

A Platinum(II) Diamino- β -cyclodextrin Complex: A Crystallographic and Solution Study. Synthesis and Structural Characterization of a Platinum(II) Complex of 6A,6B-Diamino-6A,6B-dideoxycyclomaltoheptaose

Vincenzo Cucinotta,[†] Giulia Grasso,[‡] Sonia Pedotti,[‡] Enrico Rizzarelli,^{*,§} Graziella Vecchio,^{*,§} Benedetto Di Blasio,^{⊥,||} Carla Isernia,[⊥] Michele Saviano,^{*,||} and Carlo Pedone^{||}

Dipartimento di Scienza degli Alimenti, Università di Napoli "Federico II", Via Università' 100, 80055 Portici, Napoli, Italy, Istituto per lo Studio delle Sostanze Naturali di Interesse Alimentare e Chimico Farmaceutico, CNR, v.le A. Doria 6, Catania, Italy, Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 8, 95125 Catania, Italy, Facoltà di Scienze Ambientali, Seconda Università di Napoli, via Arena, 22, Caserta, Italy, and Biocrystallography Research Centre, CNR, Dipartimento di Chimica, Università "Federico II" di Napoli, via Mezzocannone 4, I-80134 Naples, Italy

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The new platinum(II) complex of 6A,6B-diamino-6A,6B-dideoxycyclomaltoheptaose was synthesized and characterized by spectroscopy (NMR, FAB MS, UV, c.d.) and X-ray diffraction analysis. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 26.970(2)$, $b = 15.102(2)$, and $c = 16.142(2)$ Å. The Pt(II) has a square-planar coordination with two chlorine atoms and two amino groups in a cis disposition. The complexation with the Pt(II) induces a distortion of the cavity. The hydrogen bonds on the secondary hydroxyl groups, which involve the functionalized rings, are longer and consequently weaker than the other hydrogen bonds.

Introduction

Cyclodextrins (CDs) are a series of oligosaccharides consisting of D-glucopyranose units (generally six, seven, or eight) α -1,4 linked in a cyclic array.^{1,2} The main feature of the more common CDs and their derivatives is that these molecules are good hosts toward guests ranging from very polar molecules such as inorganic anions, water and alcohols, to apolar molecules such as hydrocarbons.^{1–4} The nature of the weak forces involved in the host–guest complex formation has been investigated. The cooperation of these forces often determines a very specific interaction of the CD with the guest.^{5,6} The functionalization of CDs can modify the nature of the binding interactions and increase the selectivity of the interaction.^{6,7}

Metal ion–CDs systems have been investigated, reviewed, and classified according to the CDs present in the first, second, or third coordination sphere of the metal ion.⁸

The inclusion complexes of the CDs with organotransition-metal complexes have been studied,^{8–14} and a number of solid-state structures have been reported.^{9,10,12,14} Examples are the inclusion complex of the antitumour cyclobutane-1,1-dicarboxylatediamineplatinum(II) (carboplatinum)⁹ with α -CD and of the trialkylphosphaneplatinum(II) with β -CD.¹⁰ In both these cases, the structure of the inclusion complex permits to the platinum(II) ion to stay outside the cavity, probably as a consequence of its ionic charge.

The CDs functionalized by appropriate groups can act as first coordination sphere ligands and their metal complexes have been largely investigated^{15–28} as abiotic molecular receptors,^{22–24}

[†] Università di Napoli "Federico II".

[‡] Istituto per lo Studio delle Sostanze Naturali di Interesse Alimentare e Chimico Farmaceutico.

[§] Università di Catania.

[⊥] Seconda Università di Napoli.

^{||} Biocrystallography Research Centre.

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metallo enzyme models, or potential drugs.²⁵ Among these, the first example of platinum(II) complexes has been recently reported by some of us.²⁶ We have synthesized the β -CD functionalized on a primary position with the ethylenediamine or propylenediamine, and we have characterized the platinum(II) complexes of these ligands. However these complexes have shown a low antitumour activity.²⁶

Recently, attempts have been made to selectively accumulate *cis*-platinum or other pharmacological compounds in the tissues (drug targeting) to reduce toxicity maintaining therapeutic efficacy. Crown ethers have been proposed to increase the solubility of some drugs and to increase the membrane permeability.²⁹

Here we report the synthesis and the characterization of the platinum(II) complex with the 6A,6B-diamino-6A,6B-dideoxycyclomaltoheptaose, a new CD derivative recently synthesized by some of us.³⁰

The disposition of the two amino groups permits a prediction of a *cis* complex which can be considered an analogous of the known *cis*-platinum. The *cis* arrangement of the two nitrogens, which can strongly complex to the Pt(II), is a very important requisite for the anticancer activity of the platinum(II) complexes.³¹ The presence of a sugar residue as the ligand determines a higher solubility in water in comparison with the *cis*-platinum, as shown for other Pt(II) complexes containing sugar residues.

Experimental Section

K_2PtCl_4 was purchased from Sigma. Merck Lichroprep Rp-8 (40–63 μ m) was used for reversed-phase column chromatography. TLC was carried out on silica gel plates (Merck 60-F254). CD derivatives were detected with anisaldehyde reagent. 6A,6B-Diamino-6A,6B-dideoxycyclomaltoheptaose (A,B-CDNH₂) was synthesized as reported elsewhere.³⁰

NMR spectra were recorded with a Varian UNITY 400 spectrometer equipped with a SUN SPARC station 330, at 400 MHz ¹H and at 100.6 MHz ¹³C without reference compound.

Electronic spectra and c.d. spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer and on a J-600 dichrographs, respectively.

Both the NMR and electronic spectra were carried out on freshly prepared solutions. No change was observed on the spectra carried out on the same solution few days after its preparation. The presence of chloride (0.5 M) in the solutions did not modify the spectra.

Synthesis of Dichloro 6A,6B-Diamino-6A,6B-dideoxycyclomaltoheptaose Platinum(II) ([Pt(A,B-CDNH₂)₂Cl₂]). An aqueous solution (0.5 mL) of K_2PtCl_4 (0.017 g) was added to a solution of ABCDNH₂ (0.47 g) in water, under stirring. The reaction was carried out under nitrogen at 60 °C for 3 h; after that no further variation of the UV spectrum of the reaction mixture was observed. The solvent was

Table 1. Crystal Data and Structure Refinement Parameters

empirical formula	PtCl ₂ C ₄₂ H ₇₂ N ₂ O ₃₃ ·13H ₂ O
crystal size	0.3 × 0.2 × 0.2 mm ³
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁
unit-cell dimensions	<i>a</i> = 26.970(2) Å <i>b</i> = 15.102(2) Å <i>c</i> = 16.142(2) Å
volume	6575(1) Å ³
<i>Z</i>	4
molecular weight	1633.2 uma
density (calculated)	1.649 g/cm ³
absorption coefficient	5.75 mm ⁻¹
wavelength/temp	1.541 84/293 K
scan type	ω -2 θ
index ranges	0 ≤ <i>h</i> ≤ 33; 0 ≤ <i>k</i> ≤ 18; 0 ≤ <i>l</i> ≤ 19
reflections collected	6880
independent reflections	6846
obsd reflections [<i>I</i> ≥ 3 σ (<i>I</i>)]	4656
refinement method	full-matrix least-squares on <i>F</i>
data/restraints/parameters	4656/0/848
goodness of fit on <i>F</i>	2.506
final <i>R</i> indexes [<i>I</i> ≥ 3 σ (<i>I</i>)]	<i>R</i> = 0.049, <i>R</i> _w = 0.053
largest diff peak and hole	0.54 and -0.413 e Å ⁻³

evaporated. The resulting solid was purified by chromatography using an Rp 8 column and a linear gradient of H₂O–EtOH (0→10%) as the eluent. Yield 80%. *R*_f = 0.2 (PrOH/H₂O/AcOEt/NH₃ 5:3:1:2). ¹H NMR (400 MHz, D₂O) 5.17–5.00 (m, 8H, H-1 and H-5N), 4.72 (m, 1H, H-5N'), 4.25–3.56 (m, 35H, H-5, -6, -3, -4, -2), 3.47 (t, 2H, H-4N, -4N'), 3.31 (d, 1H, H-6N), 2.78 (dd, 1H, H-6N'), 2.49 (t, 1H, H-6'N). ¹³C NMR (100.6 MHz, D₂O) 106.1–101.8 (1-C), 85.3–80.3 (4-C), 74.9–71.9 (2-, 3-, 5-C), 61.0–62.0 (6-C), 49.6 (6N-C or 6N'-C), 46.4 (6N'-C or 6N-C). FAB MS *m/e* 1400 (*M* + 1), 1365 (*M* – Cl + 1).

X-Ray Diffraction Analysis. Colorless crystals of [Pt(A,B-CDNH₂)₂Cl₂] were obtained at room temperature by slow evaporation of a D₂O solution. A crystal of dimensions 0.3 × 0.2 × 0.2 mm³ was used for X-ray diffraction analysis. Unit-cell parameters were determined by least-squares refinement of the setting angles of 25 carefully centered reflections in the range 15° < 2*d* in Table 1. All measurements were made on a CAD4 Enraf Nonius diffractometer with graphite-monochromated Cu K α radiation at the Centro di Studio di Biocristallografia of CNR. The data were collected at room temperature using the ω -2 θ scan technique.

A total of 6846 independent reflections were measured and corrected for Lorentz and polarization factors. No corrections for the absorption were done. Of these, only 4656 reflections were considered as "observed", having net intensity *I* ≥ 3.0 determination procedure, using the SIR92³² program. The best E-map revealed all of the non-hydrogen atoms and the oxygen atoms of some cocrystallized water molecules. Subsequent difference electron density maps revealed the positions of the water molecules. The structure was refined using the full-matrix least-squares program in the SDP package³³ on *F*_o values. The refinement was carried out on 848 parameters, including atomic coordinates and anisotropic thermal factors. All hydrogen atoms were included in their stereochemically expected positions with thermal factors equal to the equivalent *B* of the carrier atom, except those of the water molecules. The refinement of the occupancy factor of water molecules indicated a total of 13 water molecules per β -CD molecule distributed over 14 sites, 12 of which were refined with full occupancy and the remaining 2 with a site occupancy factor of 0.5. Scattering factors were taken from International Tables for X-ray Crystallography.³⁴ The structure was refined to final indexes *R* = 0.049 and *R*_w = 0.053. Refinement was ended when the shifts in the atomic

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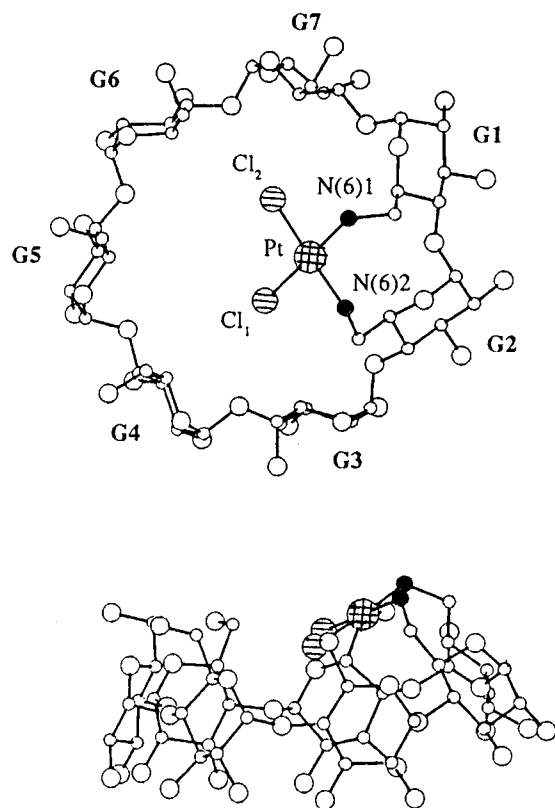


Figure 1. Molecular model of $[\text{Pt}(\text{A,B-CDNH}_2)_2\text{Cl}_2]$

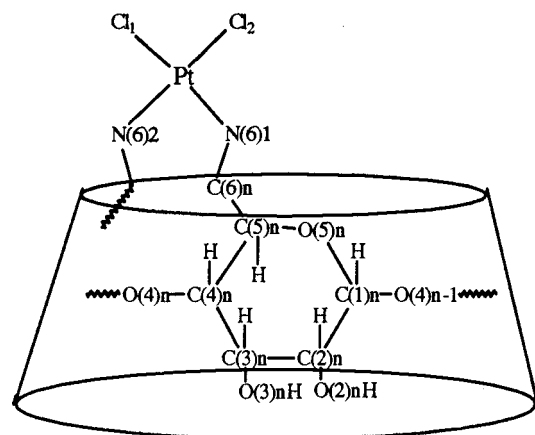


Figure 2. Atom numbering scheme of $[\text{Pt}(\text{A,B-CDNH}_2)_2\text{Cl}_2]$

coordinates and temperature factors were less than $1/5$ and $1/3$ of the corresponding standard deviations, respectively.

Results

The synthesis of the Pt(II) complex was carried out in good yield: the two amino groups in the A,B position seem to be preorganized to form the cis complex.

X-ray Analysis. The molecular model of the $[\text{Pt}(\text{A,B-CDNH}_2)_2\text{Cl}_2]$ structure is represented in Figure 1 with the indication of the numbering of the glucose residues and the numbering of the coordination atoms. The numbering of the atoms in the glucopyranosinic ring is reported in Figure 2. Geometrical data for the glucose residues are reported in Table 2. A selection of torsion angles which define the linkage bonds between the glucose units and the orientation of the primary hydroxyl groups and the Cremer and Pople puckering parameters of glucose units³⁵ are given in Table 3 and 4. Glucose units

Table 2. Geometrical Data

residue	radius (Å) ^a	distance (Å) ^b	angle (deg) ^c	tilt angle ^d	planarity ^e
G1	5.05	4.47	121.8	29.2	-0.34
G2	4.65	4.51	133.2	33.5	0.31
G3	5.01	4.35	127.2	5.8	0.09
G4	5.33	4.34	126.1	15.9	-0.22
G5	5.28	4.39	128.2	17.4	-0.13
G6	5.06	4.42	131.6	11.0	0.38
G7	5.09	4.34	127.8	8.2	-0.09

^a The radius is measured from the centre of gravity of the seven O(4) atoms to each O(4) atom. ^b The distance is defined as the O(4)_n-O(4)_{n+1} distance. ^c The angle is defined as the O(4)_{n-1}-O(4)_n-O(4)_{n+1} angle. ^d The tilt angle is defined as the angle made by O(4) atoms plane and the plane formed by O(4)_{n+1}, C(1)_n, C(4)_n, O(4)_n of each glucose residue. ^e Planarity is defined as the rms deviation of each O(4)_n atom from the least-squares plane of the seven O(4) atoms.

are in the usual ⁴C₁ chair conformation with a small degree of flexibility with the exception of the G7 glucose unit with a θ value of 12°. However, the average total puckering amplitude Q for all residues (0.56 Å) is slightly lower than the corresponding value for an ideal cyclohexane chair (0.63 Å). In addition, the parameters, which give a measure of the ring distortion, are in the range 1.29–12.0 Å. The comparison of these values with those reported for the structure of 6A,6B-diamino-6A,6B-dideoxycyclomaltoheptaose [θ range 1.2–8.6°]³⁰ reveals a major distortion of the glucose rings. All primary hydroxyl groups (O(6)_n, $n = 3,7$) assume the gauche⁻-gauche⁺ orientation (mean torsion angle O(5)-C(5)-C(6)-O(6) and C(4)-C(5)-C(6)-O(6) -65.0° and 55.4°, respectively). Consequently, these groups point "away" from the center of the cavity to form hydrogen bonds with water molecules and neighboring β -CD molecules. On the contrary, the N(6)_n ($n = 1,2$) groups present a gauche⁺-trans orientation and point "inward" toward the center of cavity.

The macrocycle structure maintains an approximative 7-fold symmetry. The seven glucosidic(4) atoms are almost coplanar with maximum deviations from the least-squares plane of 0.38, 0.34, 0.31, and 0.22 Å for the O(4) atoms of units 6, 1, 2, and 4, respectively. The O(4) atoms form a heptagon with the radii (distances between the center of gravity of the seven O(4) atoms and each O(4) atom) and side lengths (the distance between two consecutive O(4) atoms), given in Table 2, in the ranges 4.65–5.33 and 4.34–4.51 Å. The angle between three O(4) atoms of consecutive glucose units (O(4)_{n-1}-O(4)_n-O(4)_{n+1}) is on the average 128.0°. These values are in good agreement with that found for other functionalized and unfunctionalized β -CDs.^{36–38}

The dihedral angles (tilt angles) between the O(4) plane and the optimum planes of the C(1), C(4), O(4), O(4') atoms for each glucose residue are in the range 5.8–33.5° (Table 3) with the higher values for the functionalized G1 and G2 units, involved in the coordination. The intramolecular (O(2)_n-O(3)_{n-1}) hydrogen bonds (Table 5a) that stabilize the round structure of the β -CD macrocycle are in the range 2.78–2.86 Å in agreement with those expected for similar distances observed in other β -CD structures,^{30,33,34} except for that around the functionalized G1-G2 units. In fact, these units present H bonds in the range 3.08–3.46 Å, longer and consequently weaker with respect to the others.

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Table 3. Selected Torsion Angles (deg) Describing the Linkage Bonds between the Glucose Residues and the Orientations of the Primary Hydroxyl

	G1	G2	G3	G4	G5	G6	G7
C(3) _n -C(4) _n -O(4) _n -C(1) _{n+1}	139.0	117.9	132.4	127.0	121.1	118.8	143.5
C(5) _n -C(4) _n -O(4) _n -C(1) _{n+1}	-100.8	-123.2	-108.9	-111.2	-116.5	-120.3	-97.7
O(5) _n -C(1) _n -O(4) _{n-1} -C(4) _{n-1}	118.6	101.4	86.4	112.2	110.1	110.5	102.4
C(2) _n -C(1) _n -O(4) _{n-1} -C(4) _{n-1}	-119.1	-138.0	-152.9	-127.4	-127.4	-124.5	-133.4
O(5) _n -C(5) _n -C(6) _n -O(6) _n			-62.9	-69.4	-62.8	-63.7	-66.0
C(4) _n -C(5) _n -C(6) _n -O(6) _n			60.4	52.2	57.3	55.3	52.0
O(5) _n -C(5) _n -C(6) _n -N(6) _n	83.2	56.5					
C(4) _n -C(5) _n -C(6) _n -N(6) _n	-155.8	176.1					

Table 4. Puckering Parameters of Glucose Units

	G1	G2	G3	G4	G5	G6	G7
<i>Q</i> (Å)	0.56	0.57	0.55	0.56	0.55	0.57	0.55
<i>θ</i> (deg)	4.02	5.19	4.23	1.29	2.54	3.26	12.00

In Figure 3, an ORTEP view of the platinum(II) coordination is shown. In Table 6, the geometrical details of the Pt(II) coordination mode are reported. The Pt(II) atom displays the square-planar coordination with the two chlorine atoms and the two nitrogen atoms (N(6)1 and N(6)2) in a *cis* disposition. Within experimental errors, the bond lengths and bond angles do not present appreciable differences from similar systems reported in literature.³⁸ The four atoms coordinated to the metal ion lie in a plane with a very small (less than 0.023 Å) deviation from it, with the metal ion lying below this plane (0.028 Å). The coordination plane points inward toward the cavity. In fact, the square plane forms a dihedral angle with the O(4)_n plane of 28.1° with distances between the Cl(1), Cl(2), and Pt atoms and the O(4) plane being 2.08, 2.30, and 2.91 Å, respectively.

In the crystal state, as shown in Figure 4, the [Pt(A,B-CDNH₂)Cl₂] molecules form dimers symmetry related by a 2₁ screw axis, which are linked by hydrogen bonds involving the secondary hydroxyl groups. Along this direction, this arrangement gives rise to polymeric rows, held together by H bonds between primary and secondary hydroxyl atoms and by water molecules, bridging symmetry-related macrocycles. The intramolecular hydrogen bonds are shown in Figure 5. It is noteworthy that the presence of hydrogen bonds between the N(6)_n (*n* = 1, 2) and O(6)4 and O(5)5 atoms (N(6)1...O(6)4 3.09 Å, N(6)2...O(5)5 2.96 Å) further stabilize the crystal packing.

The intermolecular H bonds involve also the two chlorine atoms which act as acceptors of the H bond from the O-H groups of the Ow₁₀ and Ow₁₁ water molecules (Table 5c). In particular, the Ow₁₀ bridges the two chlorine atoms, while the other water molecule (Ow₁₁) is located in the CD cavity together with the Ow₇ and Ow₉ water molecules. In the literature, it is reported that in the β-CD cavity can be accommodated eight water molecules. For the Pt(II) complex, the steric hindrance of the coordination plane on the top of the β-CD cavity reduces the number of water molecules inside the rim cavity to three molecules.

In the crystal, except Ow₉ and Ow₁₂, which are only linked to other water molecules, all the remaining water molecules are H-bonded to hydroxyl groups, nitrogen atoms, and/or chlorine atoms.

Solution Studies. The ¹H NMR spectrum of [Pt(A,B-CDNH₂)Cl₂] (Figure 6) was assigned on the basis of the DQF-COSY spectra.

The complexation with platinum(II) induces large shifts of the peaks, due to the protons of two of the seven glucopyranosinic rings, which correspond to the substituted rings. Since with the spectra it is not possible to identify A with respect to the B ring, we attributed the generic symbols N and N' for

the two substituted rings. On the ¹H NMR spectra the resonances at 2.49(t) and 3.31(d) ppm are assigned to the two H-6N and the resonance at 2.78(dd) ppm is assigned to one of the H-6N'. The other H-6N' is in the 2,4 region at ca 3.6 ppm, as identified by the COSY spectra, and this strong downfield shift suggests that this proton is directed toward the cavity. Furthermore the COSY spectra identify the signals for the 5N and 5N' protons at 5.14 and 4.70 ppm, respectively. The resonance at 3.47 ppm is assigned to the 4-N,N' protons. In addition, the usual groups of the peaks of β-CD are present at 4.10–3.80 ppm for H-3,5,6 and 3.75–3.55 ppm for the H-2,4. Both the H-5 of the two functionalized rings show downfield shifts in comparison with the ligand alone. Furthermore, 5N and 5N' have different chemical shifts.

Three peaks are observed in the UV spectra in the 270–500 nm region. The transition assignment of the bands follows that proposed for analogous complexes.⁴⁰ They are ascribable to the spin-allowed and spin-forbidden d-d transitions, ¹A_{1g} → ³E_g (367 nm, ε = 48) ¹A_{1g} → ¹A_{2g} (307 nm, ε = 133), and ¹A_{1g} → E_g (274 nm, ε = 193). The c.d. spectra of [Pt(A,B-CDNH₂)Cl₂] show four bands, corresponding to the absorption bands described for analogous complexes.^{40,41} The band at 410 nm is not observed in the UV-vis spectra, due to its too low value. C.d. spectra were also obtained in the presence of increasing concentrations of 1-adamantanol (see Figure 7) and show how this substance influences the c.d. spectra of [Pt(A,B-CDNH₂)Cl₂]. It is known that 1-adamantanol is strongly included in the CD cavity, and it is widely used as a competitive guest.^{42–44} Thus, these spectra suggest that a contribution to the chirality of this complex is due to the interaction of the metal ion with the cavity which can act as a second-sphere coordination ligand.^{44,45} Furthermore, the 1-adamantanol inclusion should force the coordination plane out of the cavity and therefore form a smaller angle with the O4 mean plane. Thus, the observed increased intensities of all the c.d. bands at increasing concentrations of 1-adamantanol suggest that the chirality of this complex increases at decreasing angles between the two planes.

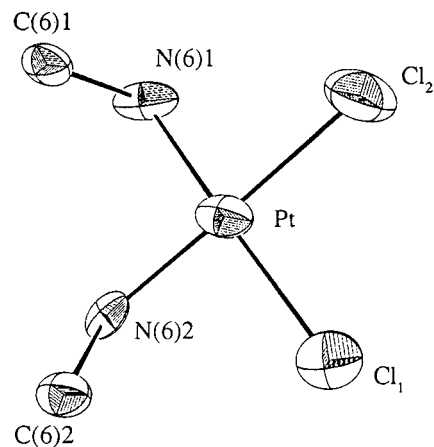
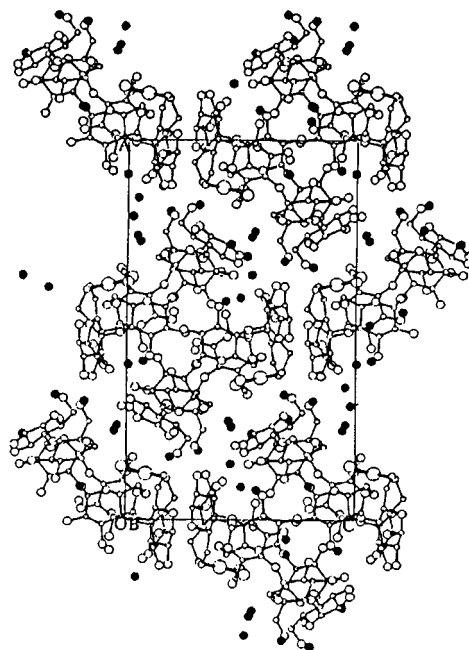
Concluding Remarks

Interestingly, the ¹H NMR results show that (i) the protons of the two substituted glucopyranosinic rings are strongly affected by the platinum(II) complexation, but each one in a different way from the other, and (ii) the remaining five glucopyranosinic rings are also affected, though only slightly. Both these spectral features parallel that observed at the solid state, as can be seen from the data in Table 3. Therefore, the

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Table 5. Inter- and Intramolecular H-Bonds

A. O(2) _n –O(3) _{n-1} Distances			
		dist (Å)	
O(2)1	O(3)7	3.08	
O(2)2	O(3)1	3.28	
O(2)3	O(3)2	3.46	
O(2)4	O(3)3	2.79	
O(2)5	O(3)4	2.84	
O(2)6	O(3)5	2.74	
O(2)7	O(3)6	2.82	
B. Intermolecular β -CD Interactions			
		dist (Å)	sym
O(2)1	O(3)4	3.22	$-x, -y - 1/2, -z - 1/2$
O(2)1	O(2)5	3.29	$-x, -y - 1/2, -z - 1/2$
O(3)1	O(6)5	2.92	$x - 1/2, -y - 1/2, -z$
N(6)1	O(6)4	3.09	$1/2 - x, -y, 1/2 + z$
N(6)2	O(5)5	2.96	$1/2 - x, -y, 1/2 + z$
O(3)2	O(2)6	2.77	$-x, y + 1/2, -z - 1/2$
O(2)3	O(2)6	3.21	$-x, y + 1/2, -z - 1/2$
O(2)3	O(3)6	2.92	$-x, y + 1/2, -z - 1/2$
O(6)3	O(6)7	3.36	$x, y + 1, z$
O(3)4	O(3)7	2.97	$-x, y + 1/2, -z - 1/2$
C. β -CD and Water Molecules Interactions			
		dist (Å)	sym
Cl ₁	Ow10	3.48	x, y, z
Cl ₁	Ow11	3.26	x, y, z
Cl ₂	Ow10	3.15	x, y, z
O(2)1	Ow1	2.92	$x - 1/2, -y - 1/2, 1 - z$
O(2)1	Ow2	3.33	$x - 1/2, -y - 1/2, -z$
O(3)1	Ow4	3.33	$x - 1/2, 1/2 - y, -z$
O(3)1	Ow13	2.75	$-x, y - 1/2, 1/2 - z$
O(3)1	Ow14	2.95	$x - 1/2, -y - 1/2, -z$
N(6)1	Ow1	3.47	$1/2 - x, -y, z - 1/2$
O(2)2	Ow4	2.93	$x - 1/2, 1/2 - y, -z$
O(2)2	Ow8	3.06	$x - 1/2, 1/2 - y, -z$
O(2)2	Ow13	2.74	$-x, y - 1/2, 1/2 - z$
O(3)2	Ow8	2.91	$x - 1/2, 1/2 - y, -z$
N(6)2	Ow1	2.97	$1/2 - x, -y, z - 1/2$
O(2)3	Ow2	2.69	$x - 1/2, 1/2 - y, -z$
O(3)3	Ow6	2.72	$-x, y + 1/2, -z - 1$
O(6)3	Ow4	2.74	$1/2 - x, 1 - y, 1/2 + z$
O(6)3	Ow5	2.74	x, y, z
O(2)4	Ow3	2.72	$-x, y + 1/2, -z - 1/2$
O(3)4	Ow14	2.63	$1/2 - x, -y, z - 1/2$
O(6)4	Ow1	2.83	$x, y, z - 1$
O(6)4	Ow8	2.66	x, y, z
O(2)5	Ow10	2.73	$1/2 - x, -y, z - 1/2$
O(3)5	Ow2	2.72	$1/2 - x, -y, z - 1/2$
O(6)5	Ow4	3.07	$x, y - 1, z$
O(2)6	Ow5	3.23	$1/2 - x, -y, z - 1/2$
O(3)6	Ow3	2.81	$-x, y - 1/2, -z - 1/2$
O(6)6	Ow5	2.72	$x, y - 1, z$
O(6)6	Ow7	2.80	x, y, z
O(2)7	Ow11	2.78	$1/2 - x, -y, z - 1/2$
O(3)7	Ow2	2.92	$x - 1/2, -y - 1/2, -z$
O(6)7	Ow4	3.26	$1/2 - x, -y, 1/2 + z$
D. Water–Water Interactions			
		dist (Å)	sym
Ow1	Ow2	2.74	$x, y, z + 1$
Ow3	Ow9	2.70	x, y, z
Ow3	Ow13	2.64	$-x, y - 1/2, 1/2 - z$
Ow4	Ow7	2.80	$x, y + 1, z$
Ow5	Ow8	3.06	x, y, z
Ow5	Ow12	2.82	$1/2 - x, -y, 1/2 + z$
Ow6	Ow9	2.78	x, y, z
Ow6	Ow11	2.88	x, y, z
Ow7	Ow8	2.86	$x, y - 1, z$
Ow7	Ow12	2.80	x, y, z
Ow9	Ow11	3.34	x, y, z
Ow10	Ow14	2.66	x, y, z
Ow12	Ow13	2.64	$x, y - 1, z - 1$

**Figure 3.** Detail of the Pt(II) coordination mode, showing the 50% probability thermal ellipsoids and the atom-labeling scheme.**Figure 4.** Crystal packing of the [Pt(A,B-CDNH₂)Cl₂] as viewed down the crystallographic *b* axis.**Table 6.** Selected Bond Lengths (Å) and Angles (deg) of the Coordination Mode of Pt(II)

Distances (Å)			
Pt–Cl ₁	2.310(4)	Pt–N(6)1	2.05(1)
Pt–Cl ₂	2.301(4)	Pt–N(6)2	2.06(1)
Angles (deg)			
Cl ₁ –Pt–Cl ₂	91.6(2)	Cl ₂ –Pt–N(6)1	87.4(3)
Cl ₁ –Pt–N(6)1	177.2(3)	Cl ₂ –Pt–N(6)2	178.1(3)
Cl ₁ –Pt–N(6)2	90.3(3)	N(6)1–Pt–N(6)2	90.4(4)

structure of the complex in aqueous solution must be very similar to that observed in the crystal.

As compared to the other structures of metal ion–CDs systems reported in literature,⁸ the [Pt(A,B-CDNH₂)Cl₂] complex here reported presents the innermost position within the cavity. In our opinion, this fact is not related to a particular affinity between the Pt(II)–Cl(1)–Cl(2) moiety and the CD cavity, but it is simply the result of the steric constraints due to the amino group coordination, as can be seen from the high values of the tilt angles (Table 2) of the substituted rings. Nevertheless, with a further distortion of angles and lengthening of bonds, particularly in the coordination plane, this plane can form a lower angle with the O4 plane, as shown by the c.d.

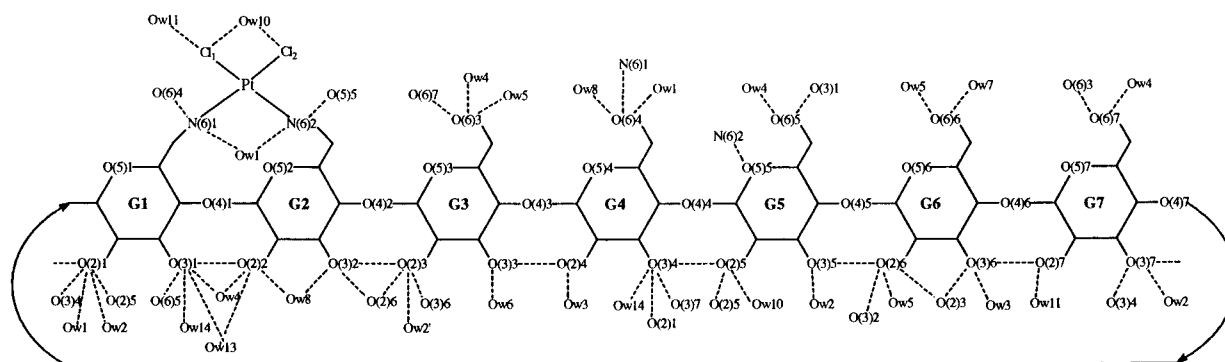


Figure 5. Hydrogen-bond scheme in $[\text{Pt}(\text{A,B-CDNH}_2)\text{Cl}_2]$

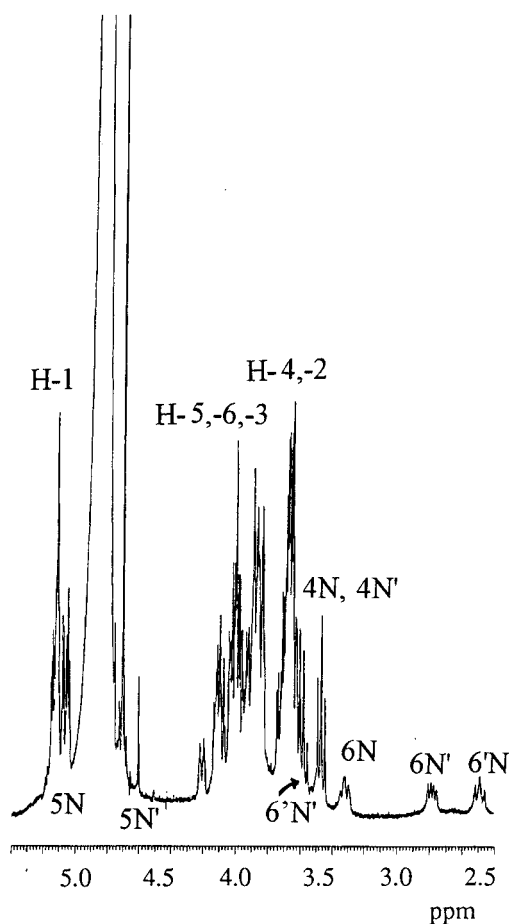


Figure 6. ^1H NMR (400 MHz, D_2O) spectra of $[\text{Pt}(\text{A,B-CDNH}_2)\text{Cl}_2]$

results in the presence of 1-adamantanol. In this system, the tendency of this guest to be included forces the platinum(II) out of the cavity, counterbalancing the destabilizing effect of the distortions thus occurring.

As regards the chirality, the c.d. titration results show that there is a contribution from the cavity. This contribution is that which is influenced by 1-adamantanol and the increase of the Cotton effect of all the bands should be related to a decrease

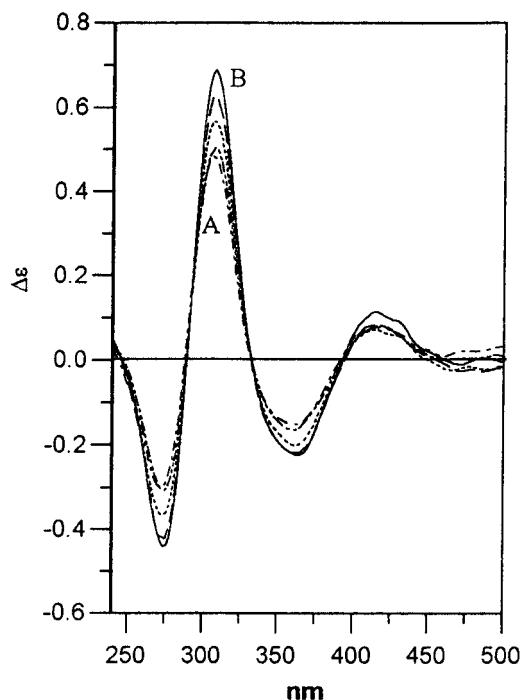


Figure 7. C.d. spectra of $[\text{Pt}(\text{A,B-CDNH}_2)\text{Cl}_2]$ alone (A) and at increasing concentration of 1-adamantanol (from A to B [$1\text{-adamantanol}] = (0\text{--}3.4) \times 10^{-3}$ M)

in the angles between the coordination plane and the O4 mean plane.

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Supporting Information Available: Tables of bond angles, bond distances, torsional angles, and general parameter displacement parameters (12 pages). Ordering information is given on any current masthead page.

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