Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1254$
$S = 1.124$
2205 reflections
200 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 10.629P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.613$ e Å^{-3}
$\Delta\rho_{\min} = -0.465$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00044 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.912 (2)	Cu—O2	1.999 (2)
Cu—N1	1.927 (3)	Cu—O3^{i}	2.458 (2)
Cu—N2	1.992 (2)		
O1—Cu—N1	92.42 (10)	N2—Cu—O2	91.21 (10)
O1—Cu—N2	91.98 (10)	O1—Cu—O3^{i}	115.78 (11)
N1—Cu—N2	172.24 (11)	N1—Cu—O3^{i}	96.75 (10)
O1—Cu—O2	160.98 (11)	N2—Cu—O3^{i}	87.08 (9)
N1—Cu—O2	82.59 (10)	O2—Cu—O3^{i}	83.11 (10)

Symmetry code: (i) $\frac{5}{4} - y, \frac{1}{4} + x, -\frac{3}{4} - z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1996). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Siemens, 1996*a*) and *XP* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*96.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclopentadienylcaesium by High-Resolution X-ray Powder Diffraction

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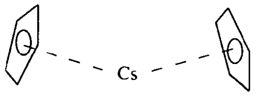
Abstract

The structure of solid (η^5-cyclopentadienyl)caesium, [Cs(C_5H_5)], has been refined by high-resolution powder X-ray diffraction. Atomic parameters based on the isostructural Rb analogue were used in the starting model. The compound crystallizes in space group *Pnma*, with $Z = 4$ and unit cell parameters $a = 11.3664\,(2)$, $b = 8.8648\,(2)$ and $c = 5.7200\,(1)$ Å. [Cs(C_5H_5)] shows a polymeric zigzag chain, a so-called multidecker structure, with an average Cs—Cp$_{\text{centroid}}$ distance of 3.140 (5) Å. [Cs(C_5H_5)] contains a single chain along the *a* axis. The chains are bent with a Cp$_{\text{centroid}}$—Cs—Cp$_{\text{centroid}}$ angle of 129.7 (1)°.

Comment

The cyclopentadienyl anion, $C_5H_5^-$ (Cp), is one of the most important ligands in organometallic chemistry and can form compounds with virtually any metallic element (Wilkinson, Stone & Abel, 1982). The structure refinement of cyclopentadienylcaesium (CsCp), (I), has been carried out as part of a general study of solid base-free cyclopentadiene–alkali metal compounds.



(I)

Preparation of single crystals of (I) has proved to be impossible due to its poor solubility in non-coordinating solvents. Powder diffraction studies have been performed on [Rb(C_5H_5)] (RbCp) (Dinnebier, Olbrich, van Smaalen & Stephens, 1996), which led to the structure solution of two polymorphic phases (in *Pnma* and *Pbca*). Visual inspection of the powder pattern of CsCp showed it to be isostructural with one of the Rb-containing phases. The crystal structure of CsCp has, therefore, been refined in space group *Pnma* using the atomic parameters of the Rb analogue as a starting model.

The main structural feature of CsCp is the polymeric chain along the *a* axis consisting of an infinite array of bent sandwiches. In this chain, the symmetry of the sandwich is *m* with the mirror plane running through the Cs atom and the centres of the Cp rings. The bond distances to the C atoms show very little variation (< 1.6%) which leads to almost perfect η^5-Cp—Cs bonding. The large coordination sphere of the Cs^+ ion can not be satisfied completely by the two 'face-on' bonded Cp ligands. In addition, 'side-on' van der Waals interactions to C and/or H atoms exist, made possible by the bending.

The bent conformation and the local environment of the Cs cations are similar to that found in $[PPh_4][Cp_3Cs_2]$ (Harder & Prosenc, 1996), although the bent angle is somewhat smaller (115.6°). In comparison to the other base-free alkali metallocenes, the bent angle of the cation has been found to be strongly dependent on radius and polarizability. While LiCp and NaCp are not bent, the bent angles of CsCp (129.7°) and RbCp (about 131°) deviate more from 180° than does that of KCp (about 138°) (Dinnebier, Behrens & Olbrich, 1997; Dinnebier, Olbrich, van Smaalen & Stephens, 1996).

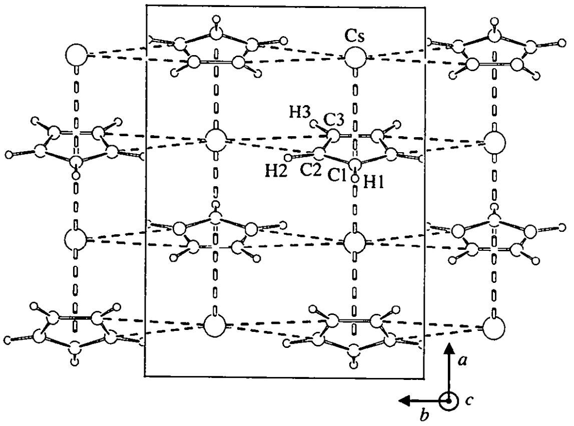


Fig. 1. Unit-cell projection down the *c* axis of CsCp showing the 'face-on' bonded Cp ligands and 'side-on' van der Waals interactions.

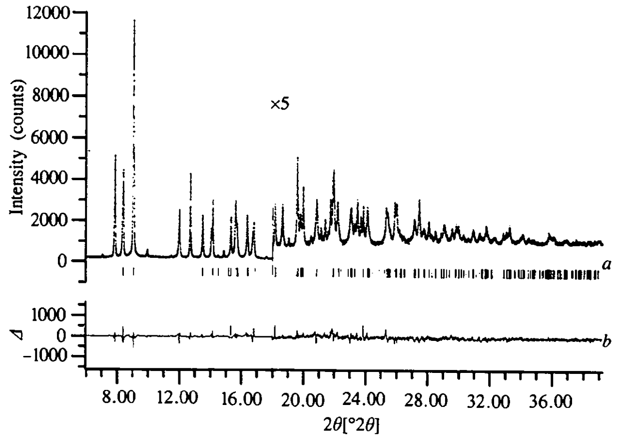


Fig. 2. Rietveld plot for CsCp showing calculated (lines), observed (diamonds, top) and difference (lower) profiles. Reflection positions are indicated by markers.

Experimental

All manipulations of solvents and substances were carried out under an atmosphere of dry argon using standard Schlenk and vacuum techniques. Cyclopentadienylcaesium was prepared as described in the literature (Harder & Prosenc, 1996). Caesium metal reacted with monomeric cyclopentadiene in THF at room temperature. The colourless solution was filtered and most of the solvent was distilled off until the product started to precipitate. Cyclopentane was added to complete precipitation. The white product was dried at 348 K and 3 × 10^{-5} Torr (yield 75%).

Crystal data

$[Cs(C_5H_5)]$
M_r = 198.00
Orthorhombic
Pnma
a = 11.3664 (2) Å
b = 8.8648 (2) Å
c = 5.7200 (1) Å
V = 576.35 (2) Å^3
Z = 4
D_x = 2.281 Mg m^{-3}

Synchrotron radiation
λ = 0.69006 Å
Cell parameters from 291 reflections
θ = 3.0–19.6°
μ = 6.23 mm^{-1}
T = 298 K
Powder
Specimen prepared at 298 K
White

Data collection

Huber two-circle diffractometer
$\theta/2\theta$ transmission scans
Beamline X3B1, NSLS, BNL (USA)
Specimen mounting: 0.7 mm glass capillary
Specimen mounted in transmission mode

Absorption correction: none
$2\theta_{min}$ = 6.01, $2\theta_{max}$ = 39.21°
Increment in 2θ = 0.005°
Monochromator: Si(111) double monochromator
Analyzer: Ge(111) analyzer crystal

Refinement

Refinement on profile intensities
R_{F^2} = 0.075
R_F = 0.059
R_p = 0.0545
R_{wp} = 0.0746
S = 1.406
Excluded region(s): none
Profile function: Thomson–Cox–Hastings–Pseudo-Voigt profile function with asymmetry correction due to axial divergence

291 reflections
35 parameters
H atoms riding
$w = 1/[y(obs)]^{1/2}$
$(\Delta/\sigma)_{max}$ = 0.1
Extinction correction: none
Preferred orientation correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Cs	0.8629 (1)	1/4	0.9831 (3)	0.060 (1)
C1	0.5742 (5)	1/4	0.9288 (14)	0.026 (2)
C2	0.6042 (4)	0.3789 (4)	0.7964 (8)	0.026 (2)
C3	0.6527 (5)	0.3297 (3)	0.5823 (9)	0.026 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cs—C1	3.296 (6)	Cs—*Cp* †	3.123 (5)
Cs—C1$^{\rm i}$	3.364 (6)	Cs—*Cp*$^{\rm i}$	3.157 (6)
Cs—C2	3.331 (5)	Cs—C2$^{\rm ii}$	3.765 (6)
Cs—C2$^{\rm i}$	3.374 (5)	Cs—C3$^{\rm ii}$	3.773 (6)
Cs—C3	3.386 (5)	C1—C2	1.412 (4)
Cs—C3$^{\rm i}$	3.389 (6)		
Cp—Cs—*Cp*$^{\rm i}$	129.71 (1)		

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

† *Cp* is the centroid of the cyclopentadienyl ring.

The structure of CsCp was refined by Rietveld (1969) analysis. A starting model based on the isostructural Rb compound in space group *Pnma* was used. The lattice parameters, the two Lorentzian peak-shape parameters of the pseudo-Voigt function (Thompson, Cox & Hastings, 1987), two asymmetry parameters due to axial divergence (Finger, Cox & Jephcoat, 1994) and the zero-point correction were refined first using the le Bail technique (le Bail, Duroy & Fourquet, 1988). Anisotropic broadening was found and refined along the chain axis. Since the shape of the Cp ring is known in very narrow limits, this additional information was used to stabilize the refinement by setting up a rigid body. In order to allow the Cp ring to relax within the plane, the length of the C—C vector was refined as an additional parameter. Refinement continued using the Rietveld technique with the scale factor, the variation of the atomic and displacement parameters. Anisotropic displacement parameters were refined for the Cs atom only. Neither absorption nor preferred orientation corrections was found to be necessary. The H atoms were included at calculated positions but were not refined.

Data collection: *SUPER* program. Cell refinement: *FULLPROF* (Rodriguez-Carvajal, 1990). Data reduction: *GUFI* (Dinnebier, 1993). Program(s) used to refine structure: *GSAS* (von Dreele & Larson, 1990). Molecular graphics: *SCHAKAL*86 (Keller, 1986). Software used to prepare material for publication: *Word for Windows* 6.0.

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Lists of raw powder data have been deposited with the IUCr (Reference: NA1280). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(ethylenediamine-*N*,*N*′)zinc(II) Dinitrate

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Abstract

The Zn$^{\rm II}$ atom in $[\rm Zn(C_2H_8N_2)_3](NO_3)_2$ has a distorted octahedral geometry of D_3 symmetry with three ethylenediamine bidentate ligands completing the coordination.

Comment

The $[\rm Ni(en)_3]^{2+}$ complex, where en is ethylenediamine (Swink & Atoji, 1960; Korp, Bernal, Palmer & Robinson, 1980) spontaneously resolves to give a dinitrate crystal in an uniaxial and enantiomorphic space group, allowing the single-crystal circular dichroism to be measured directly. The corresponding $[\rm Zn(en)_3]^{2+}$ complex also spontaneously resolves into one of two optical isomers, with the conformer in this determination found to be $(\Delta\lambda\lambda\lambda)$, the same as for the corresponding