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# Halogen bonding in crystal structure of bis(1,4,7,10-tetraoxacyclododecane- $\kappa^4\text{O},\text{O}',\text{O}'',\text{O}'''$ ) cesium triiodide, $\text{C}_{16}\text{H}_{32}\text{CsI}_3\text{O}_8$

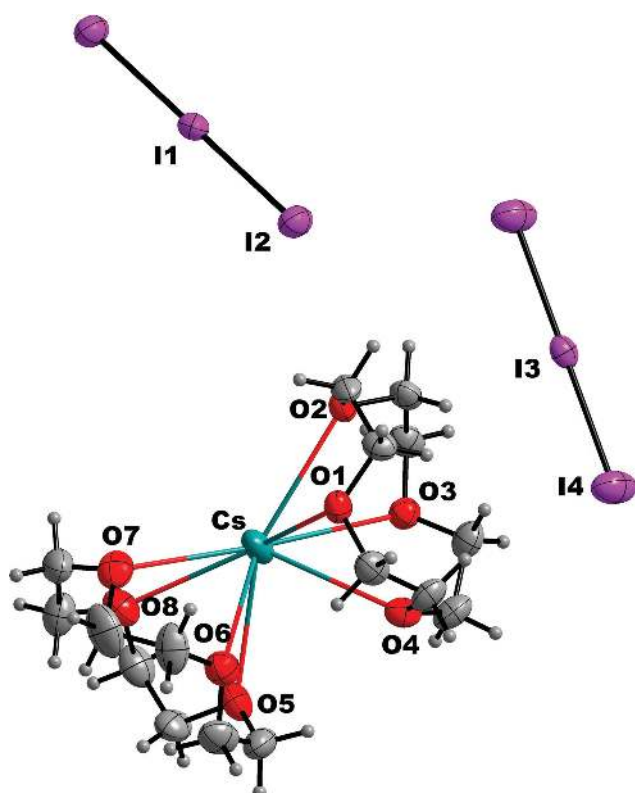


Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**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)
$\mu$ :	4.8 mm <sup>-1</sup>
Diffractometer, scan mode:	KappaCCD, $\omega$
$\theta_{\max}$ , completeness:	26.5°, 90%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	4853, 4853,
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4166
$N(\text{param})_{\text{refined}}$ :	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)  $\text{I}_2$  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  $[\text{Cs}(12\text{-crown-4})_2]\text{I}_3$ .

## 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%.

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## Abstract

$\text{C}_{16}\text{H}_{32}\text{CsI}_3\text{O}_8$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 10.7930(5)$  Å,  $b = 11.5610(5)$  Å,  $c = 12.4880(5)$  Å,  $\alpha = 73.050(10)^\circ$ ,  $\beta = 88.870(10)^\circ$ ,  $\gamma = 66.060(10)^\circ$ ,  $V = 1353.62(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0578$ ,  $wR_{\text{ref}}(F^2) = 0.1875$ ,  $T = 293(2)$  K.

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

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*

**Table 2 (continued)**

Atom	x	y	z	$U_{iso}^*/U_{eq}$
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<sub>3</sub><sup>-</sup> 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-I-I]<sup>-</sup> with halogen bonding like the previously reported triiodides 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<sup>-1</sup> for the triiodide, which is available in our previous compounds [14] and in the very recently reported cyclic I<sub>10</sub><sup>-2</sup> anion [15]. The later showed another strong line at 172 cm<sup>-1</sup> due to weak

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

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## References

1. Brandenburg, K.: *DIAMOND*. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2015).
2. Enraf-Nonius: *CAD4 EXPRESS*, Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands (1994).
3. Sheldrick, G. M.: SHELXT – integrated space-group and crystal structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with *SHELXL*. *Acta Crystallogr.* **C71** (2015) 3–8.
5. Kaiho, T.: Iodine chemistry and applications. (Ed. T. Kaiho), John Wiley & Sons, Inc.: Hoboken, NJ, USA (2015), ISBN: 978-1-118-46629-2.
6. Aoki, S.; Yamakawa, K.; Kubo, K.; Takeshite, J.; Takeuchi, M.; Nobuoka, Y.; Wada, R.; Kikuchi, M.; Sawai, S.: Antibacterial properties in silicone membranes after a simple two-step immersion process in iodine and silver nitrate solutions. *Biocontrol Sci.* **23** (2018) 97–105.
7. Zhang, S.; Kai, C.; Liu, B.; Zhang, S.; Wei, W.; Xu, X.: Facile fabrication of cellulose membrane containing polyiodides and its antimicrobial properties. *Appl. Surf. Sci.* **500** (2020) 144046.
8. Lundin, J. G.; MsGann, C. L.; Weise, N. K.; Estrella, L. A.; Balow, R. B.; Streifel, B. C.; Wynne, J. H.: Iodine binding and release from antimicrobial hemostatic polymer foams. *React. Funct. Polym.* **135** (2019) 44–51.
9. Viswanathan, K.; Babu, D. B.; Jayakumar, G.; Raj, G. D.: Antimicrobial and skin wound dressing application of molecular iodine nanoparticles. *Mater. Res. Express* **4** (2017) 104003.
10. Edis, Z.; Haj Bloukh, S.: Preparation, structural and spectroscopic characterization of a pentaiodide  $[Rb(12-Crown-4)_2]I_5$ . *Z. Naturforsch.* **68b** (2013) 1340–1346.
11. Edis, Z.; Haj Bloukh, S.: Preparation and structural and spectroscopic characterization of triiodides  $[M(12-Crown-4)_2]I_3$  with  $M = Na$  and  $Rb$ . *Z. Naturforsch.* **69b** (2014) 995–1002.
12. van Megen, M.; Reiss, G. J.:  $I_6^{2-}$  Anion composed of two asymmetric triiodide moieties: a competition between halogen and hydrogen bond. *Inorganics* **1** (2013) 3–13 and references cited therein.
13. Bartashevich, E. V.; Grigoreva, E. A.; Yushina, I. D.; Bulatova, L. M.; Tsirelson, V. G.: Modern level for the prediction of properties of iodine-containing organic compounds: iodine forming halogen bonds. *Russ. Chem. Bull. Int. Ed.* **66** (2017) 1–12.
14. Edis, Z.; Haj Bloukh, S.; Abu Sara, H.; Bhakhoa, H.; Rhyman, L.; Ramasami, P.: “Smart” triiodide compounds: does halogen bonding influence antimicrobial activities? *Pathogens* **8** (2019) 182.
15. Reiss, G. J.: A cyclic  $I_{10}^{2-}$  anion in the layered crystal structure of theophyllinium pentaiodide,  $C_7H_9I_5N_4O_2$ . *Z. Kristallogr. NCS* **234** (2019) 737–739.
16. Liddle, S. T.; Izod, K.: Synthesis and characterization of 1,3-diphosphapropene and alkali-metal 1,3-diphosphaallyl complexes and unexpected 1,3-rearrangement of a cesium 1,3-diphosphaallyl complex to a cesium secondary phosphanide. *Organometallics* **23** (2004) 5550–5559.