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PREPARATION AND PROPERTIES OF INCLUSION COMPOUNDS OF CYCLODEXTRINS WITH ORGANOTRANSITION METAL COMPLEXES

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ABSTRACT

Inclusion compounds of transition metal complexes of cycloocta-1,5-diene (cod) and norbornadiene (nbd) with cyclodextrins were prepared. Two-to-one (cyclodextrin:guest) inclusion compounds were obtained in high yields by the treatment of β-cyclodextrin (β-CD) with $[(L)RhCl]_2$ (L = nbd or cod) and 1:1 inclusion compounds were obtained by the reaction of β-CD with $(cod)PtX_2$ (X = Cl, Br, or I) in high yields, while γ-CD formed 1:1 inclusion compounds with $(cod)PtX_2$ (X = Br or I). The formation of inclusion compounds is selective. α-CD did not form inclusion compounds with any transition-metal complexes with cycloocta-1,5-diene. Thermogravimetric measurements show that the complexes are stabilized by inclusion in cyclodextrin cavities. The inclusion compounds were characterized by ^{1}H-NMR, IR, UV, and circular dichroism spectra.

INTRODUCTION

Recently the importance of second-sphere coordination, noncovalent coordination, to transition metal complexes has been recognized [1] and much attention has been directed toward the field of supramolecular chemistry. Inclusion compounds of transition metal complexes with crown ethers [2] and cryptands [3, 4] have been reported and have attracted much attention because of their unique structures and properties. However, in these cases the guest complexes are limited to complexes with protic ligands, such as the ammine, water, or acetonitrile ligand in the first coordination sphere. There have been no reports on inclusion compounds with neutral transition-metal complexes without protic ligands, but such coordination may be possible when the host molecules have hydrophobic cavities to accommodate these lipophilic ligands. One of the most promising candidates for such a host is cyclodextrin.

Cyclodextrins (CDs), which are cyclic molecules consisting of 6 to 8 glucose units (α-, β-, γ-CD, respectively), are known to form inclusion complexes with various compounds [5]. Nevertheless, there are few reports on inclusion compounds with transition-metal complexes. In previous communications we reported the preparation and properties of ferrocene and its analogs [6-11]. Now we wish to report the preparation and properties of new cyclodextrin inclusion compounds of cyclic olefin-metal complexes which are frequently used in a variety of organic syntheses.

EXPERIMENTAL

Materials

Cyclodextrins (α-CD, β-CD, and γ-CD) were obtained from Hayashibara Biochemical Laboratories Inc. They were purified by recrystallization from water, and their purities were checked by elemental analysis and optical rotation. Cycloocta-1,5-dienerhodium chloride dimer was prepared from cycloocta-1,5-diene and rhodium chloride by a procedure similar to that described previously [12]. Cycloocta-1,5-dieneplatinum dichloride was prepared by a procedure described previously [13]. Cycloocta-1,5-dieneplatinum dibromide and diiodide were prepared by treatment of cycloocta-1,5-dieneplatinum dichloride with excess potassium bromide or potassium iodide.

Preparation of Inclusion Compounds

Inclusion compounds of alkene-metal complexes with cyclodextrins were prepared by adding fine crystals of the complexes to a stirred saturated aqueous solution of the CD at 40°C. The product which precipitated was washed with water to remove the remaining CD, and dried *in vacuo.* Nonincluded metal complexes were removed by washing the residue with THF.

Measurements

Infrared spectra were taken on a Hitachi 295 spectrometer, and UV spectra were recorded on a Shimadzu UV-202 spectrophotometer. ^{1}H-NMR spectra were run on a Bruker 360 MHz spectrometer. Circular dichroism spectra were recorded on a JASCO J-205 spectropolarimeter. Thermogravimetric analysis was made by using a Shimadzu thermal analyzer DT-30. Atomic absorption analysis was made by using a Shimadzu A-610S atomic absorption/flame spectrophotometer.

RESULTS AND DISCUSSION

Table 1 shows results of the preparation of inclusion compounds of CD-alkene-metal complexes. β-CD formed 2:1 (CD:guest) inclusion compounds with di-μ-chlorobis(cycloocta-1,5-diene)dirhodium, [(cod)RhCl]$_2$, and di-μ-chlorobis(norbornadiene)dirhodium, [(nbd)RhCl]$_2$, in high yields, γ-CD formed 2:1 inclusion compounds with [(cod)RhCl]$_2$ in 29% yield, but it did not form inclusion compounds with [(nbd)RhCl]$_2$ which is smaller than [(cod)RhCl]$_2$. It is noteworthy that [(nbd)RhCl]$_2$ was specifically included in β-CD. β-CD also formed inclusion compounds with dihalogeno-(cycloocta-1,5-diene)platinum complexes, (cod)PtX$_2$ (X = Cl, Br, I), in high yields. γ-CD formed inclusion compounds with (cod)PtI$_2$ quantitatively, whereas it did not form inclusion compounds with (cod)PtCl$_2$. With (cod)PtBr$_2$ it gave the inclusion compounds in low yield, indicating that γ-CD appears to discriminate among the guest compounds, by size, especially of the halogen part. All the inclusion compounds were stoichiometric 1:1 or 2:1 (host to guest) complexes, depending on the size of the guest compounds.

We could not obtain inclusion compounds of any neutral alkene-metal complexes tested with α-CD. Examination of C.P.K. molecular models shows that these alkene-metal complexes are a little too large to be fully included in the α-CD cavity.

The inclusion compounds were characterized by elemental analysis and their IR, UV, and ^{1}H-NMR spectra. The ^{1}H-NMR spectrum of the β-CD-[(cod)] RhCl]$_2$ inclusion compounds in D$_2$O showed two sets of resonances, apparently for two different CD species (Fig. 1). One of them is superimposable with that of free β-CD and the other, which could represent complexed

TABLE 1. Preparation of Inclusion Compounds of Alkene-Metal Complexes with Cyclodextrins

	Product					
	α-CD		β-CD		γ-CD	
	Yield, %	CD:guest	Yield, %	CD:guest	Yield, %	CD:guest
$[(cod)RhCl]_2$	0	–	90	2:1	29	2:1
$[(nbd)RhCl]_2$	0	–	100	2:1	0	–
$(cod)PtCl_2$	0	–	99	1:1	0	–
$(cod)PtBr_2$	0	–	100	1:1	14	1:1
$(cod)PtI_2$	0	–	90	1:1	100	1:1

CD, showed large shifts of the signals for H-1, H-2, and H-5 of β-CD to lower frequencies and of that for H-3 to higher frequency. This implies that exchange between free and complex CD is slow on the NMR time-scale. Stoichiometries were determined by elemental analysis, including atomic absorption analysis of the metal contents, and from the ^{1}H-NMR spectra. All the inclusion compounds obtained in this work were stoichiometric 1:1 or 2:1 (host to guest) complexes depending on the size of the guest compounds.

The inclusion compounds were thermally stable. β-CD-$[(cod)RhCl]_2$, for example, did not liberate the guest when heated at 200°C *in vacuo*. Under these conditions the alkene complex sublimes. Thermogravimetric analyses showed that the inclusion compound was stable up to 280°C and decomposed at around the melting point (decomposition point) of β-CD (Fig. 2).

Figures 2 and 3 show absorption and circular dichroism spectra of the inclusion compounds measured in aqueous solution. A large induced Cotton effect was observed in the case of the β-CD-$[(cod)RhCl]_2$ inclusion compound, while a very weak induced Cotton effect was observed with the γ-CD inclusion compound, indicating that the guest compound was fixed well in the β-cyclodextrin ring.

According to C.P.K. molecular models, cycloocta-1,5-diene- and norbornadiene-metal complexes appear to fit well into the β-CD cavity as shown in Fig. 4. Whereas $[(nbd)RhCl]_2$ and $(cod)PtCl_2$ are too small to fit in the γ-CD cavity, $[(cod)RhCl]_2$ and $(cod)PtX_2$ (X = Br or I) are large enough to fit in

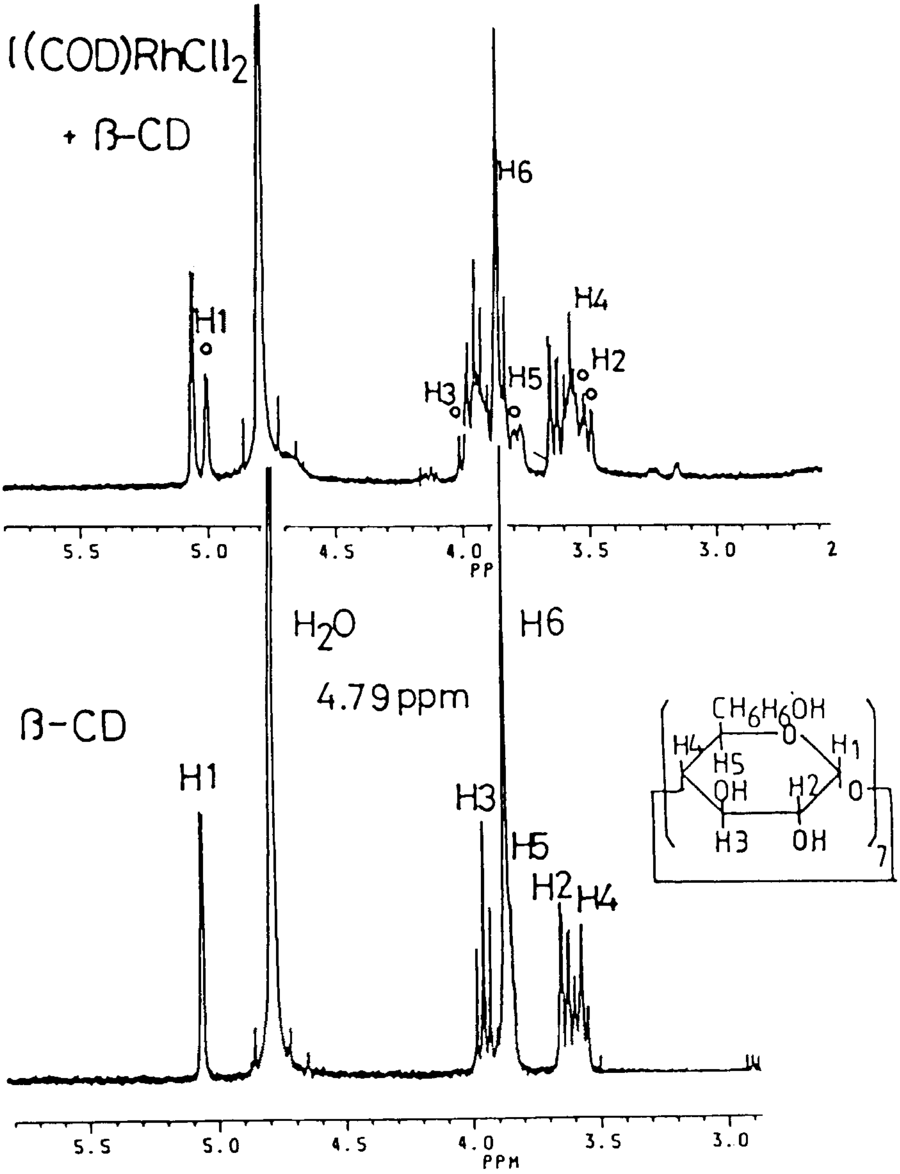


FIG. 1. ^{1}H-NMR spectra of β-CD-[(cod)RhCl]$_2$.

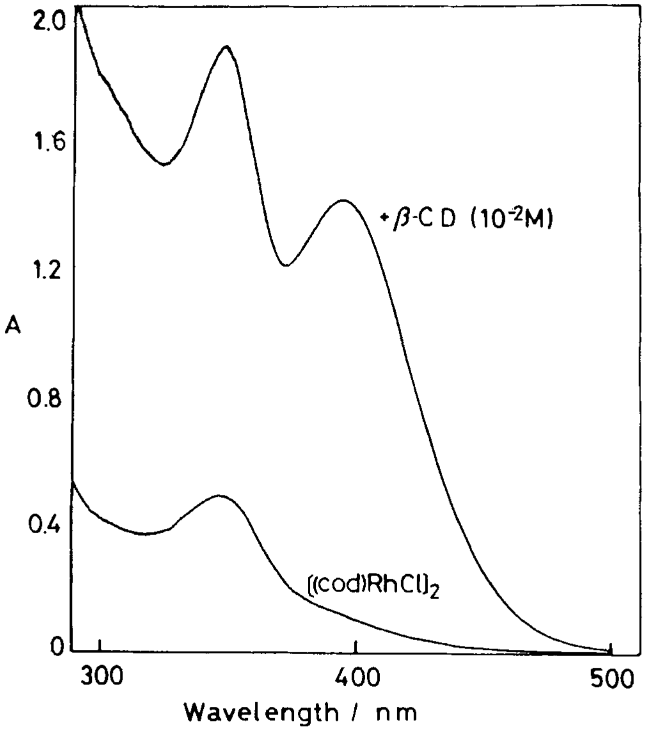


FIG. 2. Absorption spectra of [(cod)RhCl]$_2$ in the presence of β-CD.

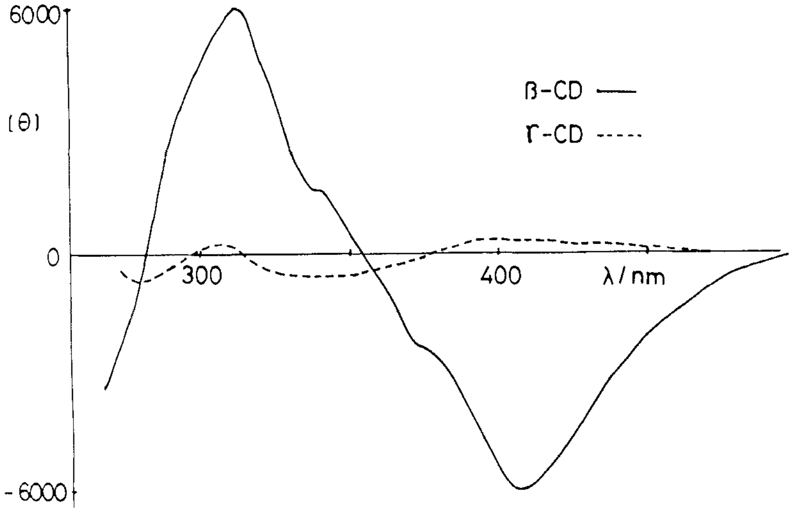
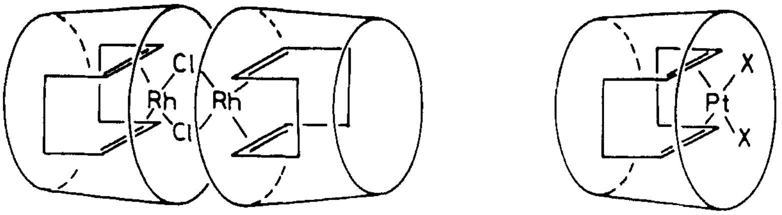


FIG. 3. Circular dichroism spectra of β-CD-[(cod)RhCl]$_2$.



2β-CD-[(cod)RhCl]$_2$

CD-(cod)PtX_2

FIG. 4. Proposed structures of β-CD-[(cod)RhCl]$_2$ and β-CD-(cod)PtX_2 (X = Cl, Br, and I).

the γ-CD cavity. The proposed structures for the β-CD-[(cod)RhCl]$_2$ and β-CD-(cod)PtX_2 complexes are shown in Fig. 4.

REFERENCES

[1] H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl., 25,* 487 (1986).

[2] H. M. Colquhoun, S. M. Doughty, J. F. Stoddart, and D. J. Williams, *Ibid., 23,* 235 (1984).

[3] D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *Ibid., 23,* 821 (1984).

[4] J-P. Lecomte, J-M. Lehn, D. Parker, J. Guilhem, and C. Pascard, *J. Chem. Soc., Chem. Commun.*, p. 296 (1983).

[5] M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry,* Springer-Verlag, New York, 1977.

[6] A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, p. 645 (1984).

[7] A. Harada and S. Takahashi, *J. Inclusion Phenomena, 3,* 791 (1984).

[8] A. Harada and S. Takahashi, *J. Chem. Soc.,Dalton Trans.*, In Press.

[9] A. Harada, K. Saeki, and S. Takahashi, *Chem. Lett.*, p. 1157 (1985).

[10] A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, p. 1229 (1986).

[11] A. Harada, M. Takauchi, and S. Takahashi, *Chem. Lett.*, p. 1893 (1986).
[12] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, p. 4735 (1957).
[13] D. Drew and J. R. Doyle, *Inorg. Synth.*, *13*, 47 (1972)