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FT-IR and Raman Spectral Evidence for Metal Complex Formation with β-Cyclodextrin as a First Sphere Ligand

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Abstract. Changes occurring in the FT-IR and Raman spectra of β-CD when complexed to Mn(III), in a compound formulated as $Mn_2(OH)_2CD$, may be taken as indicating the formation of a complex in which β-CD is acting simultaneously as a first and second sphere ligand.

Key words. Cyclodextrin, Manganese(III), FT-IR, Raman.

1. Introduction

Although transition metal complexes, having cyclodextrin (CD) as a second sphere ligand, have been prepared and in many cases successfully characterized [1], relatively little work has been carried out on complexes having CD as a first sphere ligand. Binuclear metal complexes of Mn(III) and Cu(II) have been reported and bridged structures proposed [2, 3] which feature first sphere coordination by β-CD. Of the various techniques employed in the study of these latter compounds only electronic spectroscopy has been successful in detecting complex formation. Reliable techniques, independent of *d–d* electron transitions, are therefore required (i) to detect complexation and (ii) to supply structural evidence.

Here, we report the FT-IR and Raman spectra of β-CD and the Mn(III) complex and propose the application of this technique to detect complex formation involving β-CD as a first sphere ligand and also to supply evidence for the structure.

2. Experimental

The Mn(III) complex (Mn_2CD) was prepared and purified according to the method of Nair and Dismukes [2]. However, vacuum drying was found to be necessary to remove final traces of solvent. The compound was subsequently washed with ethanol–water (1 : 1) and air dried. The metal content of the complex was determined using a Shimadzu Atomic Absorption/Flame Emission spectrophotometer (Model AA–670). This method confirmed the ratio Mn(III) : β-CD to be 2 : 1.

FT-IR spectra were recorded on solid samples (potassium bromide discs) using a Perkin Elmer Infrared Fourier Transform spectrometer (Model 1710).

Raman spectra of solid samples were obtained by excitation with the 488.0 nm blue line of an argon-ion laser, 250 mW (Jobin Yvon Ramanor HG2 instrument).

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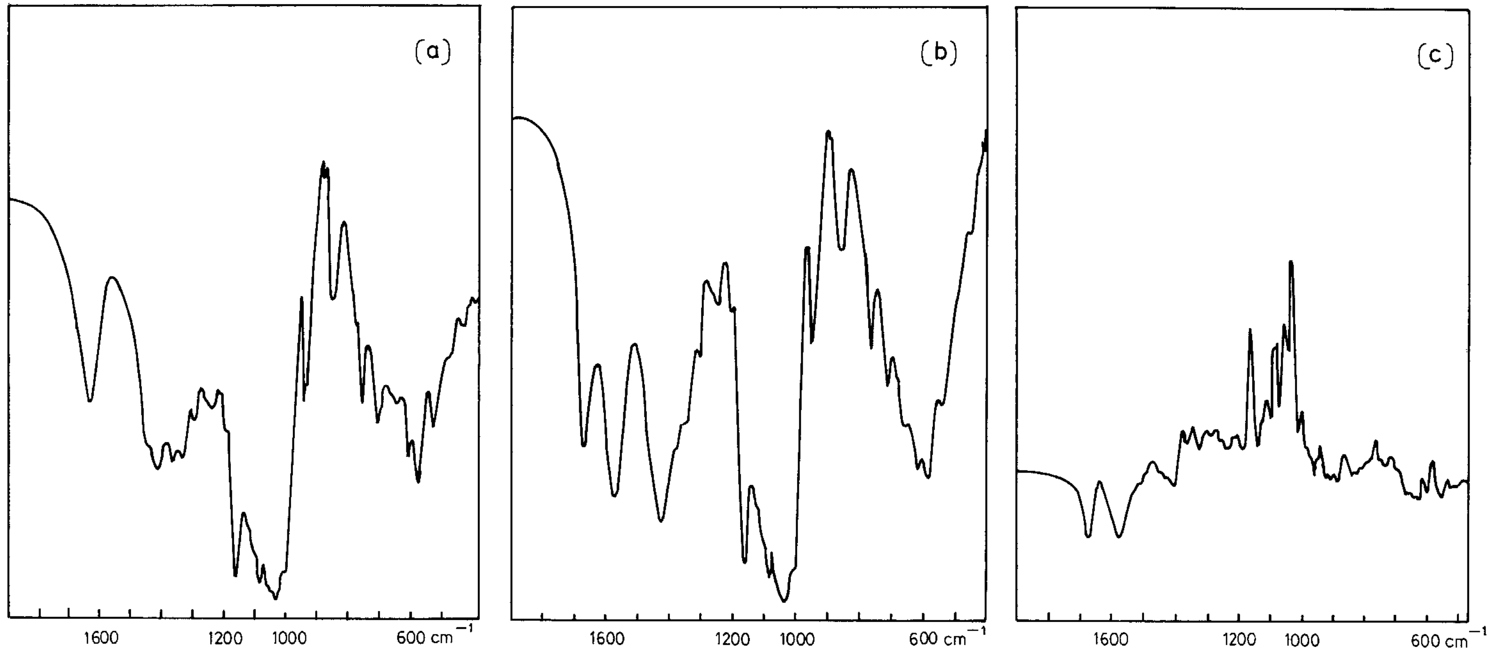

Fig. 1. The FT-IR spectra (%T) of (a) β-CD, (b) Mn_2CD and (c) the difference spectrum.

A spinning cell was used for the complex. Spectra were recorded using the following slit widths; β-CD = 500/1000(2)/500 μ and Mn_2CD = 800/1400(1)/800 μ.

3. Results and Discussion

Figure 1 shows the FT-IR spectra of β-CD, Mn_2CD and the difference spectrum in the 1900–400 cm^{-1} region. Table I lists the frequencies of the bands for each compound, with assignments where possible [4].

The FT-IR spectrum of Mn_2CD shows a band at 1566 cm^{-1} which is absent in the spectrum of β-CD itself. This band is difficult to assign at this stage. Some possible assignments are (i) a shifted band of the β-CD spectrum, (ii) an inactive mode becoming active on complexation, or (iii) a vibrational mode associated with the complexed water molecules.

The difference spectrum shows clearly the presence of the new band at 1566 cm^{-1}. Although not required in this case, results obtained with other similar complexes suggest that difference spectroscopy is essential to show the presence of new bands.

Appreciable changes occur in relative intensities and in the general shape of the bands in the region 1500–1200 cm^{-1}. Absorption in this region is assigned to C—H,

Table I. IR absorption frequencies (cm^{-1}) of β-CD and Mn_2CD.

β-CD	Mn_2CD	Assignment
1647	1661	complexed water
–	1566	
1463sh*	1455	CH_2 bending
1418	1415	O—H in-plane bending
1369	1369sh	C—H bending
1338	1338	O—H in-plane bending
1303	1304	C—H bending/wagging
1262sh	1262sh	O—H in-plane bending
1245	1246	O—H in-plane bending
1198	1203	O—H in-plane bending
1158	1157	antisymmetric C—O—C (glycosidic) stretch
1102sh	1102sh	antisymmetric C—O—C (glycosidic) stretch
1082	1081	coupled C—C stretch/C—O stretch
1029	1030	coupled C—C stretch/C—O stretch
999	999sh	coupled C—C stretch/C—O stretch
947	948	ring vibration
911sh	911sh	ring vibration
889	892	
859	847	C_1 group vibration
757	758	ring breathing vibration
709	708	ring vibration
653	651	O—H out-of-plane bending
610	612	ring vibration
579	581	ring vibration
531	535	ring vibration
437	444	ring vibration

* sh = shoulder.

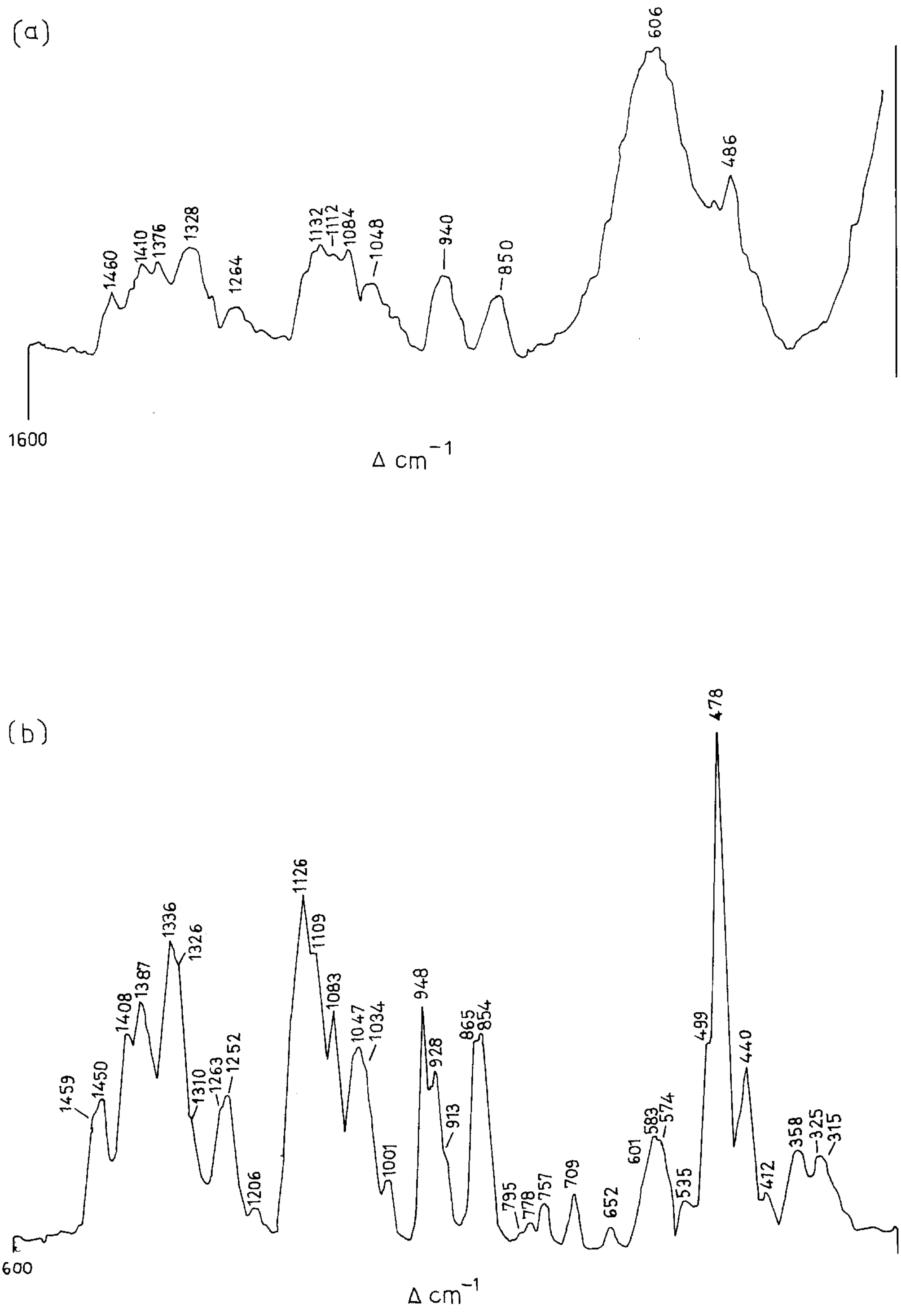

Fig. 2. The Raman spectra of (a) Mn_2CD and (b) β-CD.

CH_2 and O—H bending modes [4]. Perturbations of the latter modes would certainly be expected in the presence of second sphere coordination [5] via hydrogen bonding between the secondary 2- and 3-hydroxyl groups of β-CD and the hydroxyls of the proposed bridged structure.

A change in relative intensity of the bands at 651 and 708 cm^{-1} was observed and is in accordance with the literature [2].

Figure 2 shows the Raman spectra of β-CD and Mn_2CD in the region 1600–200 cm^{-1}. The spectrum of β-CD is very similar to that reported for α-CD [6]. Mn_2CD was found to be a weaker scatterer than the parent though the signal/noise ratio remained high. On comparison, it can be seen that there are many common features in the Raman spectra of Mn_2CD and β-CD. A particularly strong band at 606 cm^{-1}, however, is shown only in the spectrum of the complex, while the intense β-CD band at 478 cm^{-1} is absent. The band at 606 cm^{-1} is unlikely to arise directly from metal–oxygen vibrational modes, since these normally vibrate in the 300–400 cm^{-1} region [7]. The high intensity of this band would be inconsistent with the highly polar nature expected for the metal–oxygen bonds. A more probable assignment is to the skeletal vibration which is assigned to the 478 cm^{-1} band in the β-CD spectrum [6]. The shift to higher frequency may be explained by increased rigidity of the CD skeleton in the complex.

The bands at 315, 325 and 358 cm^{-1} in the β-CD spectrum are absent in that of the complex. One interpretation is that these bands have also shifted to higher frequency. This interpretation would also be consistent with the proposed bridged structure, as these bands have their origin in the skeletal and torsional modes of the CD ring [6].

Further detailed study of the Raman spectra in the region 300–600 cm^{-1} may provide an insight into the extent of interaction between the chelate ligand and the metal ion.

The results obtained to date indicate that this technique may be generally applicable to metal complexes of β-CD.

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