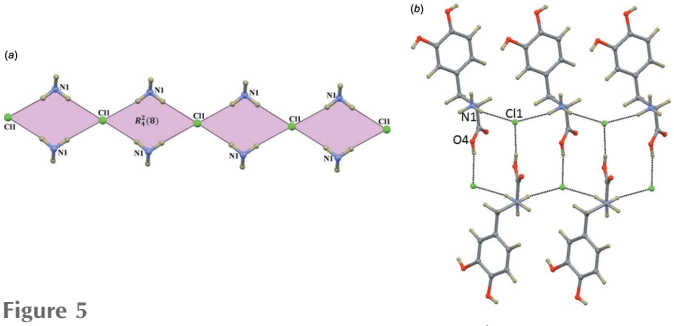


Figure 5
(*a*) Part of the crystal structure of (II) showing the $R_2^4(8)$ motif formed by intermolecular N—H···Cl hydrogen bonds (see Table 1), and (*b*) part of the crystal structure of form (I) dopa HCl showing the cyclic motif formed by N—H···Cl and O—H···Cl hydrogen bonds.

in many amino acid–carboxylic acid/metal complexes (Sharma *et al.*, 2006; Selvaraj *et al.*, 2007; Balakrishnan, Ramamurthi & Thamotharan *et al.*, 2013; Balakrishnan, Ramamurthi, Jeyakanthan *et al.*, 2013; Sathiskumar *et al.*, 2015*a*,*b*,*c*; Revathi *et al.*, 2015) is that the amino acid molecules aggregate in head-to-tail sequences of the type $\cdots NH_3^+—CHR—COO^-\cdots NH_3^+—CHR—COO^-\cdots$ in which α-amino and α-carboxylate groups are brought into periodic hydrogen-bonded proximity in a peptide-like arrangements. Similar arrangements (as layers) are observed in the title compound, in which α-amino (atom N1) and α-carboxylate (atom O3) groups interact *via* an N—H···O hydrogen bond. Adjacent layers are interconnected by strong O—H···O hydrogen bonds. The former N—H···O and the latter O—H···O interactions collectively form an $R_4^4(18)$ ring motif (Fig. 4). Similar interactions are presented in dopa and the HCl form (I).

As shown in Table 1, the amino group (*via* H1*A* and H1*B*) of the dopa molecule participates in N—H···Cl interactions with two different Cl^- anions. As observed in the bromide counterpart (III), these interactions interconnect the cations and anions into a chain of cyclic motifs that enclose $R_2^4(8)$ rings and runs parallel to the *b* axis (Fig. 5*a*). Forms (I) and (II) of the dopa HCl structures differ in the formation of cyclic motifs. In form (I), two N—H···Cl hydrogen bonds link the cations and anions into a chain. Adjacent chains are interconnected through O—H···Cl interactions (carboxylic acid···Cl). Collectively, these interactions generate cyclic motifs (Fig. 5*b*).

The side-chain hydroxy groups (O1—H1*O* and O2—H2*O*) of the dopa molecules are involved in O—H···O hydrogen-bonding interactions, the former with the carbonyl oxygen atom (O3) and the latter in a bifurcated mode with two different hydroxy (O1 and O2) oxygen atoms of adjacent dopa

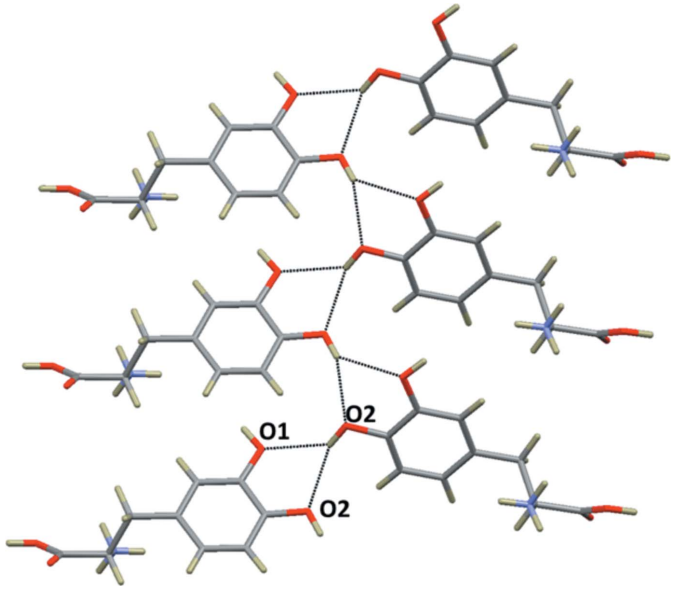


Figure 6
Adjacent dopa layers are interlinked by side chain–side chain interactions in (II) through intermolecular O—H···O hydrogen bonds (see Table 1).

layers (Fig. 6). These interactions are invariant in the dopa structures reported earlier.

4. Hirshfeld surface analysis

The Hirshfeld surfaces (HS) and the decomposed two-dimensional fingerprint plots have been generated, using the program *CrystalExplorer* (Wolff *et al.*, 2012), to investigate the similarities and differences in the crystal packing amongst polymorphs. The two different views of the HS diagram for the complete unit of dopa molecules along with the Cl^- anion and the two-dimensional fingerprint plots are shown in Fig. 7.

The analysis suggests that the O···H contacts contribute more (41.6%) to the crystal packing when compared to other contacts with respect to the dopa molecules in the title compound. The relative contributions of H···H, C···H and H···Cl contacts are 29, 18.6 and 6.2%, respectively, with respect to the complete unit of dopa molecule. These contacts are nearly identical in the case of the bromide counterpart. The H···Cl and O···Cl contacts contributions to the Hirshfeld surface area for the Cl ion are 71.9 and 13.7%, respectively. In the bromide counterpart (III), the corresponding contacts are found to be 64.1 (H···Br) and 10.2% (O···Br). It is clearly seen that these contacts are lower in the bromide counterpart (III) when compared to the title salt (II).

In form (I) of the dopa HCl structure, the relative contributions of O···H, H···H, C···H and H···Cl contacts are 40.5, 25.2, 17.1 and 14.1%, respectively, with respect to the cationic dopa molecule. It is worthy to note that O···H and H···H contacts are reduced by 1.1–3.8% when compared to form (II). The H···Cl contact is increased by 7.9% in (I) when compared to (II) of the dopa HCl structure. In (I) anionic Cl^-, the relative contribution of H···Cl contacts is found be 90.4%. This is approximately 18.5 and 26% higher when compared to (II) and its bromide counterpart (III). These contacts are used to discriminate between forms (I) and (II).

5. Synthesis and crystallization

L-dopa and HCl (1:1 molar ratio) were dissolved in double-distilled water and stirred well for 6 h. The mixture was filtered and the filtrate left to evaporate slowly. Colourless block-shaped crystals of the title molecular salt (II) were obtained after a growth period of 15 days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Since the title molecular salt (I) is isotypic with its bromide counterpart (III) (Kathiravan *et al.*, 2016), it was refined with the coordinates of the dopa molecule of the latter as a starting model. The Cl^- anion was located from a difference Fourier map. The amino and carboxylic acid H atoms were located from a difference Fourier map and freely refined. The OH groups of the dopa side chain and C-bound H atoms were treated as riding atoms and included in geometrically calculated positions: C—H = 0.93–0.98 and O—H = 0.82 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(O)$. The carboxylic acid O—H bond length was restrained to 0.90 (2) Å, using a DFIX option.

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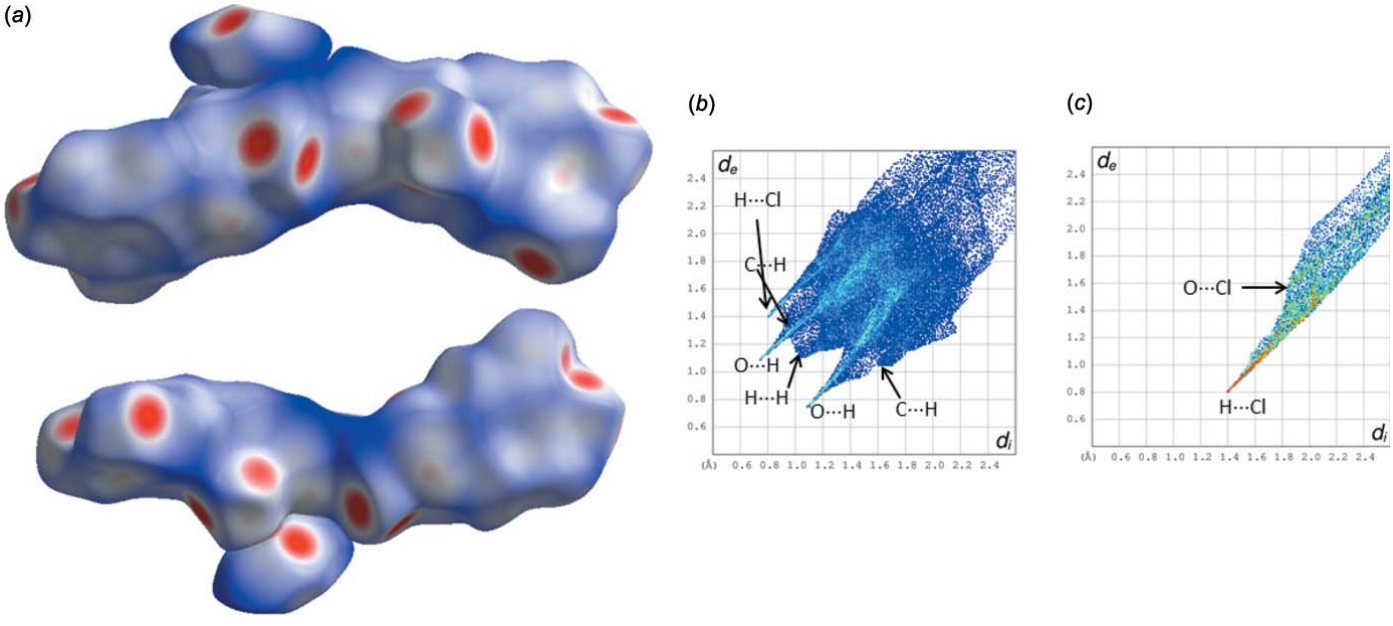

Figure 7
(*a*) Two different views of Hirshfeld surfaces of dimeric dopa molecules along with a Cl^- anion, (*b*) two-dimensional fingerprint plots for complete unit of dopa and (*c*) anionic Cl^-. Various types of contacts are indicated.

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References

André, V. & Duarte, M. T. (2014). *J. Mol. Struct.* **1076**, 238–243.
Balakrishnan, T., Ramamurthi, K., Jeyakanthan, J. & Thamotharan, S. (2013). *Acta Cryst.* E**69**, m60–m61.
Balakrishnan, T., Ramamurthi, K. & Thamotharan, S. (2013). *Acta Cryst.* E**69**, o57.
Bernstein, J. (2002). *Polymorphism in Molecular Crystals*. Oxford University Press.
Bernstein, J. (2011). *Cryst. Growth Des.* **11**, 632–650.
Bruker (2004). *APEX2*, *SAINT* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chan, S. W., Dunlop, R. A., Rowe, A., Double, K. L. & Rodgers, K. J. (2012). *Exp. Neurol.* **238**, 29–37.
Guranda, D. T. & Gil'deeva, G. N. (2010). *Pharm. Chem. J.* **44**, 254–260.
Jandacek, R. J. & Earle, K. M. (1971). *Acta Cryst.* B**27**, 841–845.
Kathiravan, P., Balakrishnan, T., Venkatesan, P., Ramamurthi, K., Percino, M. J. & Thamotharan, S. (2016). *Acta Cryst.* E**72**, 1544–1548.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mostad, A., Otternsen, T. & Rømming, C. (1971). *Acta Chem. Scand.* **25**, 3549–3560.
Mostad, A. & Rømming, C. (1974). *Acta Chem. Scand.* B**28**, 1161–1168.
Nangia, A. (2008). *Acc. Chem. Res.* **41**, 595–604.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Revathi, P., Balakrishnan, T., Ramamurthi, K. & Thamotharan, S. (2015). *Acta Cryst.* E**71**, 875–878.
Sathiskumar, S., Balakrishnan, T., Ramamurthi, K. & Thamotharan, S. (2015*a*). *Acta Cryst.* E**71**, 217–219.
Sathiskumar, S., Balakrishnan, T., Ramamurthi, K. & Thamotharan, S. (2015*b*). *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **138**, 187–194.
Sathiskumar, S., Balakrishnan, T., Ramamurthi, K. & Thamotharan, S. (2015*c*). *Acta Cryst.* E**71**, 1199–1202.
Selvaraj, M., Thamotharan, S., Roy, S. & Vijayan, M. (2007). *Acta Cryst.* B**63**, 459–468.
Sharma, A., Thamotharan, S., Roy, S. & Vijayan, M. (2006). *Acta Cryst.* C**62**, o148–o152.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}NO_4^+\cdot Cl^-\cdot C_9H_{11}NO_4$
M_r	430.83
Crystal system, space group	Monoclinic, *I*2
Temperature (K)	293
a, *b*, *c* (Å)	6.1768 (3), 5.4349 (3), 28.7651 (16)
β (°)	98.140 (4)
V (Å^3)	955.92 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.30 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.927, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14303, 2982, 2623
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.777
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.094, 1.05
No. of reflections	2982
No. of parameters	151
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.57, −0.21
Absolute structure	Flack *x* determined using 1021 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.033 (17)

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *Mercury* (Macrae *et al.*, 2006), *SHELXL2014/7* (Sheldrick, 2015) and *publCIF* (Westrip, 2010). Structure solution – isomorphous replacement.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. The University of Western Australia.

supporting information

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Crystal structure and Hirshfeld surface analysis of 1-carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium chloride 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate: a new polymorph of L-dopa HCl and isotypic with its bromide counterpart

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Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*/*SAINT* (Bruker, 2004); data reduction: *SAINT*/*XPREP* (Bruker, 2004); program(s) used to solve structure: structure solution – isomorphous replacement; program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2014/7* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

1-Carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium chloride 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate

Crystal data

$C_9H_{12}NO_4^+\cdot Cl^-\cdot C_9H_{11}NO_4$
M_r = 430.83
Monoclinic, *I*2
a = 6.1768 (3) Å
b = 5.4349 (3) Å
c = 28.7651 (16) Å
β = 98.140 (4)°
V = 955.92 (9) Å^3
Z = 2
F(000) = 452
D_x = 1.497 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7161 reflections
θ = 3.8–31.1°
μ = 0.25 mm^{-1}
T = 293 K
Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and *φ* scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.927, T_{max} = 0.959
14303 measured reflections
2982 independent reflections
2623 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 33.5°, θ_{min} = 2.9°
h = −8→9
k = −7→7
l = −39→40

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.094
S = 1.05
2982 reflections
151 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.236P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

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

Refinement. Refined as a two-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.3951 (2)	1.2691 (3)	0.33134 (6)	0.0290 (3)	
H1O	0.4509	1.3678	0.3510	0.044*	
O2	0.3026 (2)	0.9556 (3)	0.26334 (5)	0.0299 (3)	
H2O	0.2767	0.8411	0.2448	0.045*	
O3	1.4771 (2)	0.5509 (3)	0.41112 (5)	0.0329 (4)	
O4	1.32315 (19)	0.6323 (4)	0.47766 (4)	0.0276 (3)	
H4O	1.467 (5)	0.623 (16)	0.489 (3)	0.07 (2)*	0.5
N1	0.9230 (2)	0.6219 (4)	0.44032 (5)	0.0192 (3)	
H1A	0.937 (4)	0.751 (7)	0.4608 (11)	0.038 (8)*	
H1B	0.933 (3)	0.498 (5)	0.4608 (8)	0.013 (5)*	
H1C	0.784 (5)	0.629 (7)	0.4261 (10)	0.043 (7)*	
C1	0.8763 (3)	0.8689 (4)	0.34670 (6)	0.0203 (4)	
C2	0.7324 (3)	1.0590 (4)	0.35439 (7)	0.0216 (4)	
H2	0.7691	1.1672	0.3793	0.026*	
C3	0.5418 (3)	1.0860 (3)	0.32596 (6)	0.0202 (4)	
C4	0.4932 (3)	0.9175 (4)	0.29009 (6)	0.0207 (4)	
C5	0.6340 (3)	0.7289 (4)	0.28237 (7)	0.0237 (4)	
H5	0.5961	0.6194	0.2577	0.028*	
C6	0.8254 (3)	0.7042 (4)	0.31046 (7)	0.0238 (4)	
H6	0.9217	0.5784	0.3056	0.029*	
C7	1.0881 (3)	0.8448 (4)	0.37635 (7)	0.0231 (4)	
H7A	1.1137	0.9888	0.3963	0.028*	
H7B	1.2030	0.8373	0.3566	0.028*	
C8	1.0974 (2)	0.6136 (4)	0.40704 (6)	0.0170 (3)	
H8	1.0707	0.4692	0.3866	0.020*	
C9	1.3196 (3)	0.5949 (4)	0.43384 (6)	0.0193 (4)	
Cl1	1.0000	0.12970 (14)	0.5000	0.0428 (2)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0242 (7)	0.0254 (7)	0.0347 (8)	0.0052 (6)	−0.0053 (6)	−0.0063 (6)
O2	0.0210 (6)	0.0325 (8)	0.0314 (8)	0.0000 (6)	−0.0127 (5)	−0.0043 (6)
O3	0.0148 (5)	0.0560 (11)	0.0263 (7)	0.0060 (6)	−0.0025 (5)	−0.0092 (7)
O4	0.0137 (5)	0.0486 (9)	0.0186 (6)	0.0019 (7)	−0.0049 (4)	−0.0034 (7)

N1	0.0122 (6)	0.0258 (8)	0.0185 (7)	−0.0008 (6)	−0.0015 (5)	0.0018 (8)
C1	0.0176 (7)	0.0246 (9)	0.0175 (8)	−0.0016 (7)	−0.0022 (6)	0.0054 (7)
C2	0.0201 (7)	0.0237 (9)	0.0192 (8)	−0.0031 (7)	−0.0028 (6)	−0.0007 (7)
C3	0.0180 (7)	0.0205 (10)	0.0210 (8)	−0.0009 (7)	−0.0007 (6)	0.0025 (7)
C4	0.0178 (7)	0.0240 (9)	0.0188 (8)	−0.0028 (7)	−0.0029 (6)	0.0025 (7)
C5	0.0240 (9)	0.0258 (10)	0.0197 (9)	−0.0012 (8)	−0.0021 (7)	−0.0029 (7)
C6	0.0216 (8)	0.0265 (10)	0.0224 (9)	0.0041 (7)	0.0003 (7)	0.0007 (7)
C7	0.0151 (7)	0.0291 (10)	0.0233 (9)	−0.0042 (7)	−0.0038 (6)	0.0065 (8)
C8	0.0122 (6)	0.0215 (8)	0.0161 (7)	−0.0002 (7)	−0.0022 (5)	−0.0005 (7)
C9	0.0130 (6)	0.0237 (10)	0.0197 (8)	0.0003 (7)	−0.0033 (5)	−0.0012 (7)
Cl1	0.0677 (5)	0.0189 (3)	0.0390 (4)	0.000	−0.0016 (4)	0.000

Geometric parameters (Å, º)

O1—C3	1.369 (2)	C1—C7	1.463 (2)
O1—H1O	0.8200	C2—C3	1.343 (2)
O2—C4	1.329 (2)	C2—H2	0.9300
O2—H2O	0.8200	C3—C4	1.380 (3)
O3—C9	1.269 (2)	C4—C5	1.382 (3)
O4—C9	1.274 (2)	C5—C6	1.341 (3)
O4—H4O	0.90 (3)	C5—H5	0.9300
N1—C8	1.540 (2)	C6—H6	0.9300
N1—H1A	0.91 (3)	C7—C8	1.532 (3)
N1—H1B	0.89 (3)	C7—H7A	0.9700
N1—H1C	0.90 (3)	C7—H7B	0.9700
C1—C6	1.376 (3)	C8—C9	1.479 (2)
C1—C2	1.401 (3)	C8—H8	0.9800
C3—O1—H1O	109.5	C6—C5—C4	119.90 (18)
C4—O2—H2O	109.5	C6—C5—H5	120.0
C9—O4—H4O	103 (5)	C4—C5—H5	120.0
C8—N1—H1A	114.6 (18)	C5—C6—C1	118.60 (18)
C8—N1—H1B	113.7 (14)	C5—C6—H6	120.7
H1A—N1—H1B	99 (2)	C1—C6—H6	120.7
C8—N1—H1C	115.1 (18)	C1—C7—C8	111.52 (15)
H1A—N1—H1C	105 (3)	C1—C7—H7A	109.3
H1B—N1—H1C	108 (3)	C8—C7—H7A	109.3
C6—C1—C2	121.15 (15)	C1—C7—H7B	109.3
C6—C1—C7	118.24 (18)	C8—C7—H7B	109.3
C2—C1—C7	120.58 (17)	H7A—C7—H7B	108.0
C3—C2—C1	120.37 (17)	C9—C8—C7	108.25 (15)
C3—C2—H2	119.8	C9—C8—N1	110.92 (13)
C1—C2—H2	119.8	C7—C8—N1	111.19 (16)
C2—C3—O1	123.21 (17)	C9—C8—H8	108.8
C2—C3—C4	117.50 (17)	C7—C8—H8	108.8
O1—C3—C4	119.29 (15)	N1—C8—H8	108.8
O2—C4—C3	114.24 (17)	O3—C9—O4	129.22 (14)
O2—C4—C5	123.27 (17)	O3—C9—C8	117.83 (15)

C3—C4—C5	122.47 (16)	O4—C9—C8	112.93 (14)
C6—C1—C2—C3	−0.8 (3)	C2—C1—C6—C5	0.0 (3)
C7—C1—C2—C3	177.45 (18)	C7—C1—C6—C5	−178.29 (19)
C1—C2—C3—O1	−179.42 (18)	C6—C1—C7—C8	−69.7 (2)
C1—C2—C3—C4	1.3 (3)	C2—C1—C7—C8	112.0 (2)
C2—C3—C4—O2	−179.88 (17)	C1—C7—C8—C9	176.83 (16)
O1—C3—C4—O2	0.8 (3)	C1—C7—C8—N1	−61.1 (2)
C2—C3—C4—C5	−1.1 (3)	C7—C8—C9—O3	−67.7 (2)
O1—C3—C4—C5	179.57 (18)	N1—C8—C9—O3	170.10 (19)
O2—C4—C5—C6	179.00 (19)	C7—C8—C9—O4	110.8 (2)
C3—C4—C5—C6	0.4 (3)	N1—C8—C9—O4	−11.4 (3)
C4—C5—C6—C1	0.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3^{i}	0.82	1.98	2.746 (2)	155
O2—H2*O*···O1^{ii}	0.82	2.33	2.999 (2)	140
O2—H2*O*···O2^{ii}	0.82	2.16	2.8730 (8)	146
O4—H4*O*···O4^{iii}	0.90 (3)	1.50 (3)	2.373 (2)	161 (8)
N1—H1*A*···Cl1^{iv}	0.91 (3)	2.35 (4)	3.249 (2)	167 (3)
N1—H1*B*···Cl1	0.89 (3)	2.31 (3)	3.178 (2)	166 (2)
N1—H1*C*···O3^{v}	0.90 (3)	1.93 (3)	2.7901 (19)	160 (3)

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