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INCLUSION COMPOUND OF α-CYCLODEXTRIN/DIQUINUCLIDINIUM CATION $[Q_2H]^+$

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In this work, we report the syntheses and characterization of a new crystalline inclusion compound of α-cyclodextrin using diquinuclidinium cation ($[Q_2H]^+$) like guest. Elemental analysis, ^{13}C CP-MAS NMR spectroscopy and powder X-ray diffraction analysis confirm the inclusion process. The guest specie $[Q_2H]^+$ corresponds to the adduct of a heterocyclic base with its conjugated cation in a symmetric linear arrangement $[Q\text{-}H\text{-}Q]^+$. This complex $[Q_2H]^+$ appears to be held in the host cavities only by weak van der Waals interactions.

Keywords: cyclodextrins; inclusion compounds; quinuclidinium

INTRODUCTION

Cyclodextrins are cyclic oligosaccharides consisting 6, 7, 8 glucopyranose units, usually referred to α-, β- or γ-cyclodextrins, respectively. These naturally occurring compounds have relatively rigid doughnut-shaped structures, and constitute very useful momomolecular hosts in supramolecular chemistry. Molecules of adequate size, shape and suitable chemical functionality can be held within the cavity of a particular cyclodextrin. The inclusion complexation occurs when the electrostatic, van der Waals, hydrophobic interactions and hydrogen bonding [1–4] are favourable. The cyclodextrins and their inclusion compounds can be crystallized from water and studied by X-ray crystallography as empty molecules or as host-guest complexes. "Channel" or "cages" structures are formed depending of the size and ionic or molecular character of the substrate, in which the cyclodextrin molecules are stacked [2,5].

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The cyclodextrin inclusion compounds, particularly the ones leading to supramolecular self-assemblies continue to be a fascinating topic in actual organic chemistry as they serve as models for understanding molecular recognition and as precursors for designing novel nanomaterials for electronics and biological applications [4].

Previously, we reported the synthesis and structural properties of inclusion compounds with cyclodextrin and secondary dialkylamine showing channel structures with a hexagonal lattice. ^{13}C-MAS NMR spectra show different resonance signals for the homologous carbon atom of both dialkylamine branches that evidences the non-symmetric location of the amine in the cyclodextrin matrix channe [5].

In this paper we report the syntheses and characterization of a new ionic inclusion compound of the α-cyclodextrin using the homo conjugated diquinuclidinium ion as guest.

EXPERIMENTAL

Commercially available reagents were used as received. The product was obtained from a mixture of quinuclidine/quinuclidine. HCl in methanol and saturated solutions of α-cyclodextrin in water/methanol at room temperature. Diquinuclidinium guest: α-cyclodextrin host molar ratios used in the experiments were always somewhat greater than the stoichiometric relation found for the products. Microcrystals were separated immediately, washed with hot acetone and dried under vacuum at 50°C. Diquinuclidinium : α-cyclodextrin ratios were determined by both elemental microanalysis (Perkin Elmer 240C microanalyzer) and ^{1}H-NMR spectroscopy of dimethyl-d_6 sulfoxide solutions, determining the following stoichiometry : 1 diquinuclidinium$^{+}\cdot Cl^{-}$: 3 α-CD, Scanning Electron Microscopy (SEM) was realized in a Phillips EM100 Microscopy. Solution ^{1}H and ^{13}C high resolution NMR spectra were recorded on a Bruker AMX-300. The ^{13}C cross-polarization magic angle spinning (CP MAS) NMR spectra were recorded on a Bruker AMX-300 spectrometer at a frequency of 75.432 MHz for ^{13}C. The number of scans was 5000 with 6.2 μs 90° pulses, 1 ms cross-polarization contact time, 50 ms acquisition time during proton decoupling and 5 s recycle delay. The polycrystalline powder samples were spun at frequency of 3.5 kHz using a Bruker CP MAS Probe. The chemical shifts are given relative to tetramethylsilane (TMS), determined *via* the use of internal standard. Powder X-ray diffractograms were recorded in the range $2^{\circ} < 2\theta < 30^{\circ}$ on a Siemens D-5000 diffractometer using Cu-K_α radiation (40 KV, 30 mA) and a graphite monochromator ($\lambda = 1.5418$ Å). Samples were ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting a preferred orientation. For all the products the

diffractograms indicated absence of any other crystalline phases than those of reported inclusion compound.

RESULTS AND DISCUSSION

Analytical as well as further characterization of the products clearly show that the specie $[Q_2H]^+$ can be accommodated by α-cyclodextrin matrix to form a stable inclusion compound with channel structure at room temperature which are similar to those obtained from the inclusion of the other guest Figure 1 [6]. Crystal inspection by Scanning Electron Microscopy (SEM) shows thin hexagonal needles. This morphology is consistent with a hexagonal crystalline system, Figure 2. All peaks in the diffractograms of α-CD-$[Q_2H]^+$ inclusion compound can be indexed on the basis of a hexagonal lattice with parameter values close to $a = b \approx 27\,Å$, $c \approx 16\,Å$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ corresponding to channel structure of α-cyclodextrin matrix in which guest molecules are stacked [6]. A typical indexed diffractogram for the α-CD inclusion compound is shown in Figure 3. Considering the size of quinuclidine molecule and the dimensions of van der Waals cavity of α-cyclodextrin is possible to propose a structure with the diquinuclidinium ion included in two α-cyclodextrin units. Figure 1 shows a schematic representation of the inclusion of $[Q_2H]^+$ in α-cyclodextrin.

The cyclodextrin molecules takes on the shape of a cone with C2 and C3 hydroxyls groups located around the larger opening and the more reactive C6 hidroxyl aligned around the smaller opening [1–3]. The arrangement of C6 hydroxyl opposite to the hydrogen bonded C2 and C3 hidroxyl forces the oxygen bonds into close proximity within the cavity, leading to an electron rich, hydrophobic interior. In the synthesized inclusion compound the matrix channel is formed by these cones unities which interact through van der Waals forces and are ordered to encounter the similar

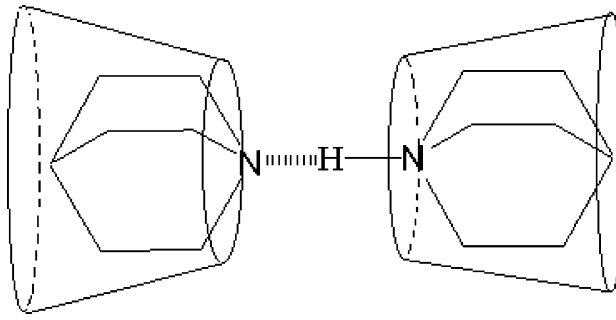

FIGURE 1 Schematic representation of α-CD-$[Q_2H]^+$ inclusion compound.

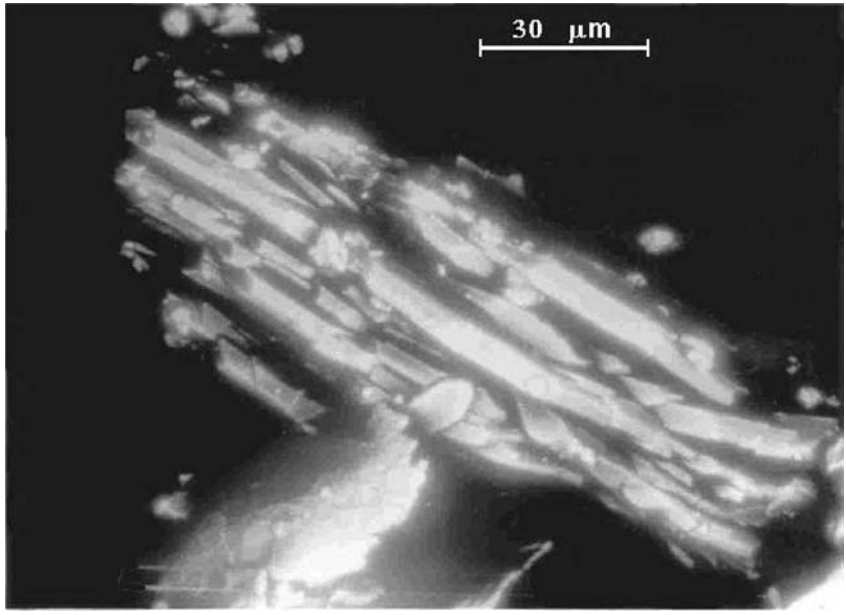

FIGURE 2 Crystal inspection by Scanning Electron Microscopy (SEM) showing the thin hexagonal needles.

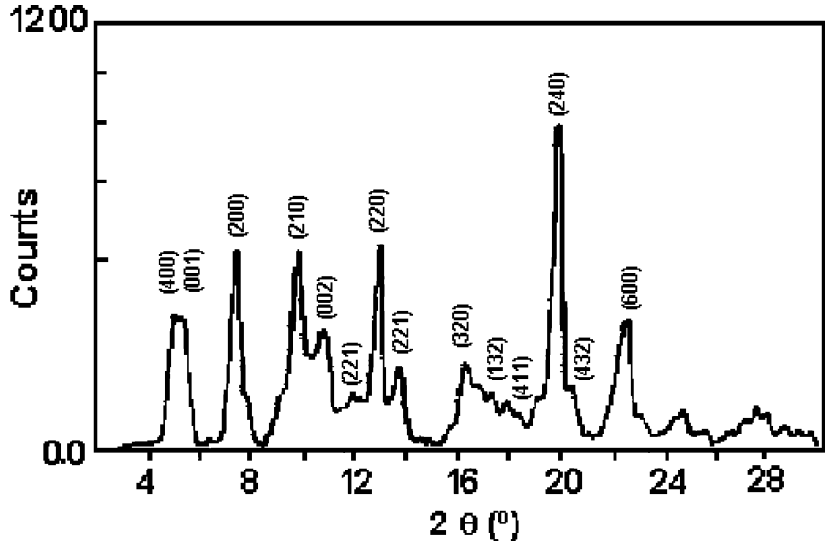

FIGURE 3 A typical indexed diffractogram for the α-CD-$[Q_2H]^+$ inclusion compound.

TABLE I Chemical Shifts (ppm) of $[QH]^+$ Inserted in the α-cyclodextrin and Quinuclidine in $CDCl_3$

Guest $[Q_2H]^+$ assignment	Medium $CDCl_3$ 10% v/v α-CD	
$C_{1\alpha}$	47.79	48.05
C_2	26.76	27.04
C_3	20.88	21.04

end of neighbouring units (larger opening-larger opening). In the inclusion of the $[Q_2H]^+$,$-NH^+N-$ group of the guest could be located at the extreme boundary of a cyclodextrin unit, in the rich electron space density with the alkyl bicycle located in the non polar and poor electron density zone of the cyclodextrins cavities. The ^{13}C-chemical shifts of the amine carbon atoms inside of the cavity of cyclodextrin are higher than for the amine in diluted solution of $CDCl_3$, that is consistent with a weaker interaction with the medium in the inclusion compound than the amine dissolved in a relatively inert solvent (Table I). Figure 4 shows the ^{13}C CP MAS NMR spectrum of the γ-CD-$[Q_2H]^+$ inclusion compound. Similar results have been obtained with urea-secondary alkylamines systems, where the ^{13}C-chemical shifts of the amines inserted in urea matrix are similar to the corresponding for a free amine or at least for an amine in a weak interactions medium like amine dissolved in an inert solvent [7]. The highest

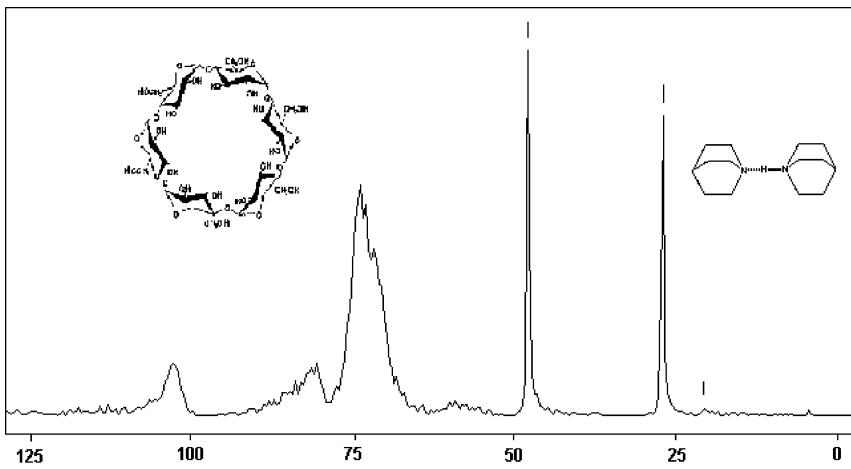

FIGURE 4 ^{13}C CP MAS NMR spectrum of the α-CD-$[Q_2H]^+$ inclusion compound.

^{13}C-chemical shifts corresponding to the C_1–C_2 carbon atom, probably due that the terminal carbon atoms are located between the cones outer of the cyclodextrins.

From the results discussed above, it can be concluded that cyclodextrin, in presence of $[QH]^+$ and Q, form solids inclusion compounds accommodating the guest $[Q_2H]^+$ in channels.

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