FT–IR and Raman Spectra of a Series of Metallo-β-Cyclodextrin Complexes

MARY McNAMARA and NOEL R. RUSSELL⋆
Department of Chemistry, Dublin Institute of Technology, College of Technology, Kevin Street, Dublin 8, Ireland

Abstract. A series of metallo-β-CD complexes were prepared and formulated as $[M_2(OH)_2\beta\text{-}CD\cdot2\,H_2O]^{n-}$. Changes in the FT–IR and Raman Spectra of β-CD on coordination may be taken as evidence for complexation and support for a hydroxy bridged binuclear structure. Further support was obtained from uv/visible and magnetic moment measurements.

Key words. β-Cyclodextrin, Metallo-complex, FT–IR, Raman, Binuclear.

1. Introduction

There are many examples reported in the literature [1] of metallo-complexes in which cyclodextrin (CD) acts as a second sphere ligand. Also, several papers have reported metallo-complexes with modified CDs acting as first sphere ligands through sites on the substituent moiety, often with simultaneous second sphere interaction [2]. β-CDs functionalised with polyamines form complexes [3] with Zn(II), Cu(II) and Mg(II) in which the metal ion is outside the CD cavity.

The work reported here follows a previous report [4a] and is mainly concerned with metallo-complexes formed by the reaction of unmodified β-CD with metal ions in alkaline solution. Only two examples of this behaviour have already been reported involving Mn(III) [4] and Cu(II) [5] ions. These complexes analysed for a M : CD ratio of 2 : 1. Binuclear hydroxy-bridged structures were proposed in which each metal ion is bonded to O-2 and O-3 of adjacent pyranose rings of the β-CD (Figure 1).

In this work a series of metallo-β-CD complexes were synthesised and formulated using AA and optical rotation techniques as $[M_2(OH)_2\beta\text{-}CD\cdot2\,H_2O]$ for Cr(III) and $Na_2[M_2(OH)_2\beta\text{-}CD\cdot2\,H_2O]$ for Co(II), Ni(II) and Cu(II). It was found that the techniques employed for Cu(II) and Mn(III) complexes [5, 4b] were not generally useful in recognising complex formation. Hence FT–IR and Raman spectroscopy, backed up by uv/visible and magnetic moment measurements, were employed and found to be more informative.
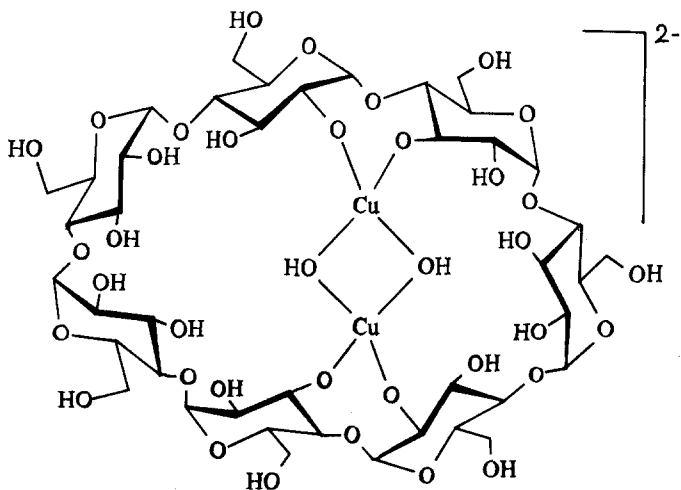

⋆ Author for correspondence.

Fig. 1.   Proposed [5] binuclear bridged structure of $[M_2(OH)_2 \cdot \beta\text{-}CD]^{n-}$ type complexes.

2. Experimental

2.1. MATERIALS

β-Cyclodextrin (Chinoin) was recrystallised from deionized, distilled water and dried at 120°C. The following analar grade metal salts were used without further purification: $Cr(NO_3)_3 \cdot 9H_2O$ (B.D.H.), $CoCl_2 \cdot 6H_2O$ (Interchem), $NiCl_2 \cdot 6H_2O$ (Reidel-de-Haen) and $Cu(CH_3CO_2)_2 \cdot H_2O$ (Merck). Dimethylformamide (Reidel-de-Haen) and dimethylsulphoxide (Aldrich) were distilled off calcium sulphate and flushed with dry nitrogen immediately prior to use.

2.2. PREPARATIONS

A series of metallo-complexes of β-CD were synthesised using either of two procedures as appropriate; the aqueous preparation of Matsui *et al.* [5] for Cr(III), Co(II) and Cu(II) complexes and the non-aqueous method of Nair and Dismukes [4(b)] for the Ni(II) complex. Slight modifications to the published procedures were adopted where necessary. In the case of Co(II), the entire synthesis was carried out in a nitrogen atmosphere. For the Ni(II) complex, final traces of organic solvent were removed by heating (50–60°C) under vacuum. All of the complexes were isolated as pale-coloured powders. They are soluble in water but are only stable at high pH values, decomposing rapidly in acidic media. The complexes are also slightly soluble in DMF and DMSO.

2.3. INSTRUMENTAL ANALYSIS

The metal ion content of the complexes was determined using a Shimadzu atomic absorption/flame emission spectrophotometer (Model AA-670) with a Shimadzu graphic printer (Model PR-4). The β-CD content was determined by fully dissociating the complexes in acid solution and determining the optical rotation using a

Bellingham and Stanley digital polarimeter (Model P10). For the metal and β-CD determinations alike, both the standard addition and normal calibration methods were employed.

2.4. INFRARED AND RAMAN SPECTROSCOPY

FT–IR spectra were recorded on KBr discs using a Perkin-Elmer Fourier transform infrared spectrometer (Model 1710). Raman spectra were obtained with the 488.0 nm line of an argon-ion laser (250 mW) on a Jobin Yvon Ramanor HG2 instrument using a spinning cell.

2.5. UV/VISIBLE AND NMR (EVANS METHOD) SPECTROSCOPY

UV/Visible spectra were obtained using a Shimadzu spectrometer (Model UV-160). Magnetic moments were determined via the Evans method [6] on a Bruker 80 MHz instrument (Model AW 80) using coaxial tubes. In the case of the Cu(II) complex it was necessary to use a Jeol 270 MHz (Model JMN GX 270) instrument in order to resolve the lines.

3. Results

Table I lists the data obtained for the determination of the metal and β-CD content for the series of metallo-β-CD complexes.

Table II lists the FT–IR frequencies for the series of metallo-β-CD complexes. Data for the Mn(III) complex [4a] and β-CD [7] are included for comparison. Figure 2 shows the FT–IR spectra of the series of metallo-β-CD complexes, together with the corresponding difference spectra.

Table II also lists the Raman frequencies (in the range 1460–865 cm^{-1}) for the series of metallo-β-CD complexes. Data obtained for β-CD [4a] is included for comparison. Figure 3 shows the corresponding Raman spectra in the 865–200 cm^{-1} range. It is useful to compare these spectra with the corresponding ones for the Mn(III)-β-CD complex and for β-CD [4a].

Table III lists the visible absorption bands and the effective magnetic moments as obtained using the Evans NMR technique. Again data for the Mn(III) complex are included for comparison.

Table I. Results of the determinations of the metal content and β-CD content of the metallo-β-CD complexes

M	%M		%β-CD		%Na	
	calc.	found	calc.	found	calc.	found
Cr(III)	7.968	7.987	86.664	86.702	–	–
Mn(III)	8.382	8.386	86.275	86.304	–	–
Co(II)	8.636	8.634	86.864	86.863	3.369	3.399
Ni(II)	8.603	8.605	82.893	82.783	3.370	3.430
Cu(II)	9.249	9.206	82.307	82.329	3.346	3.404

Table II. FT–IR absorption frequencies (cm⁻¹) and Raman frequencies of β-CD and metallo-β-CD complexes

FT–IR Frequencies (cm⁻¹)						Raman frequencies (cm⁻¹)				
β-CD [7]	Cr(III)	Mn(III) [4a]	Co(II)	Ni(II)	Cu(II)	β-CD	Cr(III)	Co(II)	Ni(II)	Cu(II)
3369	3402	3392	3378	3378	3397					
–	3240sh	–	3170sh	3270sh	3235sh					
1647	1657	1661	1650	1655	1663					
–	1575sh	–	1580sh	1580sh	1610					
–	1494sh(1505)	1566(1568)	1495sh(1515)	1497	1530					
–	–	1507sh*	–	–	–					
1463sh	1470sh	–	1465sh	1465sh	–	1459sh	1458	–	1458	–
–	–	1455sh	–	–	1450sh	1450	–	1451	–	1453
1418	1410	1415	15412	1414	1416	–	–	–	–	–
–	–	–	–	–	–	1408	–	1408sh	–	1405
–	1386*	1395	1393*	1394*	1388	1387	1382	1377	–	1376
1369	1370	1369	1365	1371	1369	–	–	–	–	–
–	1359*	1351*	1360*	1360*	1352*	–	–	–	–	–
1338	–	1338	1338sh	1340sh	1335	–	–	–	–	–

1334	1334	1332	1336	1336	–	–	–	–	–	–
–	–	–	–	1326sh	–	–	–	–	–	–
–	–	–	–	1321*	1319*	1320*	1318*	1320*	–	–
–	–	–	–	1310sh	1303sh	1310sh	1302sh	1304	1303sh	1303
–	–	–	–	–	1282*	1287*	1292*	1281*	1287*	–
1256	1261	1252	1260	1263sh	–	–	–	–	–	1262sh
–	–	–	–	1252	–	–	–	–	–	–
–	–	–	–	–	1245sh	1248	1245ssh	1246	1247	1245
–	–	–	–	–	1215sh*	1227*	1227*	1223*	1223*	–
1202	1201	1208	1205	1206	1198sh	1210sh	1204	1203sh	1205sh	1198sh
1128	1126	1122	1130	1126	–	–	–	–	–	–
–	–	–	–	1109sh	–	–	–	–	–	–
1081	1085	1077	1086	1083	–	–	–	–	–	–
1043	1047	1041	1070	1047	–	–	–	–	–	–
–	–	–	–	1034sh	–	–	–	–	–	–
1006sh	–	–	1008	1001	–	–	–	–	–	–
945	947	943	950	948	–	–	–	–	–	–
920sh	–	–	924	928	–	–	–	–	–	–
–	–	–	–	913sh	–	–	–	–	–	–
–	–	–	–	865sh	–	–	–	–	–	–

* Measured by difference spectroscopy. Frequencies in parentheses were also determined by subtraction.
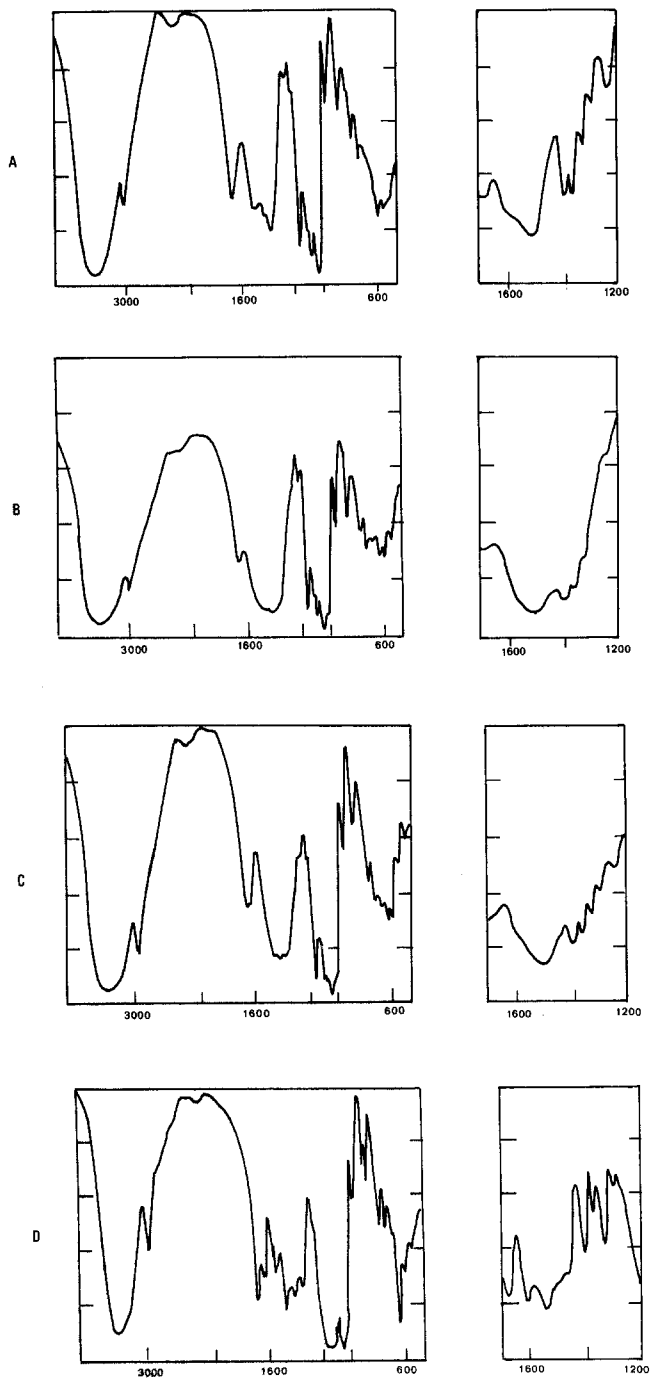
Fig. 2. The FT–IR spectra (%T) and corresponding difference spectra of (A) Cr$_2$CD, (B) Co$_2$CD, (C) Ni$_2$CD and (D) Cu$_2$CD.
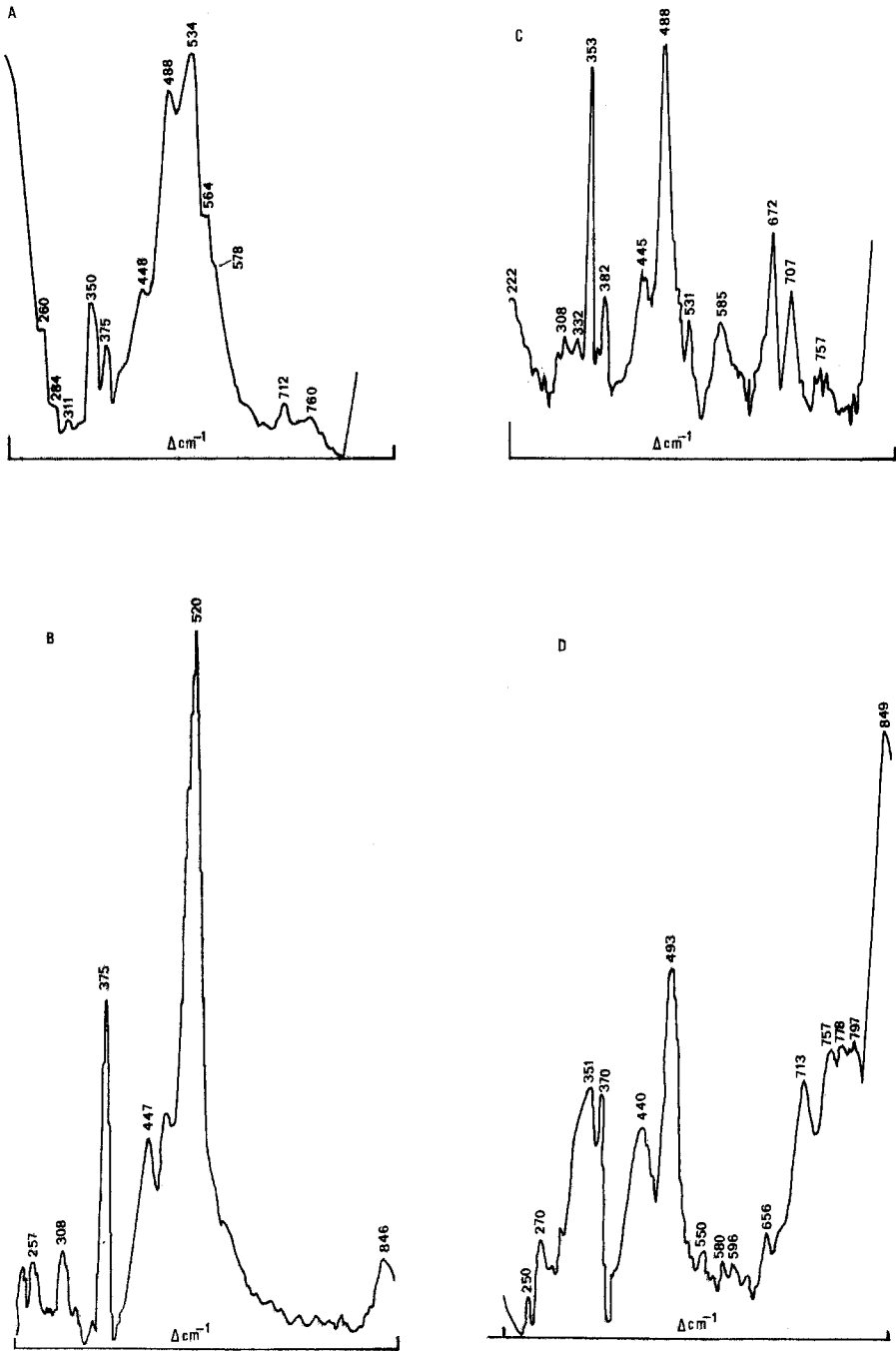
Fig. 3.   The Raman spectra of (A) Cr$_2$CD, (B) Co$_2$CD, (C) Ni$_2$CD and (D) Cu$_2$CD.

Table III. Electronic absorption spectra and effective magnetic moments of metallo-β-CD complexes

M	UV/Vis Spectra				Magnetic Moments	
	$[M_2(OH)_2CD]^{n-}$		$[M(H_2O)_6]^{n+}$		μ	$(\mu_{s.o.})$
					(B.M. per metal ion)	
	λ_{max} (nm)	ε (M cm^{-1})	λ_{max} (nm)	ε (M cm^{-1})		
Cr(III)	593	39	575	13	2.873	(3.873)
	427	45	406	15		
	–	–	265	4		
Mn(III)	482	80	476	5	3.488	(4.899)
Co(II)	–	–	1234	2	3.190	(3.873)
	622	74	625sh	0.18		
	584	77	515	4.6		
	531	57	–	–		
Ni(II)	–	–	1176	2	1.999	(2.828)
	746sh	8	725	2		
	682	10	658sf	–		
	397	33	395	5		
Cu(II)	668	33	801	7	0.83	(1.79)

sh = Shoulder.
sf = Spin-forbidden transition.

4. Discussion

4.1. FT–IR SPECTRA

(i) *4000–3000 cm^{-1} Region*

Bands in this region are normally assigned to symmetric and antisymmetric O—H stretching modes, and are extremely broad. The centre of the band shifts to higher frequencies for the complexes, a shoulder appearing on the low frequency side in some cases. The upward shift may be accounted for in terms of O—H stretching modes associated with the bridged system [8] while the shoulder may be the result of hydrogen-bonding between the bridging hydroxy groups and the 2,3-hydroxy groups of nearby pyranose rings (Figure 1), i.e. second sphere interaction [2].

(ii) *1700–1500 cm^{-1} Region*

Absorption in this region has been assigned to H—O—H deformation modes of coordinated water in aquo-halogeno complexes [9]. New bands appear in this region for all of the metallo-β-CD compelxes (Table II), which are absent from the β-CD spectrum. In some cases the presence of these bands is only confirmed in the difference spectrum (Figure 2). The appearance of two bands in this region, sometimes not well resolved, probably reflects the presence of two different types of coordinated water molecule per metal ion, one directed out of the β-CD cavity and

the other centred in the cavity. This lowers the symmetry around the metal ion from pseudo D_{4h} to pseudo C_{4v}; a conclusion supported by the electronic absorption data (Table III).

(iii) *1500–1200 cm^{-1} Region*

In this region appreciable changes in relative intensities of bands are obvious (Figure 2). Absorption in this region is assigned to β-CD hydroxy in-plane deformation modes [7]. Perturbation of these modes would certainly be expected assuming second-sphere interaction via hydrogen bonding. New bands in the 1300–1200 cm^{-1} region (Table II) were revealed by difference spectroscopy.

(iv) *1200–800 cm^{-1} Region*

There is close similarity in this region of the metallo-complex spectra (Figure 2) with that of the β-CD spectrum. Assignments in this region [7] are to stretching modes of the glycosidic group coupled with C—C and C—O stretching modes.

4.2. RAMAN SPECTRA

(i) *1600–1200 cm^{-1} Region*

Raman spectra of carbohydrates below 1600 cm^{-1} arise mainly from highly coupled vibrational modes [10]. In the region 1440–1320 cm^{-1} assignments are to combinations of C—C stretching, C—OH deformation and CH$_2$ deformation modes. It is not surprising to find small shifts of bands of approximately 6 cm^{-1} in this region for the metallo-complex spectra (Table II).

(ii) *1200–1000 cm^{-1} Region*

Bands in this region are assigned to C—OH stretching and —OH deformation modes. The complex spectra show small shifts with respect to the β-CD bands at 1126, 1083, 1047 and 1001 cm^{-1} (Table II).

(iii) *800–200 cm^{-1} Region*

Normal coordinate analysis for β-D-glucopyranose [11] suggests that bands in this region have their origin in skeletal and ring torsional modes. Significant changes occur in this region on complexation as previously observed [4a] for the Mn(III) complex. The β-CD band at 478 cm^{-1} is generally absent or extremely weak and new bands arise in the 606–478 cm^{-1} region, the exact location depending on the nature of the metal ion. A possible assignment for these new bands is to the skeletal mode assigned to the 478 cm^{-1} band in the β-CD spectrum. The torsional flexibility of the pyranose rings would undoubtedly be reduced by the formation of a binuclear hydroxy bridged system and the accompanying second sphere interaction, resulting in increased frequency for the skeletal mode. Alternatively there is evidence in the literature that the new bands may have their origin in M—OH modes associated with the hydroxy-bridged system [12].

In the case of the Co(II) complex the new bands are relatively intense (Figure 3). The visible absorption spectrum for this complex has λ_{max} at 531 nm (Table III) suggesting that the resonance Raman effect may be operating here as previously suggested in the case of the Mn(III) complex [4a], the latter having λ_{max} at 482 nm.

4.3. UV/VISIBLE AND MAGNETIC STUDIES

4.3.1. *UV/Visible Spectra*

Shifts in the visible range λ_{max} values for metal complexes are normally taken as indicative of a change in the first sphere environment of the metal ion. In all of the cases recorded here (Table III) there are significant changes in at least one of the λ_{max} values for the complex with respect to the corresponding values for the aqueous ions. The values recorded here for Cu(II) and Mn(III) are similar to those previously recorded by Matsui *et al.* [5] and Nair and Dismukes [4b], respectively. Appreciable increases in the molar extinction coefficient value in all cases for the CD complex over that for the corresponding aqueous ion is certainly indicative of a lowering in the symmetry of the ligand field. This is to be expected, as mentioned earlier because of the different environments of each of the solvent molecules.

4.3.2. *Magnetic Moments*

All of the complexes show effective magnetic moments appreciably lower than the spin only values (Table III). This apparent antiferromagnetic behaviour has been observed [13] in many complexes which contain binuclear hydroxy bridged systems. It is normally attributed to overlap of the metal d orbitals with hybridised oxygen orbitals of the bridging hydroxy groups, giving rise to a singlet ground state. Low temperature magnetic studies are required to confirm this. The Néel point for many of these complexes occurs in the range 4 to 20 K, the coupling constants (J) having small negative values of -5 to -20 cm^{-1}, ensuring appreciable population of the excited paramagnetic state even at liquid nitrogen temperatures. The presence of the bridged type system in the metallo-β-CD complexes would therefore account for their relatively low room temperature effective magnetic moments. It is envisaged that further temperature dependent magnetic studies will be performed to determine coupling constants, the values of which can in turn be related to certain structural features of the bridging systems [13].

5. Conclusion

It is clear that the FT–IR and Raman techniques are capable of detecting complex formation in CD complexes and also of providing evidence for structural aspects of these complexes. The data presented here is consistent with (i) the proposal of binuclear hydroxy-bridged complexes and (ii) the presence of simultaneous first and second sphere interaction. The electronic spectra and magnetic data are also in agreement. However, further magnetic studies over the temperature range 20 K to room temperature are required to establish that the compounds are truly antiferromagnetic.

Acknowledgement

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