CHEMISTRY LETTERS, pp. 1157-1160, 1985.

PREPARATION AND PROPERTIES OF INCLUSION COMPOUNDS OF (η^6-ARENE)TRICARBONYLCHROMIUM(0) COMPLEXES WITH CYCLODEXTRINS

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One-to-one inclusion compounds were obtained in high yields by the treatment of β- and γ-cyclodextrin(CD) with (η^6-arene)-tricarbonylchromium(0) complexes; the formation of inclusion compounds is selective.

Cyclodextrins(CDs) are cyclic molecules consisting of six, seven, and eight glucose units (α-, β-, and γ-CD, respectively). They form inclusion compounds with various compounds, ranging from nonpolar molecules to small ions. However, there are only a few reports on the inclusion compounds of organometallic complexes with cyclodextrins. In a previous communication we reported the preparation and properties of cyclodextrin-ferrocene inclusion compounds as the first example of cyclodextrin inclusion compounds of organotransition metal complexes.1) We have now found that β- and γ-cyclodextrins form inclusion compounds with (η^6-arene)tricarbonylchromium(0) complexes and that the formation of inclusion compounds is selective.

Cyclodextrin inclusion compounds of (η^6-arene)tricarbonylchromium(0) complexes were obtained by adding fine crystals of (arene)tricarbonylchromium complexes2) to a saturated aqueous solution of cyclodextrin at 60 °C with stirring.3) The product was washed with water to remove remaining cyclodextrin, and dried in vacuum. Unincluded (arene)tricarbonylchromium complexes were removed by washing the residue with benzene. During this process, the included guest was not liberated from the cyclodextrin cavity. The inclusion compounds of (η^6-arene)tricarbonylchromium(0) complexes were characterized by elemental analyses and their IR, and ^{1}H-NMR spectra.4) Stoichiometries were determined by elemental analyses, and especially the chromium contents measured by atomic absorption analyses and from the ^{1}H-NMR spectra.

Table 1. Preparation of Inclusion Compounds of CD-(η^6-Arene)tricarbonylchromium Complexes

CD	(η^6-arene)Cr(CO)$_3$ arene	Product			
		Yield	Cr		CD:guest
		%	Found(%)	Calcd(%)	
α	benzene	0	-	-	-
β	benzene	91	3.7	3.9	1:1
γ	benzene	21	3.5	3.4	1:1
α	toluene	0	-	-	-
β	toluene	87	4.3	3.8	1:1
γ	toluene	90	3.7	3.4	1:1
α	*o*-xylene	0	-	-	-
β	*o*-xylene	56	3.8	3.8	1:1
γ	*o*-xylene	96	3.8	3.4	1:1
α	*m*-xylene	0	-	-	-
β	*m*-xylene	trace	3.7	3.8	1:1
γ	*m*-xylene	84	4.2	3.4	1:1
α	*p*-xylene	0	-	-	-
β	*p*-xylene	trace	3.9	3.8	1:1
γ	*p*-xylene	81	3.7	3.4	1:1
α	mesitylene	0	-	-	-
β	mesitylene	0	-	-	-
γ	mesitylene	61	3.7	3.3	1:1
α	hexamethylbenzene	0	-	-	-
β	hexamethylbenzene	0	-	-	-
γ	hexamethylbenzene	98	3.1	3.3	1:1

Table 1 shows results on the preparation of inclusion compounds of CD-(η^6-arene)tricarbonylchromium(0) complexes, whereas no formation of inclusion compounds between hexacarbonylchromium and cyclodextrins was observed. β-CD formed inclusion compounds with tricarbonylchromium complexes of benzene, toluene, and *o*-xylene in high yields, and with those of *m*- and *p*-xylene in trace amounts, but not with those of mesitylene and hexamethylbenzene. γ-CD formed an inclusion compound with (benzene)tricarbonylchromium complex in 21% yield and with all other (arene)tricarbonylchromium complexes tested in high yields. The inclusion compound of γ-CD-tricarbonyl(hexamethylbenzene)chromium complex was obtained almost quantitatively. It should be noted that (benzene)tricarbonylchromium complex was selectively included in β-CD, while tricarbonylchromium complexes of mesitylene and hexamethylbenzene were specifically included in γ-CD. Of the tricarbonylchromium complexes of *o*-, *m*-, and *p*-xylenes, only tricarbonyl-(*o*-xylene)chromium complex was selectively included in β-CD. β-CD does not show such selectivity with uncomplexed *o*-, *m*-, and *p*-xylene.5) α-CD did not form inclusion compounds with any (η^6-arene)tricarbonylchromium complexes tested, although it formed inclusion compounds with uncomplexed benzene, toluene, and xylenes.6)

All the inclusion compounds obtained here are stoichiometric one-to-one (host to guest) complexes, even when cyclodextrin was treated with two fold molar excess of (arene)tricarbonylchromium complexes.

The inclusion compounds obtained were thermally stable. The inclusion compound of β-CD with (benzene)tricarbonylchromium complex, for example, did not liberate the guest when heated at 100 °C in vacuum, while under these conditions unincluded (benzene)tricarbonylchromium complex sublimed. Thermogravimetric analyses showed that the inclusion compound was stable up to 250 °C and decomposed at about the melting point of β-CD.

Judging from the molecular dimensions of α-CD[7)] and (arene)tricarbonylchromium complexes, (arene)tricarbonylchromium complexes are too large to be included in the α-CD cavity. Uncomplexed benzene, toluene, and xylenes can be included in the α-CD cavity axially,[8)] but a chromium tricarbonyl group hinders inclusion of the whole guest molecule. No formation of inclusion compounds with hexacarbonylchromium suggests that cyclodextrins do not interact sufficiently with the carbonyl moiety and, therefore, the inclusion of (arene)tricarbonylchromium is essentially based on preferential interactions between the arene moiety and cyclodextrin. According to this and CPK molecular model, the structure of axial inclusion (Fig. 1) may be tentatively proposed, which could interpret the selective inclusion in terms of the steric factor of the π-arene moiety. The tricarbonylchromium complexes of benzene and toluene appear to fit well into the β-CD cavity with axial orientation, whereas those of mesitylene and hexamethylbenzene are too large to be included in the β-CD cavity. The γ-CD cavity is large enough to accommodate tricarbonylchromium complexes of xylene, mesitylene, and hexamethylbenzene. *o*-Xylene complex, which is more compact than *m*- or *p*-xylene complex, fits well into the β-CD cavity.

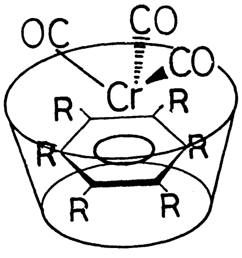

Fig.1. Proposed structure of CD-(π-arene)tricarbonylchromium complex.

The UV and circular dichroism spectra of the complexes were measured in dimethylformamide. A positive induced Cotton effect was observed at about 317 nm in the case of β-CD-(benzene)tricarbonylchromium complex. This result is in accordance with that of the β-CD-ferrocene inclusion compounds,$^{9)}$ and supports the proposed axial inclusion.

References

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2) For preparation, R. B. King, "Organometallic Syntheses," Academic Press, New York (1965), Vol.1, pp. 136-139.
3) For example, β-CD-(benzene)tricarbonylchromium complex inclusion compound was prepared by adding finely ground crystals of (benzene)tricarbonylchromium complex (0.108 g, 0.5 mmol) to an aqueous solution of β-CD ($10H_2O$ adduct, 0.328 g, 0.25 mmol) at 60 °C with stirring. The product was washed with water to remove remaining CD, and dried in vacuum. Unincluded (benzene)tricarbonylchromium was removed by washing the residue with benzene. The product was recrystallized from water or aqueous alcohol to give pale yellow crystals.
4) For β-CD(H_2O)-(benzene)tricarbonylchromium complex: mp 235-245 °C(decomp.); Found: C,44.80; H,5.95%. Calcd for $C_{51}H_{78}O_{39}Cr$: C,44.80; H,5.75%. IR ν c=o 1960, 1895 cm^{-1}; ^1H-NMR(DMSO,100 MHz) δ 5.68 (s 6H).
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(Received May 18, 1985)