

Communication

## Iodine Molecules Included in the Structure of Dibenzo-24-Crown-8, (I<sub>2</sub>)@(db24c8)

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**Abstract:** A reaction of YI<sub>3</sub>, dibenzo-24-crown-8 and iodine in ethanol yielded, as a by-product, red single crystals of (I<sub>2</sub>)@(db24c8). In the triclinic crystal, *P*-1, *a* = 485.0(1), *b* = 1203.7(3), *c* = 1280.4(2) pm,  $\alpha$  = 64.56(2)°,  $\beta$  = 86.82(2)°,  $\gamma$  = 83.89(2)°, *V* = 671.1(2) × 10<sup>6</sup> pm<sup>3</sup>, *Z* = 1, *R*<sub>1</sub> = 0.0301 for 1965 reflections with *I*<sub>0</sub> > 2σ(*I*<sub>0</sub>), iodine molecules with an I–I distance of 268.39(7) pm, slightly longer than in the gas phase, are included in a matrix of db24c8 molecules.

**Keywords:** iodine; dibenzo-24-crown-8; inclusion compound; crystal structure

### 1. Introduction

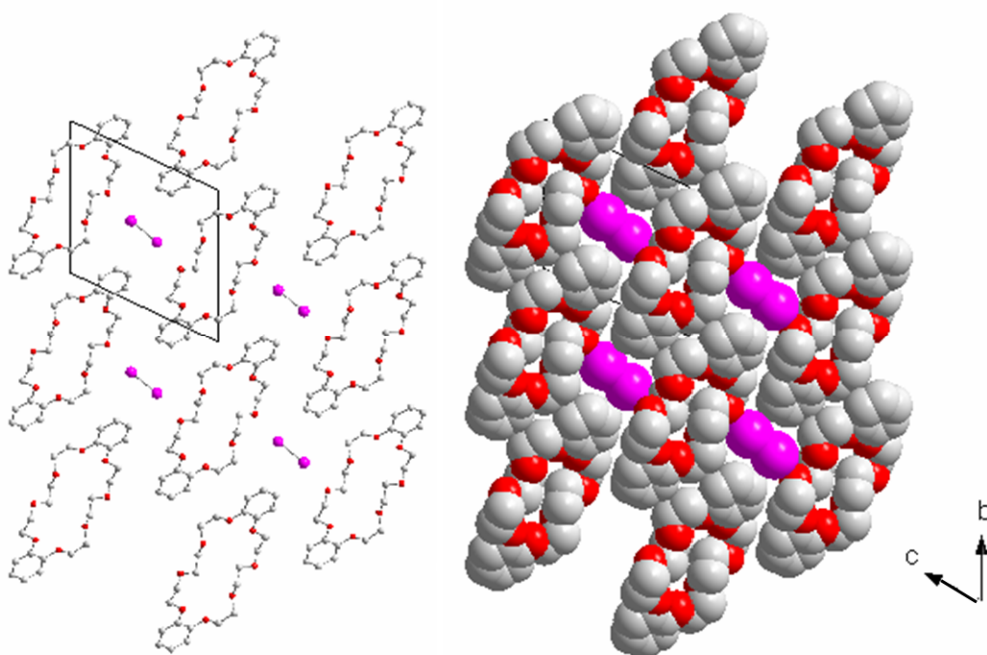
Dibenzo-24-crown-8 (db24c8) is a large crown ether which may encapsulate rather large cations in a nest-like conformation, such as in [K(db24c8)](I<sub>3</sub>) [1]. Three of these molecules may also form the second coordination shell of the large cation [Y(H<sub>2</sub>O)<sub>8</sub>(db24c8)<sub>3</sub>]<sup>3+</sup> in which the first coordination sphere is built from eight water molecules. This cation was recently found in the polyiodide salt [Y(H<sub>2</sub>O)<sub>8</sub>(db24c8)<sub>3</sub>]<sub>2</sub>(I<sub>3</sub>)<sub>3</sub>(I<sub>5</sub>)<sub>3</sub> [1]. In the course of the reactions that led to this mixed tri-/pentaiodide, we have also observed a small amount of red needles which turned out to be of the inclusion compound (I<sub>2</sub>)@(db24c8). Similar inclusion compounds of halogens and common polyethers seem not to be known. However, there are inclusion compounds of polyethers with compounds that are capable

of forming hydrogen bonds, as for example in  $(\text{PicH})_2(\text{db24c8})$  [2] (PicH = picric acid) and  $[\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_3](\text{db24c8})$  [3].

## 2. Results and Discussion

The crystal structure of  $(\text{I}_2)@(\text{db24c8})$  is triclinic, space group  $P-1$ , with a pseudo-hexagonal unit cell,  $a = 485.0(1)$ ,  $b = 1203.7(3)$ ,  $c = 1280.4(2)$  pm,  $\alpha = 64.56(2)^\circ$ ,  $\beta = 86.82(2)^\circ$ ,  $\gamma = 83.89(2)^\circ$ , hence with  $a_{\text{hex}} = b_{\text{hex}} \rightarrow b \approx c$ ,  $c_{\text{hex}} = a$ ;  $\alpha_{\text{hex}} = \beta\gamma_{\text{hex}} \rightarrow \beta \approx \gamma \approx 90^\circ$ ,  $\gamma_{\text{hex}} \approx \gamma^* \approx 120^\circ$ . There is one formula unit in the unit cell, the volume amounts to  $671.1(2) \times 10^6 \text{ pm}^3 (= \text{\AA}^3)$ . One iodine molecule resides in the center of the unit cell, surrounded by four db24c8 molecules, see Figure 1. The  $\text{I}_2$  molecules are stacked almost on top of each other with the shortest intermolecular I–I distance of  $485.0(1)$  pm =  $a$ . The intramolecular I–I distance is surprisingly short,  $268.39(7)$  pm, only slightly larger than in gaseous iodine,  $267$  pm [4,5], and shorter than in solid iodine at  $170$  K,  $271.5(6)$  pm [6,7]. Shortest distances of I to neighboring O and C atoms are  $292.8(2)$  (I1–O4) and  $374.7(2)$  pm (I1–C3), well and far beyond the sum of the van der Waals radii [8],  $264$  (I + O) and  $275$  (I + C) pm, respectively.

**Figure 1.** Perspective view of the crystal structure of  $(\text{I}_2)@(\text{db24c8})$  down  $[100]$ ; ball-and-stick and space-filling models.

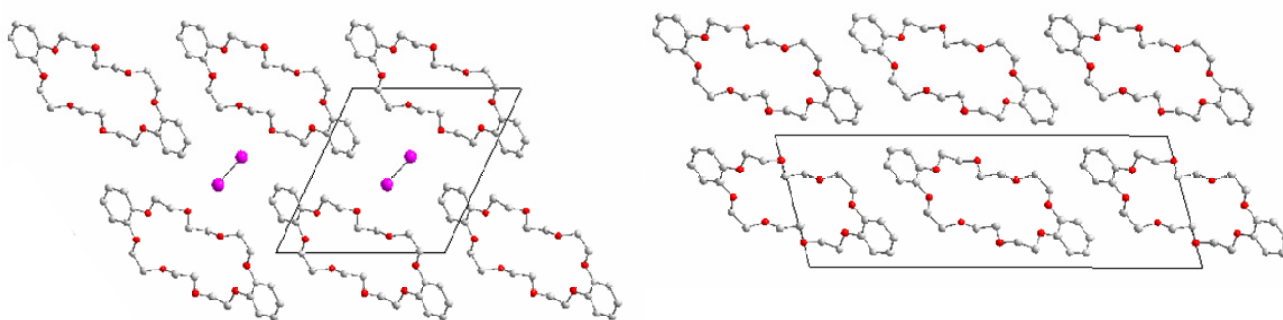


Thus,  $(\text{I}_2)@(\text{db24c8})$  can be considered as a true inclusion compound. The crystal structure of db24c8 [9] contains a rather dense peanut packing with a volume per db24c8 molecule of  $577 \times 10^6 \text{ pm}^3$ ,  $94 \times 10^6 \text{ pm}^3$  less than the volume of one formula unit of  $(\text{I}_2)@(\text{db24c8})$ . In the crystal structure of iodine [6, 7], there are four molecules per unit cell with a cell volume of  $327.2 \times 10^6 \text{ pm}^3$ . One iodine molecule, therefore, affords a volume of  $82 \times 10^6 \text{ pm}^3$  in solid iodine. In  $(\text{I}_2)@(\text{db24c8})$ , the volume per iodine molecule is, with  $94 \times 10^6 \text{ pm}^3$ , considerably larger. This is in agreement with the more gas-like I–I distance in  $(\text{I}_2)@(\text{db24c8})$ , hence with much less  $(\text{I}_2)$  to  $(\text{db24c8})$  interactions in

the inclusion compound, compared with those in solid iodine where the shortest intermolecular distances, 353.8 pm, are much shorter than twice the van der Waals radius,  $2 \times 198 = 396$  pm.

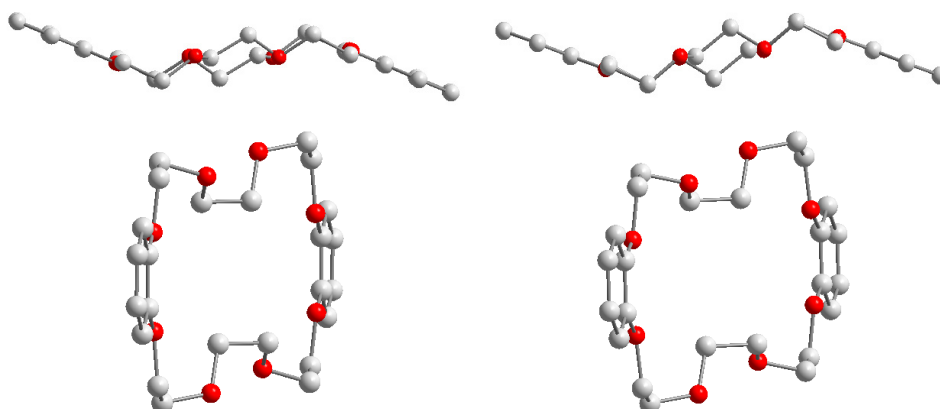
Structurally, rows of db24c8 molecules appear in the [001] direction in the crystal structure of db24c8, see Figure 2, right. These rows are arranged almost parallel to each other, with a shift according to the angle  $\beta = 104.93(1)^\circ$ . The layers that occur parallel (010) are stacked on top of each other in the [010] direction of monoclinic db24c8. Space for one iodine molecule per db24c8 molecule ( $I_2$ @db24c8) is provided through some rotation of the db24c8 molecules and a larger shift of the rows in the [010] direction of ( $I_2$ )@db24c8, see the comparison of the structures in Figure 2.

**Figure 2.** Comparison of the crystal structures of ( $I_2$ )@db24c8 (left) and db24c8 (right). Views down the short axes,  $a = 485.0(1)$  and  $b = 491.3(2)$  pm, respectively.



The conformation of the db24c8 molecules in both structures, ( $I_2$ )@db24c8 and the parent (db24c8), and their arrangement in both crystal structures are very similar. This may be seen from Figure 2 and from a comparison of the db24c8 molecules in both structures as shown in Figure 3. The C–C and C–O distances are identical within the error limits.

**Figure 3.** Comparison of the molecular structures of db24c8 molecules in the crystal structures of ( $I_2$ )@db24c8 (left) and (db24c8) (right).



### 3. Experimental Section

In a typical reaction, 0.02 g (0.1 mmol) yttrium triiodide,  $\text{YI}_3$ , previously synthesized from the elements [10], 0.09 g (0.02 mmol) dibenzo-24-crown-8 (db24c8) and 0.08 g (0.3 mmol) iodine were dissolved in 40 mL of ethanol. Slow evaporation of the solvent (beaker with perforated Parafilm<sup>®</sup>) yielded single crystals of  $[\text{Y}(\text{H}_2\text{O})_8(\text{db24c8})_3]_2(\text{I}_3)_3(\text{I}_5)_3$  together with a small amount of  $(\text{I}_2)@(\text{db24c8})$ .

Single crystals were selected under a microscope and sealed in thin-walled glass capillaries. After their quality had been checked by Laue diffraction patterns, the single crystals were transferred to a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS II) to collect a complete intensity data set at ambient temperature. Structure solution and refinement was performed with the programs SHELXS-97 (direct methods) [11,12] and SHELXL-97 [11,13], scattering factors were from International Tables for X-ray Crystallography [14]. Data corrections were carried out for Lorentz and polarization factors and absorption (numerical with the aid of the programs X-RED [15] and X-SHAPE [16]). Further details of the crystal structure determination may be obtained from the Cambridge Crystallography Data center, CCDC-837899, free of charge, on application from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for  $(\text{I}_2)@(\text{db24c8})$  ( $720.30 \text{ g mol}^{-1}$ ); diffractometer IPDS-II, Stoe, Darmstadt; Mo- $\text{K}\alpha$  (graphite monochromator,  $\lambda = 71.073 \text{ pm}$ );  $T = 293(2) \text{ K}$ ;  $2\theta_{\text{max}} = 59.32^\circ$ ; 180 images,  $0^\circ \leq \omega \leq 180^\circ$ ;  $\varphi = 0^\circ$ ,  $0^\circ \leq \omega \leq 180^\circ$ ;  $\varphi = 90^\circ$ ,  $\Delta\omega = 2^\circ$ ; indices:  $-5 \leq h \leq 6$ ,  $-16 \leq k \leq 16$ ,  $-17 \leq l \leq 17$ ; transmission (min, max) = 0.5359, 0.7874;  $\rho_{\text{calc}} = 1.738 \text{ g cm}^{-3}$ ; 13396 reflection intensities measured of which 3765 were symmetrically independent,  $R_{\text{int}} = 0.0446$ ,  $F(000) = 346$ ,  $\mu = 2.387 \text{ mm}^{-1}$ . Triclinic,  $P-1$  (no. 2),  $a = 485.0(1)$ ,  $b = 1203.7(3)$ ,  $c = 1280.4(2) \text{ pm}$ ,  $\alpha = 64.56(2)^\circ$ ,  $\beta = 86.82(2)^\circ$ ,  $\gamma = 83.89(2)^\circ$ ,  $V = 671.1(2) \times 10^6 \text{ pm}^3$ ,  $Z = 1$ .  $R$  values:  $R_1/wR_2$  for 1965 reflections with  $[I_0 > 2\sigma(I_0)]$ : 0.0301/0.0625 and for all data: 0.0804/0.0751;  $S_{\text{all}} = 0.835$ .

### 4. Conclusions

Iodine molecules with I–I distances of 268.39(7) pm, between those in gaseous iodine and solid iodine, 267 and 271.5 pm, respectively, are included in the solid-state structure of dibenzo-24-crown-8. The molecular structures of the db24c8 molecules are practically unchanged; there is a volume increase of about 16% relative to the parent crystal structure of db24c8. This increase amounts to  $94 \times 10^6 \text{ pm}^3$  which is considerably larger than the volume of  $82 \times 10^6 \text{ pm}^3$  of an iodine molecule in solid iodine. Only very weak interactions between the iodine and the db24c8 molecules in  $(\text{I}_2)@(\text{db24c8})$  are thereby attested.

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