CHEMISTRY LETTERS, pp. 275-276, 1989.

γ-Cyclodextrin as a Second Sphere Coordinating Ligand for Cobalt Cluster Complexes

Akira HARADA,* Masayuki SHIMADA, and Shigetoshi TAKAHASHI*
The Institute of Scientific and Industrial Research,
Osaka University, Ibaraki, Osaka 567

One-to-one inclusion compounds of di-, tri-, and tetranuclear cobalt complexes with γ-cyclodextrin were obtained in high yields, while α- and β-cyclodextrin did not form inclusion compounds.

Recently the importance of second sphere coordination to transition metal complexes has been recognized[1)] and much attention has been directed toward the supramolecular chemistry. Recently, inclusion compounds of transition metal complexes with crown ethers,[2)] cryptands,[3)] and cyclodextrins[4)] have been reported. However, their guest complexes have been limited to the complexes with one or two metal centers. There have been no reports on the inclusion compounds of cluster complexes with cyclodextrins(CDs). Large cavities may be required to accommodate cluster complexes. Now we found that γ-CD forms inclusion compounds with some cobalt cluster complexes though α-CD and β-CD did not form inclusion compounds with those cobalt cluster complexes. We report here the preparation and properties of inclusion compounds of di-, tri-, and tetracobalt complexes with γ-CD.

Inclusion compounds of cobalt complexes with γ-CD were prepared by adding fine crystals of complexes to an aqueous solution of γ-CD at 30 °C with stirring under a nitrogen atmosphere. The precipitated products were washed with water to remove remaining CD and dried in vacuum. Non-included cluster complexes were removed by washing the residue with hexane. During this process, the included guest was not liberated from the CD cavity.

Table 1 shows the results on the preparation of inclusion compounds of cobalt complexes with γ-CD. γ-CD formed inclusion compounds with cobalt cluster complexes (**1**, **2**) and dinuclear complex (**4**) in high yields but it did not form any inclusion compound with complex (**3**). α-CD and β-CD did not form inclusion compounds with any cobalt cluster complexes tested. The inclusion compounds were characterized by elemental analysis and their IR, UV, and ^{1}H-NMR spectra. Stoichiometries were determined by elemental analysis, including atomic absorption analysis of the metal contents, and from their ^{1}H-NMR and UV spectra. All the inclusion compounds obtained in this work are stoichiometric one-to-one inclusion compounds.

Cobalt cluster complexes are stabilized when they are included in the cavity of γ-CD. Thermogravimetric analysis shows that non-included cluster complex (**1**) decomposes at 120 °C, while the inclusion compound of (**1**) with γ-CD decomposes

Table 1. Preparation of inclusion compounds of cobalt complexes with cyclodextrins

Complex	Yield/%		
	α-CD	β-CD	γ-CD
1	0	0	74
2	0	0	67
3	0	0	0
4	0	0	73

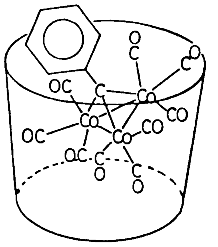
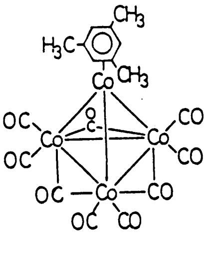


Fig. 1. Proposed structure of the inclusion compound of cobalt cluster complex with γ-CD.

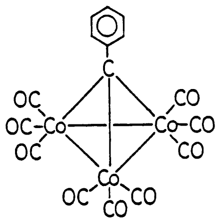
gradually above 200 °C.

Cobalt clusters included in the CD cavity could be recovered by heating aqueous solutions of the inclusion compounds and then extracted with organic solvents.

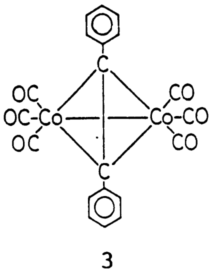
Judging from the molecular dimensions of CDs and the cobalt cluster complexes, these cluster complexes are too large to fit in α-CD and β-CD, but γ-CD is large enough to accommodate these cluster complexes. The complex (**3**) has a phenyl group at each end which may hinder inclusion of the whole guest molecule. Proposed structure for the inclusion compound of cluster complex (**1**) is shown in Fig. 1.



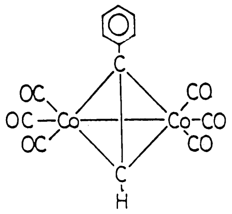
1



2



3



4

References

1) H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, Angew. Chem., Int. Ed. Engl., 25, 487 (1986).
2) D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, Angew. Chem., Int. Ed. Engl., 24, 786 (1985); D. R. Alston, T. H. Lilley, and J. F. Stoddart, J. Chem. Soc., Chem. Commun., 1985, 1600.
3) J.-P. Lecomte, J.-M. Lehn, D. Parker, J. Guihem, and C. Pascard, J. Chem. Soc., Chem. Commun., 1983, 296.
4) A. Harada and S. Takahashi, J. Chem. Soc., Chem. Commun., 1984, 645; A. Harada, Y. Hu, S. Yamamoto, and S. Takahashi, J. Chem. Soc., Dalton Trans., 1988, 729; D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, Angew. Chem., Int. Ed. Engl., 24, 786 (1985); A. Harada and S. Takahashi, J. Chem. Soc., Chem. Commun., 1986, 1229.

(Received October 31, 1988)