

Polymeric (18-crown-6)bis(2-amido-pyridinecaesium) toluene solvate

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Key indicators

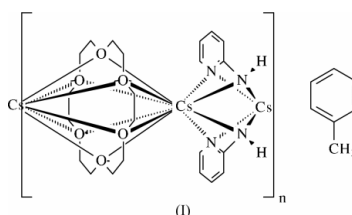
Single-crystal X-ray study
 $T = 160\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.016\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.028
 wR factor = 0.065
Data-to-parameter ratio = 19.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, *catena*-poly[[caesium(I)- μ -18-crown-6-caesium(I)-di- μ -2-amidopyridine] toluene], $[[\{\text{Cs}\{2\text{-N}(\text{H})\text{C}_5\text{-H}_4\text{N}\}]_2(\text{C}_{12}\text{H}_{24}\text{O}_6) \cdot (\text{C}_6\text{H}_5\text{CH}_3)]_\infty]$ or $[\text{Cs}_2(\text{C}_5\text{H}_5\text{N}_2)_2(\text{C}_{12}\text{H}_{24}\text{O}_6)] \cdot \text{C}_7\text{H}_8$, crystallizes as a toluene solvate. The polymeric structure is constructed from dimeric amido-bridged Cs_2N_2 four-membered rings with additional supporting coordination by bridging pyridyl N atoms. Each dimeric unit is linked to the next in the polymeric chain by bridging $\kappa^6:k^6$ 18-crown-6 ether molecules, in which each of the six O atoms bonds to both caesium ions; each caesium is ten-coordinate. The polymer has crystallographic mirror (C_s) symmetry, the mirror running through all the caesium ions, so that there is only one unique amidopyridine ligand and each crown ligand is bisected by the mirror. Consequently, the amide ligands are arranged *cis* with respect to each other, which is unusual.

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Comment

Alkali metal amides are important by virtue of their utility in proton abstraction reactions (Wakefield, 1988) and their effectiveness as ligand transfer reagents (Lappert *et al.*, 1980). They are also of major interest due to their structural diversity in solution and the solid state (Gregory *et al.*, 1991). We recently reported a series of alkali metal derivatives of 2-trimethylsilylamidopyridine (Liddle & Clegg, 2001*a,b*, 2002) with the macrocyclic polyethers 12-crown-4 and 15-crown-5, with which we probed, in a systematic manner, structural changes brought about by a change in the alkali metal cation or crown. In most cases, straightforward lithiation and, if required, metathesis reactions generated the target complexes. However, in three instances, we observed N—Si bond cleavage by the heavier alkali metal alkoxide reagent employed, and proton abstraction, to form primary pyridyl amide complexes that were either mononuclear or heterobinuclear in nature. We have subsequently investigated complexes with 18-crown-6, but have encountered difficulties in preparing crystals of suitable quality. However, we have successfully characterized the title compound, (I), in the solid state, and this reveals a fourth instance of N—Si bond cleavage during the metathesis reaction.



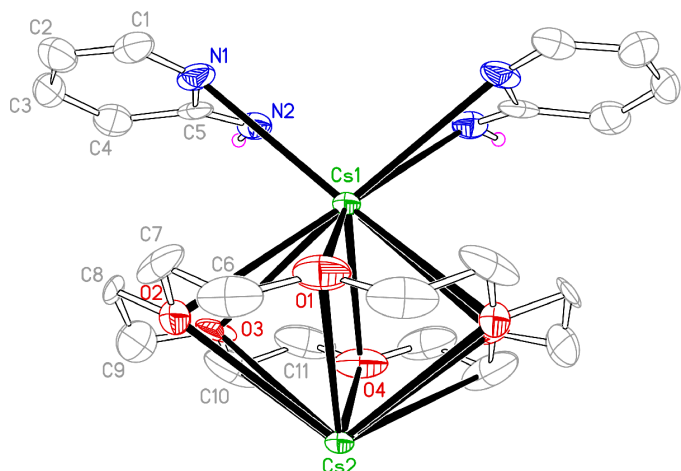


Figure 1

The asymmetric unit of (I), together with its mirror image, with atom labels and 30% probability ellipsoids. The toluene molecule and H atoms other than that on the amide group have been omitted for clarity.

Metathesis of $C_5H_4N-2-N(Li)SiMe_3$ with caesium 2-ethylhexoxide in the presence of one equivalent of 18-crown-6 generates, after crystallization, the title complex in which only half a molecule of 18-crown-6 is present for each caesium amide (Fig. 1). The structure contains Cs–amide dimers featuring Cs_2N_2 four-membered rings, which are a common structural motif in alkali metal amide chemistry, with additional coordination by bridging pyridyl N atoms. Each dimeric unit is linked to the next by bridging $\kappa^6:\kappa^6$ 18-crown-6 molecules to generate a chain polymer (Fig. 2). The amides are arranged *cis* with respect to each other as a consequence of lying on each side of a crystallographic mirror plane, which passes through all the caesium ions and bisects each crown ligand. A *trans* arrangement with a centrosymmetric M_2N_2 ring is by far the most common observation for this type of ring. A molecule of toluene per dimer unit crystallizes in the structure, but is unexceptional in all respects. The Cs–O bond lengths span the range 3.210 (10)–3.490 (10) Å; this compares well with the only other example in the Cambridge Structural Database (Allen, 2002) of a bridging $\kappa^6:\kappa^6$ 18-crown-6 molecule with caesium, where caesium is not bonded to another crown (Rabe *et al.*, 1999). The Cs–amide mean bond length of 3.209 (5) Å and the mean Cs–pyridyl bond length of 3.241 (9) Å are typical of such bonds.

Experimental

The title compound was prepared by a metathesis reaction between $C_5H_4N-2-N(Li)SiMe_3$ [obtained *in situ* from 2-trimethylsilylamino-pyridine (0.48 g, 2.89 mmol) and *n*-butyllithium (1.15 ml of a 2.5 M solution in hexanes, 2.89 mmol)] and caesium 2-ethylhexoxide (0.76 g, 2.89 mmol) in the presence of 18-crown-6 (0.76 g, 2.89 mmol) in THF solution, in an analogous manner to that described previously (Liddle & Clegg, 2001*a,b*, 2002); yield 0.89 g, 86%. Crystals were obtained by slow cooling from 373 to 298 K of a solution in toluene also containing hexamethylphosphoramide. NMR: δ_H ($[^2H]_8$ THF) 3.51 (24H, *s*, crown OCH_2), 4.13 (2H, *s*, *br*, N–H), 5.81 (2H, *t*, β -H), 6.45 (2H, *d*, β' -H), 7.28 (2H, *t*, γ -H) and 8.37 (2H, *d*, α -H). δ_C ($[^2H]_8$ THF) 70.55 (crown OCH_2), 109.62 (β -C), 125.69 (β' -C),

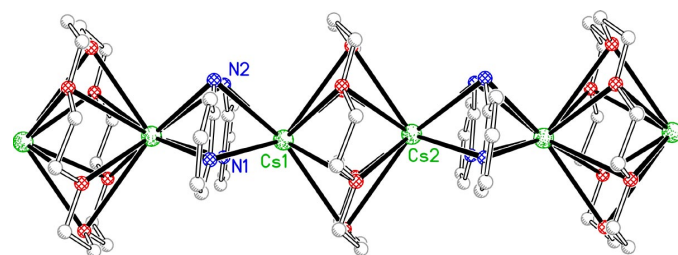


Figure 2

Part of the polymeric chain generated by the bridging crown and amidopyridine ligands.

136.36 (γ -C), 137.88 (α -C) and 149.05 (α' -C). δ_{Cs} ($[^2H]_8$ THF) 48.31. Accurate chemical microanalysis could not be obtained due to facile loss of toluene; results lie between those expected for the toluene solvate and those for the unsolvated compound.

Crystal data

$[Cs_2(C_5H_5N_2)_2(C_{12}H_{24}O_6)] \cdot C_7H_8$
 $M_r = 808.49$
 Monoclinic, *Cm*
 $a = 13.0109$ (10) Å
 $b = 17.3720$ (14) Å
 $c = 7.8427$ (6) Å
 $\beta = 107.979$ (2)°
 $V = 1686.1$ (2) Å³
 $Z = 2$

$D_x = 1.592$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5667 reflections
 $\theta = 2.4$ – 28.4 °
 $\mu = 2.21$ mm⁻¹
 $T = 160$ (2) K
 Needle, yellow
 1.30 × 0.22 × 0.12 mm

Data collection

Bruker SMART 1K CCD diffractometer
 Thin-slice ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{min} = 0.478$, $T_{max} = 0.768$
 7390 measured reflections

3879 independent reflections
 2911 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$
 $\theta_{max} = 28.5$ °
 $h = -17 \rightarrow 16$
 $k = -22 \rightarrow 23$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.065$
 $S = 0.94$
 3879 reflections
 201 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.038$
 $\Delta\rho_{max} = 0.81$ e Å⁻³
 $\Delta\rho_{min} = -0.53$ e Å⁻³
 Absolute structure: Flack (1983),
 1789 Friedel pairs
 Flack parameter = 0.46 (4)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--|------------|--------------------------|------------|
| Cs1–N1 | 3.235 (9) | Cs2–N1 ⁱ | 3.247 (9) |
| Cs1–N2 | 3.202 (5) | Cs2–N2 ⁱ | 3.216 (5) |
| Cs1–O1 | 3.243 (12) | Cs2–O1 | 3.487 (13) |
| Cs1–O2 | 3.488 (8) | Cs2–O2 | 3.272 (8) |
| Cs1–O3 | 3.315 (6) | Cs2–O3 | 3.423 (6) |
| Cs1–O4 | 3.490 (10) | Cs2–O4 | 3.210 (10) |
| N1–Cs1–N1 ⁱⁱ | 100.4 (3) | O1–Cs2–O2 | 50.80 (16) |
| N1–Cs1–N2 | 42.9 (2) | O2–Cs2–O3 | 48.29 (15) |
| N2–Cs1–N2 ⁱⁱ | 72.11 (17) | O3–Cs2–O4 | 47.51 (17) |
| O1–Cs1–O2 | 50.99 (17) | Cs1–N1–Cs2 ^{iv} | 75.75 (19) |
| O2–Cs1–O3 | 47.45 (14) | Cs1–N2–Cs2 ^{iv} | 76.64 (11) |
| O3–Cs1–O4 | 46.27 (17) | Cs1–O1–Cs2 | 70.0 (2) |
| N1 ⁱ –Cs2–N1 ⁱⁱⁱ | 99.9 (3) | Cs1–O2–Cs2 | 69.72 (16) |
| N1 ⁱ –Cs2–N2 ^j | 42.7 (2) | Cs1–O3–Cs2 | 70.05 (12) |
| N2 ⁱⁱⁱ –Cs2–N2 ^j | 71.75 (18) | Cs1–O4–Cs2 | 70.38 (19) |

Symmetry codes: (i) $x, y, 1 + z$; (ii) $x, 1 - y, z$; (iii) $x, 1 - y, 1 + z$; (iv) $x, y, z - 1$.

Crystals were air-sensitive and subject to degradation by loss of toluene, and were fragile, suffering damage on attempted cutting; therefore, a long needle was used uncut, subsequent correction being made simultaneously for absorption and the incomplete irradiation of the crystal (Sheldrick, 2002). In the presence of caesium atoms, the lighter atoms were located with lower precision. To aid refinement, restraints were applied for similarity of chemically similar bond lengths and to anisotropic displacement parameter components of bonded atoms. Relatively high displacement parameters for some atoms indicate possible disorder, but this was not resolved into separate atom sites. The methyl group of the toluene molecule was refined as disordered over two orientations, with equal occupancies. The amido H atom was located in a difference map and refined freely [$N-H = 1.11(5) \text{ \AA}$]. Other H atoms were placed geometrically and refined with a riding model, with $C-H = 0.95-0.99 \text{ \AA}$ and $U_{iso}(H) = 1.2$ or 1.5 times U_{eq} of the carrier atom. Refinement of the Flack (1983) parameter indicates that the sample is an inversion twin; the correct assignment of the uncommon space group Cm has been confirmed by use of the symmetry-checking procedures of *PLATON* (Spek, 2001).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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