Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Caesium sodium bis(formate)

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Received 18 January 2006
Accepted 25 January 2006

The title compound, CsNa(CHO_2)$_2$, was obtained from the crystallization of caesium formate in a glass container. It has a complex structure, with sodium ions octahedrally coordinated and caesium ions irregularly eight-coordinated by the formate O atoms. One Cs cation and four formate C atoms have site symmetry m and one Na cation has site symmetry $\bar{1}$, resulting in the unusual situation of $Z = 12$ for an orthorhombic structure.

Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(O–C) = 0.004 Å
R factor = 0.034
wR factor = 0.090
Data-to-parameter ratio = 19.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

During a study of the crystal structure of caesium formate (Wilson *et al.*, 2006), it was found that, if the crystallization of caesium formate by diffusion is carried out in a glass container, the crystals formed are of a mixed caesium sodium salt, CsNa(C_2HO_2)$_2$, (I).

(I)

The sodium ions were identified from the crystal structure analysis. After initial location of the Cs atoms, the chemical identity of two medium height electron-density peaks was tested by refinement. Only the assignment of Na to the peaks both satisfied stoichiometric requirements and gave satisfactory displacement parameters (as well as providing much the best R value). It is inferred that their source is the glass vials used for crystallization, and it has been shown (Wilson *et al.*, 2006) that recrystallization from polythene vials gives unchanged caesium formate. Similar extraction of sodium cations by formate solutions has been reported by Robinet *et al.* (2004).

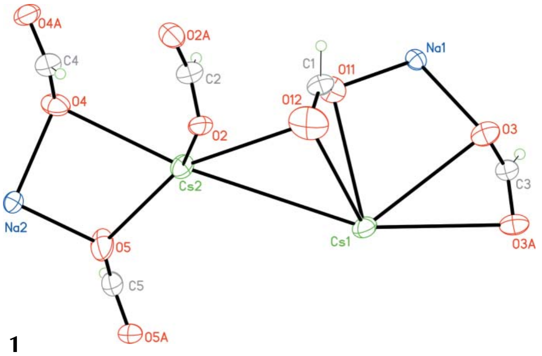

Figure 1
View of the asymmetric unit of (I) (with formate ions completed by symmetry), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Cs, H, Na and O atoms are green (large), green (small), blue and red, respectively. [Symmetry codes: $x, -\frac{1}{2} - y, z$ (for O2A and O4A); $x, \frac{1}{2} - y, z$ (for O3A and O5A)].

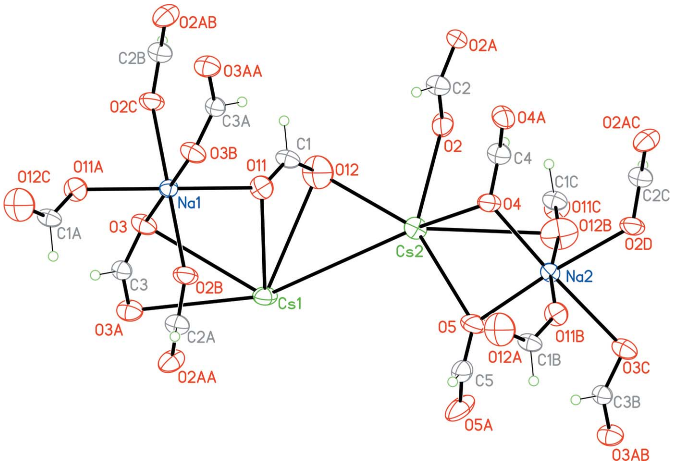

Figure 2
The structure with the Na ion coordination completed. Atom colouring as in Fig. 1. [Symmetry codes: $x, -\frac{1}{2} - y, z$ (O2A and O4A); $x, \frac{1}{2} - y, z$ (O3A, O5A, O11A, O12A and C1A); $2 - x, -y, 1 - z$ (C4A, O4B, O5B and C5A); $2 - x, \frac{1}{2} - y, 1 - z$ (O4AA and O5AA); $\frac{1}{2} + x, y, \frac{3}{2} - z$ (O11B, O12B and C1B)].

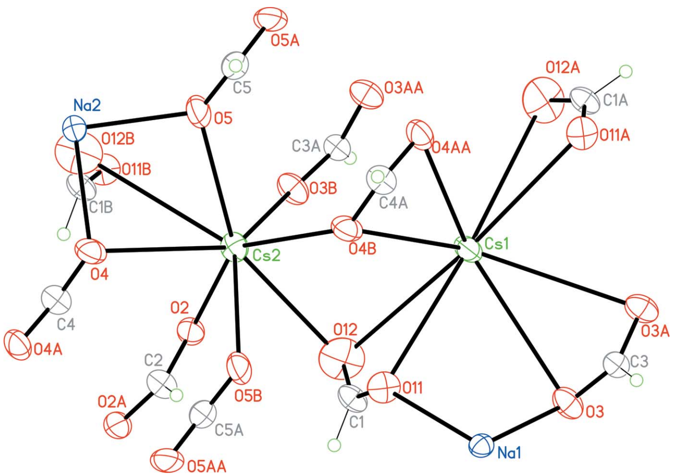

Figure 3
The structure with the Cs ion coordination completed. Atom colouring as in Fig. 1. [Symmetry codes: $x, -\frac{1}{2} - y, z$ (O2A and O4A); $x, \frac{1}{2} - y, z$ (O3A and O5A); $\frac{1}{2} + x, y, \frac{3}{2} - z$ (O11A, C1, O12C, O12B, C1C, O11C, O2D and C2C); $\frac{1}{2} + x, -1 + y, \frac{3}{2} - z$ (O2C and C2B); $\frac{3}{2} - x, -y, -\frac{1}{2} - z$ (O2B and C2A); $1 - x, -y, 1 - z$ (O3B and C3A); $2 - x, -y, 1 - z$ (O11B, C1B and O12A); $\frac{3}{2} - x, -y, -\frac{1}{2} - z$ (O2AA); $-\frac{1}{2} + x, -\frac{1}{2} - y, \frac{3}{2} - z$ (O2AB); $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{3}{2} - z$ (O2AC); $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} - z$ (O3AB); $1 - x, -\frac{1}{2} + y, 1 - z$ (O3AA); $1 + x, y, z$ (O3C and C3B)].

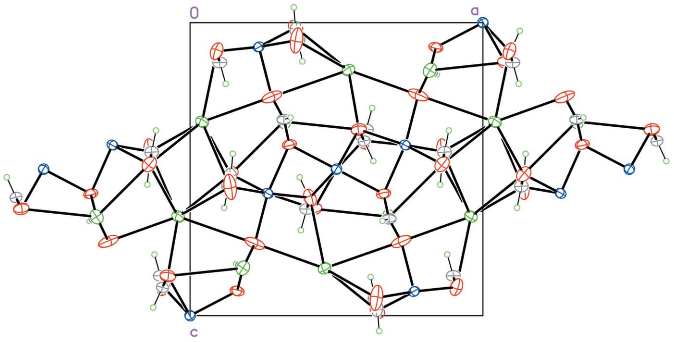

Figure 4
The packing, viewed down the b axis. Atom colouring as in Fig. 1.

In the structure of (I) (Fig. 1), both Na ions are octahedrally coordinated, with Na—O distances (Table 1) in the range 2.243 (4)–2.678 (3) Å (Fig. 2). The coordination of the Cs ions (Fig. 3) is best regarded as eight-coordinate, with Cs1 having square-antiprismatic geometry and Cs2 a less regular arrangement of ligand O atoms [Cs—O = 3.007 (3)–3.550 (4) Å], but with additional O atoms within 0.3 Å. The overall packing (Fig. 4) can be described as including chains of cations bridged by formate ions.

Experimental

AR standard caesium formate (Aldrich) was dissolved in a minimum volume of methanol in a glass vial. This (open) container was then placed inside a larger vial containing a small amount of 1-butanol and the whole system sealed immediately. Crystallization proceeded with occasional swirling of the suspension over a two-week period.

Crystal data

$CsNa(CHO_2)_2$
$M_r = 245.94$
Orthorhombic, *Pnma*
$a = 12.5812$ (3) Å
$b = 11.0509$ (3) Å
$c = 12.6024$ (3) Å
$V = 1752.16$ (8) Å^3
$Z = 12$
$D_x = 2.797$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 3$–25°
$\mu = 6.34$ mm^{-1}
$T = 180$ (2) K
Block, colourless
$0.20 \times 0.20 \times 0.15$ mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.202$, $T_{\max} = 0.387$
10798 measured reflections
2324 independent reflections

1867 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 29.1°$
$h = -15 \rightarrow 16$
$k = -15 \rightarrow 14$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.03$
2324 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.59$ e Å^{-3}
$\Delta\rho_{\min} = -1.59$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0039 (3)

Table 1
Selected bond lengths (Å).

Cs1—O11	3.193 (3)	Cs2—O12$^{\rm iv}$	3.516 (4)
Cs1—O12	3.294 (4)	Cs2—O2	3.550 (4)
Cs1—O4$^{\rm i}$	3.389 (3)	Na1—O11	2.298 (3)
Cs1—O3	3.441 (3)	Na1—O2$^{\rm ii}$	2.350 (3)
Cs1—O2$^{\rm ii}$	3.642 (4)	Na1—O3	2.553 (3)
Cs2—O4$^{\rm iii}$	3.007 (3)	Na2—O12$^{\rm iv}$	2.243 (4)
Cs2—O5	3.015 (3)	Na2—O11$^{\rm iii}$	2.313 (3)
Cs2—O3$^{\rm iv}$	3.027 (3)	Na2—O5	2.354 (4)
Cs2—O12	3.206 (4)	Na2—O4	2.416 (3)
Cs2—O4	3.386 (3)	Na2—O2$^{\rm iv}$	2.443 (3)
Cs2—O5$^{\rm iii}$	3.510 (5)	Na2—O3$^{\rm v}$	2.678 (3)

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

H atoms were placed in calculated positions and refined using a riding model [C—H = 0.95 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)]. The highest and lowest peaks on the difference map are all close to the Cs positions.

Acta Cryst. (2006). E**62**, m388–m390 Alcock *et al.* • $CsNa(CHO_2)_2$ **m389**

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

We thank Cabot Specialty Fluids for support of this work. EPSRC and Siemens plc generously supported the purchase of the *SMART* diffractometer.

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