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Metallic nanoparticle tropism of alkylthiol guest molecules included into α-cyclodextrin host

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The migration of octanethiol, decanethiol and dodecanethiol guest molecules included in the cavities of the channel-type structure of α-cyclodextrin matrix in the presence of gold nanoparticles (AuNPs) was studied by powder X-ray diffraction. This behaviour has been called *metallic nanoparticle tropism*. The phenomena behaviour can be associated to the guest (thiol group)–AuNP interaction. This is evidenced by an increase of the lattice parameters, especially the *c*-axis, because to that AuNPs induce a shift of the guest molecule left outside the (001) plane, stabilising the nanoparticle and arranging them in an ordered way.

Keywords: metallic tropism; α-cyclodextrin inclusion complexes; gold nanoparticles; α-CD–alkylthiol

Introduction

Cyclodextrin inclusion compounds (α-CD IC), particularly those leading to supramolecular self-assemblies, continue to be a fascinating topic in modern organic chemistry as they serve as models for understanding molecular recognition and as precursors for designing novel nanomaterials (*1*) and for electronics and biological applications (*2*).

On the other hand, renewed interest in metal clusters and colloidal particles has given rise to an expanding area of interdisciplinary research. For example, colloidal gold particles can be modified with cyclodextrin (CD) as molecular receptor (*3–5*) or by the phase transfer of nanoparticles in liquids of different polarity (*6, 7*).

CDs are of interest to synthetic chemists because they are chemically stable and can be modified in a regioselective manner. These molecules are of great importance in supramolecular chemistry, since they form a series of water-soluble host molecules that can be used as models for studying weak interactions. CDs are widely used in pharmaceutical science, catalysis, drug delivery and more recently in the field of chemical nanostructures (*8–10*).

It has already been reported that α-cyclodextrin matrix (α-CD) forms three types of structural packing: the so-called 'cage type', 'layer type' and 'channel type' (*8*). For the channel structure, two possible arrangements of the α-CD hosts exist, namely head-to-tail and head-to-head orientations.

Complexes with 2:1 stoichiometry between the α-CD host and guest molecules with an extended hydrocarbon chain have been studied by NMR spectroscopy and powder XRD (*11*). Valeric acid, 1-octanol (*12*), dialkylamine (*13*) and lauric acids (*14*) are examples of guest molecules that form channel inclusion compounds of hexagonal symmetry with α-CD.

By contrast, the α-CD adducts with the linear bifunctional aliphatic compounds 1,12-diaminododecane (*15*) and 12-aminododecanoic acid (*16*) crystallise to form pseudorotaxanes and have successfully been characterised by single-crystal X-ray diffraction. Despite extensive research, it has not yet been possible to determine the structure of α-CD complexes with linear monofunctional aliphatic guests. In this contribution, we report the first evidence, obtained from powder X-ray diffraction studies, of a migration of a guest molecule included in a supramolecular host structure towards the metal nanoparticle. We are calling this shift as metallic nanoparticle tropism. This migration has been attributed to the interaction between the ─SH group (guest), which is close to the edge of the opening of the channel (as a result of its hydrophilic character), with the AuNPs, producing a movement of molecules through the channel matrix of the α-CD. This shift allows the ─SH group to be exposed as a protrusive outside the plane of the crystal, allowing interaction with the metal.

The sequential movement of the guest's molecules generates a disorder with the loss of periodicity of such molecules.

Experimental section

Reagents. Chemicals in this work were used as obtained from commercial sources.

Synthesis. The three α-CD inclusion compounds (octanethiol (OT), decanethiol (DT) and dodecanethiol (DDT)) were synthesised directly by mixing alkylthiols

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Table 1. Calculated and observed X-ray powder diffraction pattern of inclusion complexes.

hkl	I_{obsd}/I_{max} (%)	d_{cal} (Å)	d_{obsd} (Å)	hkl	I_{obsd}/I_{max} (%)	d_{cal} (Å)	d_{obsd} (Å)
α-CD/OT				*2α-CD/DT*			
410	100	4.495	4.490	410	100	4.476	4.460
001	29	15.929	15.824	001	8	16.020	15.924
110	43	11.892	12.039	110	28	11.842	11.905
111	2	9.503	9.530	111	2	9.523	9.446
210	53	7.785	7.740	210	10	7.753	7.874
102	57	7.429	7.372	102	26	7.461	7.409
300	56	6.866	6.882	300	30	6.837	6.847
112	4	6.618	6.570	301	1	6.288	6.188
202	1	6.300	6.359	220	2	5.921	5.911
220	3	5.946	5.942	221	8	5.554	5.517
310	2	5.713	5.815	302	2	5.200	5.248
221	10	5.571	5.493	400	4	5.128	5.091
302	5	5.200	5.242	320	4	4.706	4.689
400	2	5.149	5.096	104	12	3.931	3.932
113	2	4.848	4.868	331	5	3.833	3.859
312	30	4.642	4.603				
500	6	4.120	4.150				
322	11	4.064	4.036				
330	13	3.964	3.949				
2α-CD/DDT							
410	100	4.451	4.449				
001	4	15.954	15.607				
110	23	11.777	11.777				
111	1	9.475	9.488				
002	3	7.977	8.102				
210	7	7.710	7.817				
102	17	7.429	7.322				
300	27	6.800	6.789				
220	2	5.889	5.879				
221	6	5.524	5.510				
400	2	5.100	5.077				
104	14	3.914	3.918				
331	3	3.812	3.831				

(1.5 mmol) with a saturated solution of α-CD (0.50 mmol) in water (10 ml) at room temperature. The immediate formation of a white precipitate shows the formation of the IC. The guest-to-α-CD molar ratio used in the experiment was 3:1, greater than the stoichiometric ratio determined by ^{1}H NMR and elemental analysis. Microcrystals were separated after 48 h, washed with hot acetone and dried under vacuum at room temperature (*17*). Microcrystals of the inclusion compound were spread on a glass surface to form a homogeneous layer prior to being exposed to sputtering. Gold was deposited on the substrate in an inert atmosphere at room temperature (*10*).

Characterisation

XRD data were collected at room temperature on a Siemens D 5000 powder diffractometer, with Cu Kα radiation in the range $2° < 2\theta < 80°$ (40 kV, 30 mA) and a graphite monochromator ($\lambda = 1.540598$ Å). Samples of α-CD/OT, 2α-CD/DT and 2α-CD/DDT inclusion compounds, and those that interacted with the nano-particles, were ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting a preferred orientation. The diffractograms of the products indicated the absence of any crystalline phases other than those of the reported inclusion compounds.

Studies of the α-CD–alkylthiols/AuNPs confirm that the basic structure of the matrix remains unchanged. The diffractograms show some additional peaks of relatively low intensity, characteristic of the fcc metal phases of gold nanoparticles (AuNPs).

The lattice parameters and refinement were calculated by the ITO method, which is the basis of the theoretical powder X-ray computer program.

Results and discussion

Analysis as well as further characterisation of the inclusion compounds clearly show that thiols $CH_3(CH_2)_nSH$ with $n = 7, 9$ and 11 can be accommodated by the α-CD to form

Table 2. Comparison of unit cell parameters of hexagonal α-CD–alkylthiol phases.

Phase	a (Å)	b (Å)	c (Å)	V (Å³)
α-CD/OT	23.78(14)	23.78(14)	15.93(11)	7804.31
2α-CD/DT	23.68(11)	23.68(11)	16.01(9)	7782.74
2α-CD/DDT	23.55(8)	23.55(8)	15.95(6)	7665.86

stable inclusion compounds with channel structures at room temperature, which are similar to those obtained from the inclusion of other guest (*13, 18*). In these inclusion complexes, the thiol guests occupy one CD unit for OT and two CD units for DT and DDT. The three guests probably present an extended linear (*zigzag*) conformation. The space periodicity along the prism's axis, calculated from the spacing of the CD matrix crystallographic layer line, is comparable with the predicted length of the guests (OT: 10.26 Å, DT: 12.80 Å and DDT: 15.28 Å, in the extended linear conformation).

The indexing of the X-ray powder diffractograms shows that the phases of the inclusion complexes correspond to a channel-type structure with a maximum reflection of $2\theta \approx 19.8°$ ($d = 4.4$ Å). All peaks can be indexed as a hexagonal lattice (6/*mmm*) whose parameters are: $a = b \approx 23.7$ Å, $c \approx 15.9$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for α-CD.

The values of the |a| and |b| cell units obtained for the α-CD complexes studied do not agree with those reported for similar guests, including dialkylamines (*13, 19*). However, the dimensions of the a and b axes obtained by us were similar to those reported in the α-CD/cyclopentanone complex, whose structure was elucidated by neutron diffraction (*20*) and with the values obtained for the
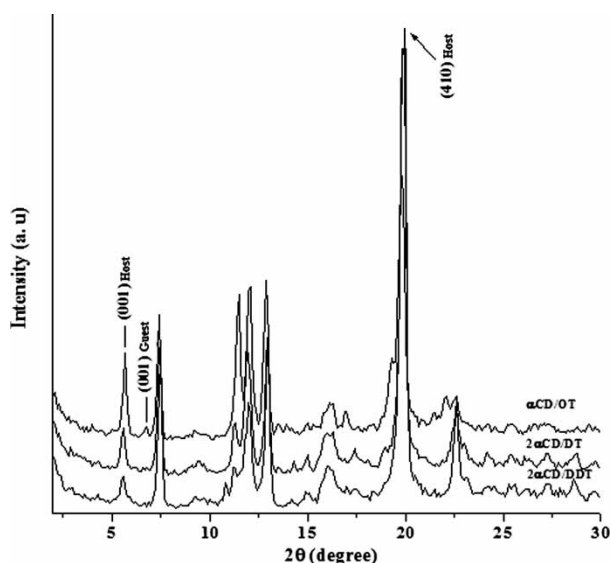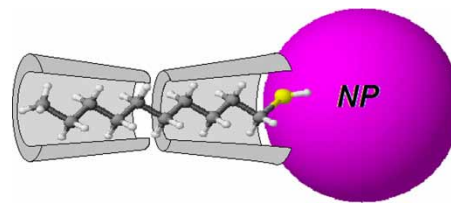

Figure 2. Schematic representation of the interaction between a nanoparticle and the CD IC.

Table 3. Lattice parameters of the inclusion complexes interacting with AuNPs.

Phase	a (Å)	b (Å)	c (Å)	V (Å³)
α-CD/OT/AuNPs	23.94(8)	23.94(8)	16.13(6)	8007.72
2α-CD/DT/AuNPs	23.79(2)	23.79(2)	16.04(2)	7862.16
2α-CD/DDT/AuNPs	23.60(4)	23.60(4)	15.84(3)	7643.55

monocrystal structure of the α-CD/octanoic acid complexes (*21*).

The observed and calculated interplanar spacing of the host lattice (d_{hkl}) and the unit cell constants are displayed in Tables 1 and 2, respectively.

Moreover, these features correspond to a 2D array of hexagonal channels along which the translation repeat unit c of about 16 Å is always the same, regardless of the size of the guest, agreeing therefore with the basic host structure observed for the α-CD–alkylthiol inclusion compounds.

The diffractograms reveal for α-CD/OT that in addition to the peaks of the host structure, one peak corresponding to the guest reflection may be identified: $2\theta = 6.80°$ ($d = 12.97$ Å; Figure 1).

This peak disappears when the guest is interacting with AuNPs due to the guest's disorder, with loss of periodicity. This disorder is a consequence of a shift of the guest towards AuNPs, which we have called metallic nanoparticle tropism (Figure 2).

The space periodicity of the guest species along the channels, which due to the good quality of the diffractograms can be unequivocally obtained for the three complexes studied (*vide supra*), is comparable with the length of the guest molecule in its most extended linear conformation.

This is evidenced by an increase in the lattice parameters, especially the c-axis, because the AuNPs induce a shift of the guest molecule, forcing it to leave the plane (001) and generating this increase (Table 3).

This peak appears only in the supramolecular structure in which the OT molecule is the guest, and it does not appear with the other two. This phenomenon has been attributed to the fact that this compound is made up of only one cone of α-CD and not two cones as in the other structures.

In the α-CD/OT complex (1:1 stoichiometry), each —SH group of the guest molecule interacts with the —OH groups that are on the edge of the α-CD, because the length

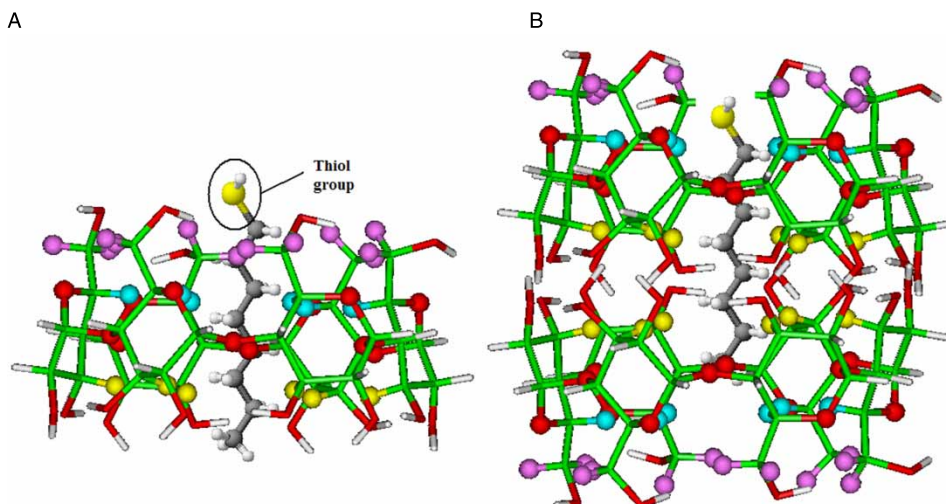Figure 1. Indexed powder X-ray diffractogram of the matrix in the three inclusion compounds at 295 K.

Figure 3. Approximate representation of two conformations of the α-CD/OT inclusion compound. (A) One α-CD interacting with a guest and (B) α-CD dimer inclusion complex.

of channel is comparable with the length of the guest, anchoring the OT molecule to the matrix and generating the periodicity. On the other hand, in the remaining complex (2:1 stoichiometry), the expected peak at a distance corresponding to 25 Å is not seen. This is probably caused by disorder at room temperature. This is shown in Figure 3.

Conclusion

This work gives the first evidence of the metallic nanoparticle tropism of a guest molecule included in a supramolecular structure. This phenomenon is caused by the interaction of the thiol group of the guest with the AuNP, stabilising and arranging the nanoparticles in an ordered way.

Note

1. On leave of absence from the Departamento de Química, Facultad de Ciencias Básicas, UMCE, Santiago, Chile.

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