

## The X-Ray Crystal Structure of a 1 : 1 Adduct between $\alpha$ -Cyclodextrin and Cyclobutane-1,1-dicarboxylatodiammineplatinum(II)

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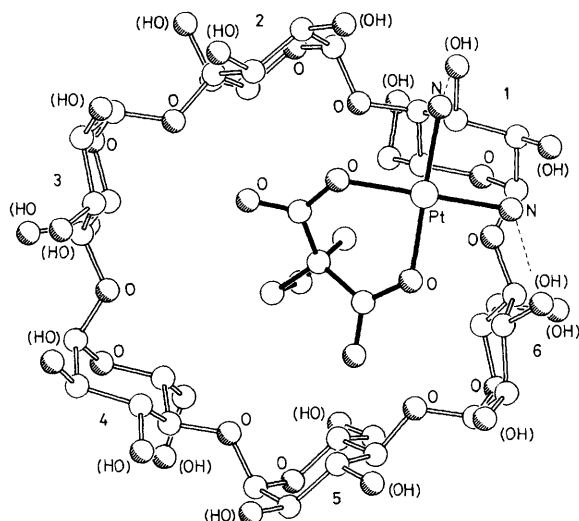
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In the second sphere co-ordination of a cyclobutane-1,1-dicarboxylatodiammineplatinum(II) by  $\alpha$ -cyclodextrin, stabilisation of the crystalline adduct is achieved by the cyclobutane ring of the guest penetrating into the cavity of the host and the ammine ligands on the guest participating in the formation of two (N-H...O) hydrogen bonds with secondary hydroxy groups at C(3) on neighbouring  $\alpha$ -D-glucopyranosidic units in the host.

The evidence presented in the preceding communication<sup>1</sup> for 1:1 adduct formation between  $\alpha$ -cyclodextrin ( $\alpha$ -CD) and cyclobutane-1,1-dicarboxylatodiammineplatinum(II) [Pt(NH<sub>3</sub>)<sub>2</sub>(CBDCA)] in aqueous solution led to speculation that the cyclobutane ring of the platinum complex is directed inside the cavity of the  $\alpha$ -CD. In order to lend support to this

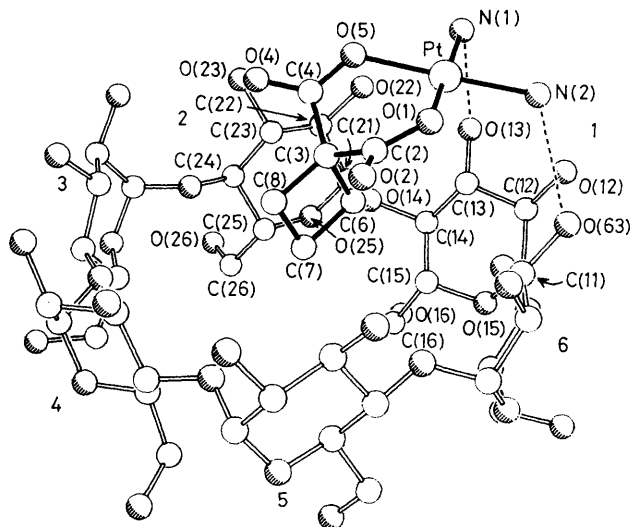
structural proposal, we sought to obtain single crystals of a 1 : 1 adduct between  $\alpha$ -CD and Pt(NH<sub>3</sub>)<sub>2</sub>(CBDCA) suitable for X-ray structural investigation. This objective has been achieved by dissolving  $\alpha$ -CD (105 mg) in water (1 ml) at 80 °C and adding Pt(NH<sub>3</sub>)<sub>2</sub>(CBDCA) until the aqueous solution was saturated with respect to the complex (34.7 mg). After



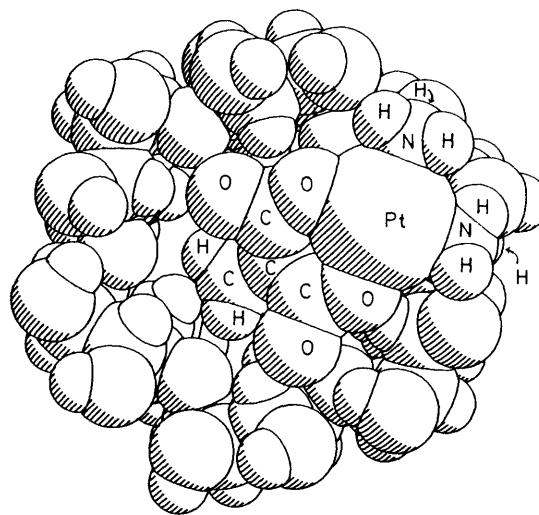
**Figure 1.** A plan view of the framework representation of  $[\text{Pt}(\text{NH}_3)_2(\text{CBDCA})\cdot\alpha\text{-CD}]$ . Note that the  $\alpha$ -D-glucopyranosidic units are numbered 1 to 6 in an anticlockwise direction.

filtering, the solution was allowed to cool during 8 h to room temperature. Slow evaporation occurred and a small amount of crystalline material was produced with m.p. 235–255 °C, which was shown in preliminary tests to contain both  $\alpha$ -CD and  $\text{Pt}(\text{NH}_3)_2(\text{CBDCA})$  and to be suitable for X-ray crystallography. Here, we report on the structure† of the penta-aquated 1:1 crystalline adduct.

Figures 1 and 2 show plan and side-on views respectively of framework representations of the 1:1 adduct. The space-filling representation in Figure 3 illustrates the penetration of the cyclobutane ring of  $\text{Pt}(\text{NH}_3)_2(\text{CBDCA})$  into  $\alpha$ -CD. The cyclodextrin has a characteristic open slightly bucket-shaped conformation with local pseudo- $C_6$  symmetry. The bound complex, whose geometry is essentially the same as that observed<sup>2</sup> for the free complex, is positioned with the cyclobutane ring oriented approximately over the centre of the  $\alpha$ -CD torus, its plane lying parallel to the '6-fold' axis of the host. The cyclobutane ring is inserted into the  $\alpha$ -CD with C(7) and C(6) lying 1.03 and 0.35 Å respectively below the mean plane of the oxygen atoms associated with the twelve secondary hydroxy groups. Carbon atom C(7) lies 0.94 Å above the mean plane of the six glycosidic oxygen atoms. The ammine ligands are oriented, for the most part, over one of the  $\alpha$ -D-glucopyranosidic units, which is, in turn, significantly more tilted with respect to the principle axis of the  $\alpha$ -CD host (Figure 1). There are two (N–H···O) hydrogen bonds between the ammine ligands and this cyclodextrin molecule,<sup>3</sup> one between N(1) and O(13) of 3.14 Å and the other between N(2) and O(63) of 2.94 Å. Surprisingly perhaps, there are no hydrogen bonds between the CBDCA carbonyl oxygen atoms



**Figure 2.** A side-on view of the framework representation of  $[\text{Pt}(\text{NH}_3)_2(\text{CBDCA})\cdot\alpha\text{-CD}]$  showing the atomic numbering scheme for the guest and two (1 and 2) of the  $\alpha$ -D-glucopyranosidic units in the host.



**Figure 3.** A plan view of the space-filling representation of  $[\text{Pt}(\text{NH}_3)_2(\text{CBDCA})\cdot\alpha\text{-CD}]$  showing the penetration of the guest into the host.

and the secondary hydroxy groups of this host cyclodextrin molecule. However, there are hydrogen bonds both from these carbonyl oxygen atoms and from the ammine hydrogen atoms to symmetry-related cyclodextrin molecules. There are also hydrogen bonds between the water molecules and both  $\alpha$ -CD hydroxy groups and the  $\text{Pt}(\text{NH}_3)_2(\text{CBDCA})$  carbonyl oxygen atoms and ammine hydrogen atoms.

The structural features which have emerged from this study support the conclusions drawn<sup>1</sup> from the solution state investigation and provide a rare example<sup>4–6</sup> of binding of a neutral organometallic guest‡ by a cyclodextrin host.<sup>7</sup>

† *Crystal data:*  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{Pt}\cdot\text{C}_{36}\text{H}_{60}\text{O}_{30}\cdot 5.5\text{H}_2\text{O}$ ,  $M = 1443.1$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 10.102(2)$ ,  $b = 13.526(4)$ ,  $c = 41.971(9)$  Å,  $U = 5735$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Cu-K}\alpha) = 56$  cm<sup>-1</sup>,  $D_c = 1.68$  g cm<sup>-3</sup>. Data were measured on a Nicolet R3m diffractometer with Cu-K $\alpha$  radiation (graphite monochromator) with  $\omega$ -scans. The structure was solved by the heavy atom method and refined anisotropically using absorption corrected data to  $R = 0.036$ ,  $R_w = 0.038$  currently for 4210 independent reflections [ $\theta \leq 58^\circ$ ,  $|F_o| > 3\sigma(|F_o|)$ ]. The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation of the communication.

‡ In a recent study (T. Matsue, D. H. Evans, T. Osa, and N. Kobayashi, *J. Am. Chem. Soc.*, 1985, **107**, 3411) of the oxidation of ferrocenecarboxylic acid (FCAH) in the presence of  $\beta$ -CD, although the anion (FCA<sup>-</sup>) is bound ( $K_a = 2200$  dm<sup>3</sup> mol<sup>-1</sup> in H<sub>2</sub>O at 20 °C) by  $\beta$ -CD, no binding of the neutral oxidised form could be detected.

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  - 5 See A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1984, 645 for the preparation of crystalline  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD-ferrocene adducts and a discussion of their properties.
  - 6 Rotaxane adducts of  $\alpha$ - and  $\beta$ -CD with  $\mu$ -( $\alpha,\omega$ -diaminoalkane)-bis[chlorobis(ethylenediamine)cobalt(III)] have been described by H. Ogino, *J. Am. Chem. Soc.*, 1981, **103**, 1303 and H. Ogino and K. Ohata, *Inorg. Chem.*, 1984, **23**, 3312.
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