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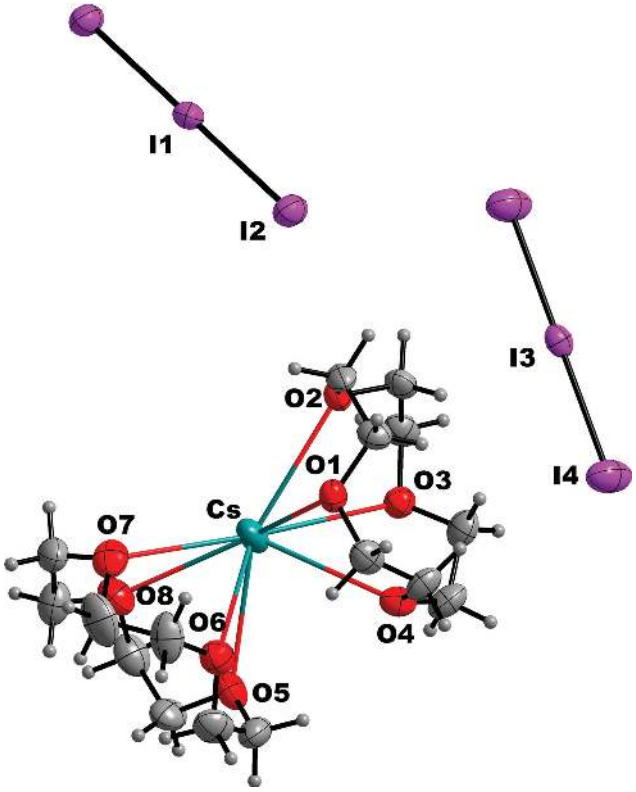
Halogen bonding in crystal structure of bis (1,4,7,10-tetraoxacyclododecane-κ⁴O,O′,O″,O‴) cesium triiodide, $C_{16}H_{32}CsI_3O_8$



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Abstract

$C_{16}H_{32}CsI_3O_8$, triclinic, $P\bar{1}$ (no. 2), $a = 10.7930(5)$ Å, $b = 11.5610(5)$ Å, $c = 12.4880(5)$ Å, $\alpha = 73.050(10)°$, $\beta = 88.870(10)°$, $\gamma = 66.060(10)°$, $V = 1353.62(16)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0578$, $wR_{ref}(F^2) = 0.1875$, $T = 293(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Reddish-brown polyhedron
Size:	0.30 × 0.25 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.8 mm^{-1}
Diffractometer, scan mode:	KappaCCD, ω
θ_{max}, completeness:	26.5°, 90%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4853, 4853,
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4166
$N(param)_{refined}$:	258
Programs:	Diamond [1], CAD-4 [2], SHELX [3, 4]

Source of material

Iodine (>=99.0%), caesium iodide, 1,4,7,10-tetraoxacyclododecan (12-crown-4) and ethanol were received from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). All the used reagents were of analytical grade and were used as purchased without further purification. The Raman spectra were measured using a Jobin Yvon U 100 spectrometer from Spectra-Physics (Argon laser at 514.5 nm). The title compound was synthesized by dissolving 0.16 g (0.63 mmol) of CsI and 0.16 g (0.63 mmol) I_2 in 10 mL ethanol/10 ml methanol mixture at room temperature. Then 0.2 mL (1.26 mmol) 12-crown-4 is added under continuous stirring. The clear solution gives after 4 days at room temperature reddish-brown crystals of $[Cs(12\text{-crown-}4)_2]I_3$.

Experimental details

A reddish-brown single crystal was selected from the mother liquor and transferred to the Kappa CCD diffractometer [2]. The measurement was done at 293 K. The structure solution, refinement and further calculations were done with the programs SHELXL [3, 4]. The data collection was undertaken several years ago using a point detector. Unfortunately, the measured section produced a completeness of only ~90%.

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cs	0.36854(8)	0.42183(7)	−0.21734(8)	0.0538(3)
I1	0.500000	0.000000	0.500000	0.0446(3)
I2	0.23561(9)	0.11040(10)	0.36787(8)	0.0626(3)
I3	0.000000	0.000000	0.000000	0.0441(3)
I4	−0.21930(11)	0.19988(12)	−0.17295(10)	0.0860(4)
O1	0.1124(8)	0.4182(8)	−0.1014(7)	0.0480(19)
O2	0.3444(8)	0.1692(8)	−0.0486(7)	0.0474(19)
O3	0.3301(8)	0.1992(8)	−0.2842(7)	0.050(2)
O4	0.0954(9)	0.4446(8)	−0.3370(7)	0.054(2)
O5	0.3400(10)	0.6302(9)	−0.4481(9)	0.063(2)
O6	0.1620(10)	0.7223(9)	−0.2905(8)	0.062(2)
O7	0.3787(11)	0.6442(11)	−0.1242(8)	0.067(3)
O8	0.5586(11)	0.5675(10)	−0.2827(9)	0.069(3)
C1	0.1054(13)	0.2993(12)	−0.0333(11)	0.052(3)
H1A	0.074901	0.259715	−0.079815	0.062*
H1B	0.041017	0.318870	0.021213	0.062*
C2	0.2463(14)	0.2037(13)	0.0270(9)	0.052(3)
H2A	0.275028	0.244174	0.073805	0.062*
H2B	0.241963	0.123426	0.076013	0.062*
C3	0.3434(13)	0.0667(11)	−0.0891(11)	0.052(3)
H3A	0.250638	0.076411	−0.100518	0.062*
H3B	0.395983	−0.019724	−0.034673	0.062*
C4	0.4050(13)	0.0770(13)	−0.1989(12)	0.058(3)
H4A	0.497468	0.067638	−0.186108	0.070*
H4B	0.409831	0.004227	−0.224964	0.070*
C5	0.2051(14)	0.2103(15)	−0.3291(12)	0.060(3)
H5A	0.153590	0.185955	−0.268890	0.072*
H5B	0.221567	0.151826	−0.375010	0.072*
C6	0.1271(15)	0.3542(16)	−0.4002(12)	0.065(4)
H6A	0.181019	0.376693	−0.459030	0.078*
H6B	0.043011	0.364145	−0.436158	0.078*
C7	−0.0169(12)	0.4564(14)	−0.2771(11)	0.057(3)
H7A	−0.021205	0.370668	−0.249384	0.068*
H7B	−0.099916	0.518725	−0.326378	0.068*
C8	−0.0058(13)	0.5038(14)	−0.1811(12)	0.060(3)
H8A	−0.005037	0.590928	−0.210338	0.072*
H8B	−0.086363	0.514050	−0.142023	0.072*
C9	0.2027(15)	0.7218(16)	−0.4755(11)	0.066(4)
H9A	0.146684	0.673581	−0.473231	0.079*
H9B	0.190630	0.779823	−0.552091	0.079*
C10	0.1542(15)	0.8040(15)	−0.4006(14)	0.072(4)
H10A	0.209740	0.852401	−0.401470	0.086*
H10B	0.060602	0.868192	−0.426528	0.086*
C11	0.1510(17)	0.7807(19)	−0.2026(17)	0.081(5)
H11A	0.122101	0.731085	−0.138136	0.097*
H11B	0.080414	0.870939	−0.228118	0.097*
C12	0.274(2)	0.7846(19)	−0.167(2)	0.099(6)
H12A	0.259277	0.826174	−0.107756	0.118*
H12B	0.304444	0.835456	−0.229550	0.118*
C13	0.5069(18)	0.6462(16)	−0.1243(12)	0.071(4)
H13A	0.570939	0.563908	−0.070946	0.085*
H13B	0.502189	0.718707	−0.097817	0.085*
C14	0.5616(16)	0.6618(17)	−0.2357(14)	0.070(4)
H14A	0.507431	0.750441	−0.286255	0.084*
H14B	0.654702	0.651959	−0.226303	0.084*
C15	0.5652(16)	0.6016(17)	−0.4012(14)	0.071(4)
H15A	0.605275	0.519782	−0.420783	0.085*
H15B	0.626941	0.644803	−0.418690	0.085*
C16	0.4349(15)	0.6893(16)	−0.4744(12)	0.067(4)
H16A	0.397861	0.775826	−0.462735	0.081*
H16B	0.450644	0.701547	−0.552887	0.081*

Nevertheless during the refinement no correlation effects were detected.

Comment

Polyiodides are interesting compounds with a rich chemistry and many applications, especially as antimicrobial agents [5]. Previously, polyiodides and iodine were incorporated into cellulose membranes [6], polymer foams [7], silicon membranes [8] and wound dressing applications in form of nanoparticles [9] due to their microbicidal actions. Only few examples of polyiodides with 12-crown-4 and alkalimetal cations have been reported previously [10, 11]. In these compounds, the crown ether and the metal cation stabilize the polyiodide structures by forming sandwich structures [10, 11]. The long time stability of a polyiodide is important for its use as antimicrobial agent to increase its long term effectiveness, durability and reduce the iodine sublimation [6]. Triiodides seem to be the most interesting class of polyiodides due to their stability. There are hundreds of examples of triiodides in the literature [12]. Halogen bonding is a major factor of stability in polyiodides within three-center-systems [13] and their resulting antimicrobial activity [14].

The asymmetric unit of the title structure contains two crystallographically independent, isolated, symmetrical, linear triiodide anions I_3^- with crystallographic inversion symmetry. The bond lengths and angles within these structures are in expected ranges and are another example of a three-center-system $[I\text{-}I\text{-}I]^-$ with halogen bonding like the previously reported triiodies in our group [14]. This three-center-system is an indicator for possible antimicrobial activities. As reported before [14], the complex compound interacts with the cell membrane of the microorganism due to electrostatic interactions and is deformed. This results in gradual free molecular iodine release from the triiodide-unit. Iodine directly attacks the pathogens by destroying their cell membrane and causing protein oxidation [5, 9, 14]. There is only one strong Raman stretching vibration at 108 cm^{-1} for the triiodide, which is available in our previous compounds [14] and in the very recently reported cyclic I_{10}^{-2} anion [15]. The later showed another strong line at 172 cm^{-1} due to weak

connections to two neighboring halogen bond donors. Usually, covalent I_2 is detected at around 180 cm^{-1} [13, 15]. All geometric parameters of the cationic cesium bis(12-crown-4) complex are in the expected ranges [16].

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