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Poly[(μ_6-6-oxidopyridinium-2-carboxylato)caesium]

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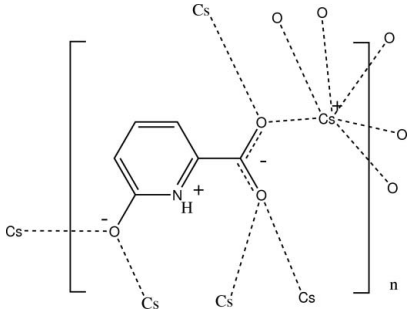
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.028; wR factor = 0.072; data-to-parameter ratio = 17.5.

The asymmetric unit of the polymeric title salt, $[Cs(C_6H_4NO_3)]_n$, comprises a Cs^+ cation and a 6-oxidopyridinium-2-carboxylate anion. The Cs^+ cation is six-coordinated by O atoms derived from two oxido and four carboxylate O atoms; each O atom in the anion bridges two Cs^+ cations. In the crystal, intermolecular N—H···O hydrogen bonding is present and contributes to the stability of the three-dimensional network generated by the bridging O atoms.

Related literature

For general background to pyridine carboxylic complexes, see: Kang (2011); Lee & Kang (2010); Hong *et al.* (2008). For the Cs—O bond lengths in caesium aryloxide complexes, see: Ungaro *et al.* (1994); Clark *et al.* (1998); Weinert *et al.* (2003).



Experimental

Crystal data

$[Cs(C_6H_4NO_3)]$
M_r = 271.01
Monoclinic, $P2_1/c$
a = 8.1746 (3) Å
b = 7.5513 (2) Å
c = 12.3843 (4) Å
β = 91.889 (1)°
V = 764.05 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.8 mm^{-1}
T = 296 K
0.10 × 0.07 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.654, T_{max} = 0.745
6897 measured reflections
1822 independent reflections
1592 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.072
S = 1.00
1822 reflections
104 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cs1—O9^{i}	2.938 (2)	Cs1—O10^{iii}	3.105 (3)
Cs1—O10^{ii}	2.991 (3)	Cs1—O11^{iv}	3.147 (2)
Cs1—O9	3.070 (3)	Cs1—O11^{v}	3.317 (2)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O11^{vi}	0.78 (3)	2.15 (3)	2.915 (4)	168 (3)

Symmetry code: (vi) $-x, -y+1, -z+1$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2010)'; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2776).

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Poly[(μ_6-6-oxidopyridinium-2-carboxylato)caesium]

Sung Kwon Kang and Yong Suk Shim

S1. Comment

During studies of lanthanide complexes of picolinic acid and their derivatives due to their interesting photoluminescent properties (Kang, 2011; Lee & Kang, 2010; Hong *et al.*, 2008), the title compound was obtained as a side-product.

The asymmetric unit of the title compound, $[Cs(C_6H_4NO_3)]_n$, comprises a Cs^+ cation and a carboxylatooxidopyridinium anion. The Cs^+ cation is coordinated to the two oxide O atoms and four carboxylate-O atoms (Fig. 1). The Cs—O bond distances lie within the range 2.938 (2) - 3.317 (2) Å (Table 1). The observed Cs—O distances are a little longer than those observed in caesium picrate complexes and caesium phenoxide complexes (Ungaro *et al.*, 1994: Clark *et al.*, 1998; Weinert *et al.*, 2003). The dihedral angle between the pyridine ring and the carboxylate group is 6.95 (19) °. In the crystal structure, the Cs atoms are linked by O atoms of the anionic ligands to form a three-dimensional network (Fig. 2) with additional stability provided by intermolecular N—H···O hydrogen bonding (Table 2).

S2. Experimental

Europium trichloride solution was prepared by dissolving $EuCl_3$ $6H_2O$ (0.37 g, 1.0 mmol; Aldrich) in absolute ethanol (20 ml) at room temperature with stirring. The ligand solution was prepared by dissolving 6-hydroxypicolinic acid (0.56 g, 4.0 mmol; Aldrich) in absolute ethanol (30 ml) at room temperature. The pH of the ligand solution was adjusted to about 6 with 2 N CsOH solution. The Eu solution was added drop wise and slowly to the ligand solution. The reaction mixture was stirred for 2 h at room temperature. Colourless crystals of (I) were obtained at room temperature over a period of a few weeks. The complex was recrystallized from distilled water.

S3. Refinement

The N—H atom was located in a difference Fourier map and refined freely. The remaining H atoms were positioned geometrically and refined using a riding model with C—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq} (C). The maximum and minimum residual electron density peaks of 1.19 and -1.14 e Å^{-3}, respectively, were located 0.83 Å and 0.71 Å from the Cs1 atom, respectively.

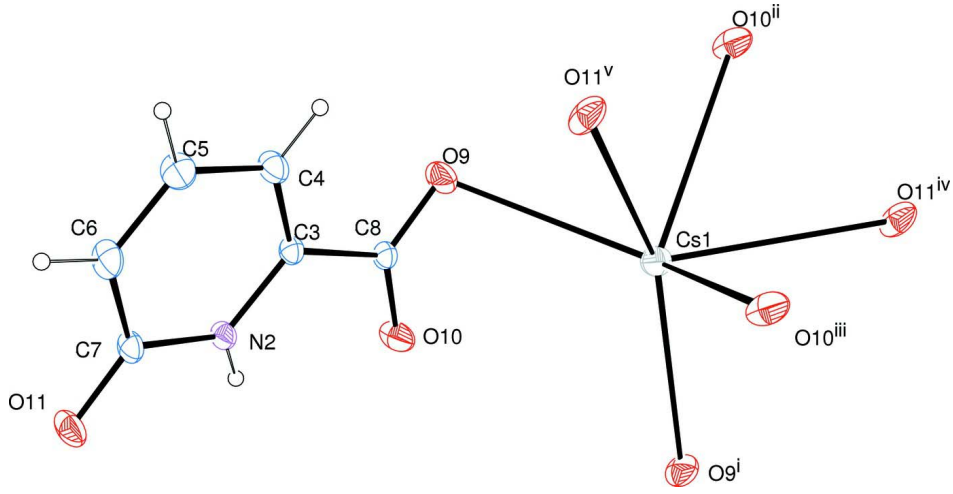

Figure 1

Molecular structure of (*I*), showing the atom-numbering scheme and 20% probability ellipsoids. [Symmetry code: (i) -*x* + 1, *y* + 1/2, -*z* + 1/2; (ii) -*x* + 1, *y* - 1/2, -*z* + 1/2; (iii) *x*, -*y* + 1/2, *z* - 1/2; (iv) *x* + 1, -*y* + 1/2, *z* - 1/2; (v) -*x*, *y* - 1/2, -*z* + 1/2].

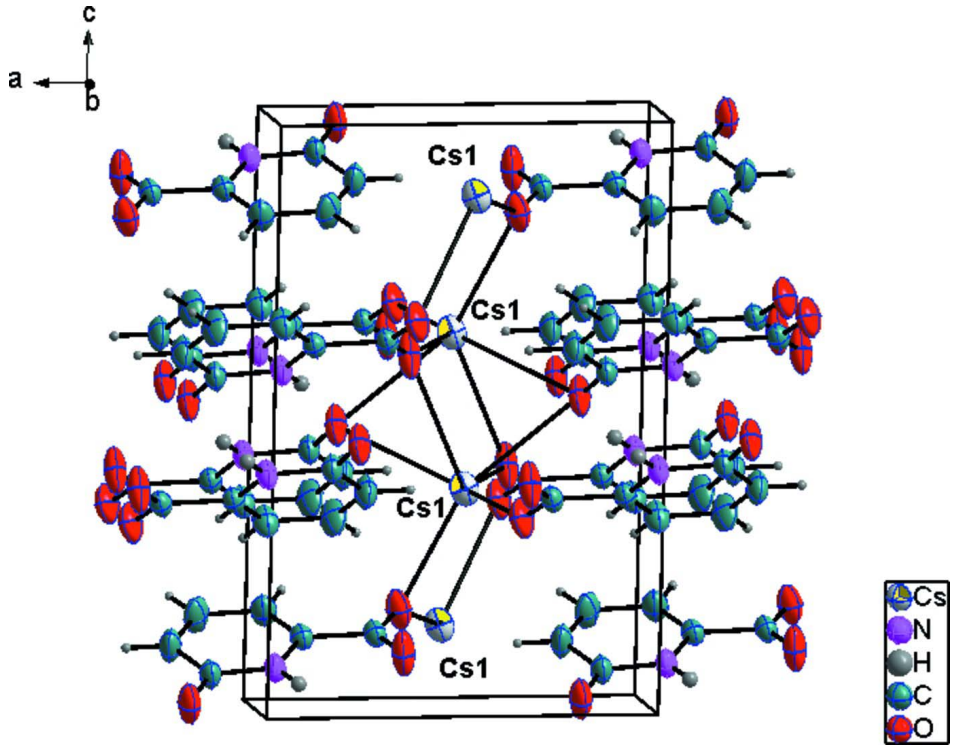

Figure 2

The three-dimensional framework of (I).

Poly[(μ_6-6-oxidopyridinium-2-carboxylato)caesium]

Crystal data

[$Cs(C_6H_4NO_3)$]
M_r = 271.01
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.1746 (3) Å
b = 7.5513 (2) Å

c = 12.3843 (4) Å
β = 91.889 (1)°
V = 764.05 (4) Å^3
Z = 4
F(000) = 504
D_x = 2.356 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 3429 reflections
θ = 2.5–28.3°
μ = 4.8 mm^{-1}
T = 296 K
Block, colourless
0.1 × 0.07 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.654, T_{max} = 0.745
6897 measured reflections

1822 independent reflections
1592 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 28.3°, θ_{min} = 2.5°
h = −3→10
k = −10→7
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.072
S = 1.00
1822 reflections
104 parameters
0 restraints

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

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.

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

	x	y	z	U_{iso}*/U_{eq}
Cs1	0.51201 (2)	0.14792 (3)	0.127051 (18)	0.04196 (11)
N2	0.0320 (3)	0.2743 (4)	0.4216 (2)	0.0304 (5)
H2	0.088 (4)	0.348 (4)	0.446 (3)	0.028 (9)*
C3	0.1062 (3)	0.1326 (4)	0.3746 (3)	0.0291 (6)
C4	0.0159 (4)	−0.0019 (5)	0.3335 (3)	0.0402 (8)
H4	0.0655	−0.0992	0.3023	0.048*
C5	−0.1567 (4)	0.0085 (5)	0.3391 (3)	0.0474 (9)
H5	−0.221	−0.0826	0.3102	0.057*
C6	−0.2296 (4)	0.1484 (5)	0.3857 (3)	0.0444 (9)
H6	−0.343	0.152	0.3888	0.053*
C7	−0.1347 (3)	0.2903 (5)	0.4302 (3)	0.0334 (7)
C8	0.2926 (3)	0.1403 (4)	0.3700 (3)	0.0298 (6)
O9	0.3603 (3)	0.0066 (3)	0.3335 (2)	0.0487 (6)
O10	0.3588 (2)	0.2803 (4)	0.3984 (2)	0.0536 (7)
O11	−0.1942 (2)	0.4235 (3)	0.4750 (2)	0.0498 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.03869 (13)	0.03507 (16)	0.05252 (19)	−0.00018 (7)	0.00759 (9)	−0.00010 (9)
N2	0.0203 (10)	0.0308 (14)	0.0402 (16)	−0.0019 (10)	0.0026 (9)	−0.0062 (12)
C3	0.0234 (12)	0.0316 (16)	0.0324 (17)	0.0012 (10)	0.0034 (10)	0.0006 (12)
C4	0.0313 (14)	0.0409 (19)	0.049 (2)	−0.0026 (12)	0.0044 (12)	−0.0145 (16)
C5	0.0316 (15)	0.049 (2)	0.061 (3)	−0.0137 (14)	−0.0003 (14)	−0.0201 (18)
C6	0.0216 (13)	0.056 (2)	0.055 (2)	−0.0055 (12)	0.0003 (13)	−0.0125 (17)
C7	0.0209 (11)	0.0393 (17)	0.0401 (19)	0.0013 (11)	0.0030 (10)	−0.0036 (15)
C8	0.0226 (12)	0.0325 (17)	0.0346 (18)	0.0020 (10)	0.0045 (10)	0.0017 (12)
O9	0.0321 (11)	0.0421 (14)	0.0725 (19)	0.0074 (10)	0.0112 (10)	−0.0090 (13)
O10	0.0235 (9)	0.0383 (14)	0.099 (2)	−0.0025 (9)	0.0070 (11)	−0.0189 (15)
O11	0.0244 (10)	0.0483 (15)	0.0772 (19)	0.0022 (10)	0.0070 (10)	−0.0231 (14)

Geometric parameters (Å, º)

Cs1—O9^{i}	2.938 (2)	C5—C6	1.352 (5)
Cs1—O10^{ii}	2.991 (3)	C5—H5	0.93
Cs1—O9	3.070 (3)	C6—C7	1.423 (4)
Cs1—O10^{iii}	3.105 (3)	C6—H6	0.93
Cs1—O11^{iv}	3.147 (2)	C7—O11	1.254 (4)
Cs1—O11^{v}	3.317 (2)	C8—O10	1.234 (4)
N2—C3	1.370 (4)	C8—O9	1.244 (4)
N2—C7	1.376 (3)	O9—Cs1^{ii}	2.938 (2)
N2—H2	0.78 (3)	O10—Cs1^{i}	2.991 (3)
C3—C4	1.345 (4)	O10—Cs1^{vi}	3.105 (3)
C3—C8	1.527 (4)	O11—Cs1^{vii}	3.147 (2)
C4—C5	1.418 (4)	O11—Cs1^{viii}	3.317 (2)
C4—H4	0.93		
O9^{i}—Cs1—O10^{ii}	138.47 (6)	C3—N2—C7	123.8 (3)
O9^{i}—Cs1—O9	109.46 (5)	C3—N2—H2	118 (3)
O10^{ii}—Cs1—O9	85.35 (7)	C7—N2—H2	119 (3)
O9^{i}—Cs1—O10^{iii}	96.96 (7)	C4—C3—N2	120.3 (3)
O10^{ii}—Cs1—O10^{iii}	101.48 (6)	C4—C3—C8	123.4 (3)
O9—Cs1—O10^{iii}	131.16 (6)	N2—C3—C8	116.3 (2)
O9^{i}—Cs1—O11^{iv}	89.05 (7)	C3—C4—C5	118.3 (3)
O10^{ii}—Cs1—O11^{iv}	59.91 (6)	C3—C4—H4	120.8
O9—Cs1—O11^{iv}	140.90 (6)	C5—C4—H4	120.8
O10^{iii}—Cs1—O11^{iv}	77.13 (6)	C6—C5—C4	121.1 (3)
O9^{i}—Cs1—O11^{v}	143.52 (6)	C6—C5—H5	119.4
O10^{ii}—Cs1—O11^{v}	76.13 (6)	C4—C5—H5	119.4
O9—Cs1—O11^{v}	78.86 (6)	C5—C6—C7	120.8 (3)
O10^{iii}—Cs1—O11^{v}	56.95 (6)	C5—C6—H6	119.6
O11^{iv}—Cs1—O11^{v}	106.75 (4)	C7—C6—H6	119.6
O9^{i}—Cs1—O10	74.53 (6)	O11—C7—N2	120.3 (3)
O10^{ii}—Cs1—O10	118.05 (6)	O11—C7—C6	124.1 (3)

O9—Cs1—O10	36.14 (6)	N2—C7—C6	115.6 (3)
O10^{iii}—Cs1—O10	129.22 (5)	O10—C8—O9	127.1 (3)
O11^{iv}—Cs1—O10	149.72 (6)	O10—C8—C3	116.8 (3)
O11^{v}—Cs1—O10	101.34 (6)	O9—C8—C3	116.0 (3)
O9^{i}—Cs1—C7^{iv}	74.04 (7)	Cs1^{ii}—O9—Cs1	107.94 (7)
O10^{ii}—Cs1—C7^{iv}	76.81 (7)	Cs1^{i}—O10—Cs1^{vi}	78.52 (6)
O9—Cs1—C7^{iv}	153.81 (6)	Cs1^{i}—O10—Cs1	91.33 (7)
O10^{iii}—Cs1—C7^{iv}	72.02 (6)	Cs1^{vi}—O10—Cs1	136.48 (6)
O11^{iv}—Cs1—C7^{iv}	16.91 (7)	Cs1^{vii}—O11—Cs1^{viii}	73.25 (4)
O11^{v}—Cs1—C7^{iv}	114.40 (7)		

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $x, -y+1/2, z-1/2$; (iv) $x+1, -y+1/2, z-1/2$; (v) $-x, y-1/2, -z+1/2$; (vi) $x, -y+1/2, z+1/2$; (vii) $x-1, -y+1/2, z+1/2$; (viii) $-x, y+1/2, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O11^{ix}	0.78 (3)	2.15 (3)	2.915 (4)	168 (3)

Symmetry code: (ix) $-x, -y+1, -z+1$.