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Preparation and properties of inclusion compounds of cobalt cluster complexes with γ-cyclodextrin *

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Abstract

Inclusion compounds of di-, tri-, and tetranuclear transition metal complexes with γ-cyclodextrin (CD) have been prepared as the first example of an inclusion compound of cyclodextrin with a metal cluster complex. High yields of crystalline one-to-one inclusion compounds were obtained by the treatment of η^2-acetylenedicobalt hexacarbonyl complexes with γ-CD. μ_3-Phenylmethylidynetricobalt nonacarbonyl, and η^6-mesitylenetetracobalt nonacarbonyl also form inclusion compounds with γ-CD. The formation of inclusion compounds is selective. γ-CD forms 1:1 host:guest inclusion compounds with η^2-phenylacetylene- and η^2-phenylmethylacetylenedicobalt hexacarbonyls, but not with the sterically larger η^2-diphenyldicobalt hexacarbonyl. Neither α-CD nor β-CD formed inclusion compounds with any of the cobalt cluster complexes tested. The metal cluster complexes included in γ-CD are thermally more stable than the free complexes.

Introduction

Metal cluster complexes consist of two or more metal atoms in which there are direct bonds between the metal atoms. A great number of metal cluster complexes have been synthesized and have received much attention as possible catalysts [1,2]. Nevertheless, there have been few examples of catalytic systems uniquely characteristic of metal clusters because under the reaction conditions of high temperature and pressure, they are assumed to be degraded to mononuclear fragments. Therefore methods for maintaining the framework of cluster complexes have been eagerly awaited. There is a large number of publications concerning metal clusters anchored to prevent fragmentation on functionalized silica surfaces or on polymer ligands [3]. Another promising candidate for maintaining the cluster framework is encapsulation of the cluster complexes into macromolecules, such as cyclodextrins, without any covalent bonds.

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Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, or eight (1–4)-linked α-D-glucopyranose residues (α-, β-, γ-CD respectively), each having a slightly different cavity diameter: α-CD 4.5-Å, β-CD 7.0 Å and γ-CD 8.5 Å. They can form inclusion compounds with a wide variety of guest molecules without any covalent bond being formed [4].

The importance of molecular recognition as evidenced by the formation of inclusion compounds has recently attracted much attention not only in the field of organic chemistry but also in the field of organometallic chemistry. Inclusion compounds of transition metal complexes with crown ethers [5], cryptands [6], calixarenes [7], and cyclodextrins [8] have been reported, and found to have unique structures and properties. In our laboratory a series of cyclodextrin inclusion compounds with organometallic complexes, such as ferrocenes, η^3-allyl palladium halide dimers, and (η^6-arene)tricarbonylchromium complexes, has been investigated [9]. We have also reported that inclusion compounds of alkyldicarbonylcyclopentadienyliron complexes with cyclodextrins undergo, in the solid state, insertion of carbon monoxide and sulphur dioxide into the Fe–R bond, and the effect of inclusion by cyclodextrin towards such insertion reactions strongly depends on the cyclodextrin used [10]. However, our studies and those of others have generally limited the guest complexes used to those with one or two metal centres without any direct metal to metal bonds. We have attempted to prepare the inclusion compounds of metal cluster complexes with cyclodextrins and have investigated the thermal stability of the complexes included in cyclodextrins.

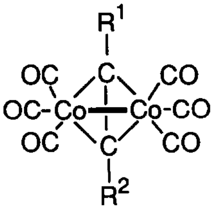
We describe here the preparation and characterization of η^2-acetylenedicobalt hexacarbonyl complex and its derivatives included in γ-cyclodextrin [11].

Results and discussion

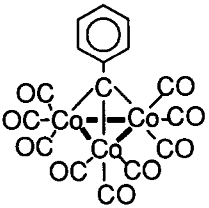
Preparation of inclusion compounds

Cocrystallization from aqueous solution is the usual method for obtaining inclusion compounds for water-soluble compounds. However this method cannot be employed for η^2-acetylenedicobalt hexacarbonyl complexes because they are almost insoluble in water. In an attempt to prepare the inclusion compounds of cobalt cluster complexes, η^2-acetylenedicobalt hexacarbonyl (**1**), its derivatives (**2–7**), μ_3-phenylmethylidynetricobalt nonacarbonyl (**8**), and η^6-mesitylenetetracobalt nonacarbonyl (**9**), we employed the following method.

A cobalt cluster complex was added to a 2-fold molar excess of saturated aqueous solution of cyclodextrin at 40 ° C with stirring. The precipitate was washed thoroughly with water to remove any remaining cyclodextrin and dried *in vacuo*. Nonincluded cobalt complex was removed by washing the residue with tetrahydrofuran. During this process, the included cobalt complex was not liberated from the cyclodextrin cavity in the cases of **1–6** and corresponding pure inclusion compounds were obtained. However a proportion of the included complexes was liberated in the cases of **8** and **9**, and we could not obtain the corresponding inclusion compounds in an analytically pure form. All of the inclusion compounds are pale brown powders except for that from η^6-mesitylenetetracobalt nonacarbonyl which is green. They are soluble in dimethylsulfoxide and decompose slowly in solution. They were characterized by elemental analyses, including atomic



1 $R^1=R^2=H$
2 $R^1=CH_3$, $R^2=H$
3 $R^1=Si(CH_3)_3$, $R^2=H$
4 $R^1=C_6H_5$, $R^2=H$
5 $R^1=R^2=CH_3$
6 $R^1=C_6H_5$, $R^2=CH_3$
7 $R^1=R^2=C_6H_5$



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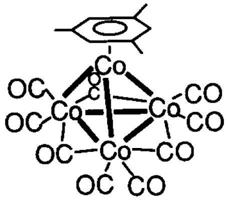

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absorption analyses for cobalt content, and by their IR and ^1H NMR spectra. Stoichiometries were determined by ^1H NMR spectra and elemental analyses.

Table 1 shows results of the preparation of inclusion compounds of cyclodextrins with cobalt cluster complexes. γ-CD, with the largest cavity diameter of the three cyclodextrins, formed inclusion compounds with di-nuclear (**1**)–(**6**), tri-nuclear (**8**), and tetra-nuclear (**9**) cobalt clusters in moderate to high yields except for the η^2-diphenylacetylene complex (**7**), the largest acetylene complex of those tested here. The smaller acetylene complexes (**2** and **5**) gave higher yields than the larger complexes (**3** and **4**). α-CD and β-CD did not form inclusion compounds with any

Table 1

Yields and spectral data of γ-CD inclusion compounds

Complex	Isolated yield of γ-CD inclusion compound (%) [a]	IR ν(CO) (cm^{-1})	^1H NMR (δ/ppm)
1	65 [b]	1895, 1960	[d]
2	78 [b]	2025, 2060, 2100	2.68 (methyl) [d]
3	42 [b]	2020, 2050, 2090	0.43 (methyl) [d]
4	51 [b]	2030, 2060	7.2–7.6 (aromatic) [d]
5	80 [b]	2020, 2050, 2090	2.51 (methyl)
6	61 [b]	2030, 2045, 2080	2.86 (methyl) 7.3–7.5 (aromatic)
7	0		
8	67 [c]	2040, 2050	6.0–6.3 (aromatic)
9	74 [c]	1835,. 1820 2070, 2000, 1970	2.05 (methyl) 5.2–5.5 (aromatic)

[a] Neither α-CD nor β-CD forms inclusion compounds with any cluster complexes tested here. [b] 1:1 inclusion compounds. [c] Not obtained in analytically pure form. Calculated for 1:1 inclusion compounds. [d] The peaks of acetylenic proton are masked under the peaks due to secondary alcohol protons of γ-CD.

Table 2

Analytical data of γ-CD inclusion compounds [a]

Inclusion compound	Molecular formula	Analysis (%) [a]		
		C	H	Co
γ-CD-**1**·$2H_2O$	$C_{56}H_{86}Co_2O_{48}$	40.93(40.88)	5.93(5.39)	7.30(7.16)
γ-CD-**2**	$C_{57}H_{84}Co_2O_{46}$	42.00(42.18)	5.25(5.22)	7.10(7.26)
γ-CD-**3**·$2H_2O$	$C_{59}H_{94}Co_2O_{48}Si$	41.08(41.26)	5.65(5.51)	7.25(6.86)
γ-CD-**4**·$2H_2O$	$C_{56}H_{86}Co_2O_{48}$	43.39(43.26)	5.67(5.27)	7.00(6.84)
γ-CD-**5**	$C_{56}H_{86}Co_2O_{46}$	42.35(42.55)	5.34(5.29)	7.42(7.20)
γ-CD-**6**·H_2O	$C_{63}H_{92}Co_2O_{48}$	43.31(43.61)	5.36(5.34)	6.40(6.79)

[a] Calculated values are given in parentheses.

cobalt cluster complex tested, although they formed inclusion compounds with uncomplexed phenylacetylene and methylphenylacetylene [12]. The examination with CPK models shows that these cluster complexes are too large to be fully included in the α-CD and β-CD cavities.

All the inclusion compounds of dinuclear cobalt complexes, η^2-acetylenedicobalt hexacarbonyl (**1**) and its derivatives (**2–6**), were stoichiometric 1:1 (host to guest) complexes, even though η^2-acetylenedicobalt hexacarbonyl complexes were treated with a 2-fold molar excess of γ-CD.

Properties of inclusion compounds

The IR and ^1H NMR spectral data of the inclusion compounds are summarized in Table 1. The IR spectra of the inclusion compounds show sharp carbonyl stretching absorptions and are very similar to those the guest complexes themselves show in solution, but are different from those in the solid state which show broad bands probably due to intermolecular interactions. These results indicate that the guest complexes are isolated from each other in the cavity as in solution.

Inclusion by cyclodextrin gives thermal stability to the metal cluster complexes. The thermogravimetric analysis revealed, for example, that the inclusion compound of **5** with γ-CD is stable up to 110 °C under an argon atmosphere, though under the same conditions the nonincluded cobalt complex decomposes at 83 °C (Fig. 1). This result was fully confirmed by the IR investigation. The IR spectrum of nonincluded **5** showed, after heated up to 100 °C, no absorption bands in the carbonyl region, indicating complete decomposition. In contrast the γ-CD inclusion compound showed after the same treatment clear strong absorption bands due to the carbonyl ligands at 2020, 2050, and 2090 cm^{-1}. The decomposition points of the inclusion compounds and the nonincluded complexes obtained by thermal analysis are summarized in Table 3. Comparison of the decomposition points T_1 and T_2 demonstrates that all the metal cluster complexes tested here are stabilized by tight inclusion within γ-CD.

According to CPK models the cobalt cluster complexes tested here are too large to be included in the α-CD or β-CD cavity, but γ-CD is large enough to accommodate them. Only η^2-diphenylacetylenedicobalt hexacarbonyl (**7**) which has a phenyl group at both ends of the acetylene ligand fails to be included as the guest. Proposed structure for the inclusion compound of **4** is shown in Fig. 2.

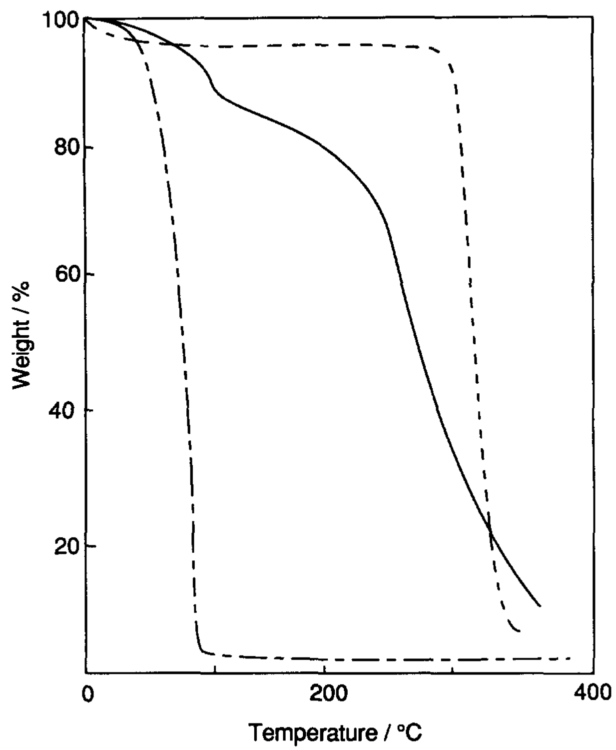

Fig. 1. Thermogravimetric analysis of inclusion compound of η^2-dimethylacetylenedicobalt hexacarbonyl with γ-CD (———), free η^2-dimethylacetylenedicobalt hexacarbonyl (— - —), and free γ-CD (- - - - - -).

Experimental section

General

All reactions were carried out under a nitrogen atmosphere. γ-CD was donated by Sanyou Kokusaku Pulp Co., Ltd. and α- and β-CDs were obtained from

Table 3
Decomposition points of γ-CD inclusion compounds and metal clusters [a]

	Dec. point (°C)		$T_1 - T_2$
	Inclusion compounds T_1	Metal clusters T_2	
1	99	77	22
2	99	81	18
3	97	77	20
4	96	79	17
5	112	83	29
6	111	83	28
8	118	85	33
9	110	84	26

[a] **1**–**6**: under an argon atmosphere; **8** and **9**: under vacuum.

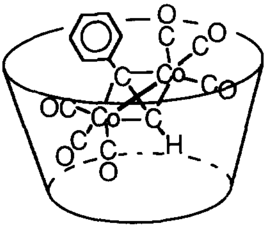

Fig. 2. Proposed structure of the inclusion compound of η^2-phenylacetylenedicobalt hexacarbonyl with γ-CD.

Nacalai Tesque, Inc. They were used without further purification. The cobalt complexes were prepared from octacarbonyldicobalt according to the methods described in the literature [13]. Infrared spectra were recorded on a Hitachi 295 spectrometer and ^{1}H NMR spectra were measured for hexadeuteriodimethylsulfoxide solutions with tetramethylsilane as an internal standard using a Brucker 360 MHz spectrometer. Thermogravimetric analysis was made with a Shimadzu DT-30 thermal analyzer. Atomic absorption analysis was made with a Shimadzu A-610S atomic absorption/flame spectrophotometer.

Preparation of inclusion compounds

The inclusion compound of η^2-dimethylacetylenedicobalt hexacarbonyl (**5**) with γ-CD was prepared by adding **5** (0.34 g, 1.0 mmol) to an aqueous solution of γ-CD (2.59 g, 2.0 mmol). After stirring for 8 h at 40 °C, the hot mixture was allowed to cool slowly overnight to room temperature. The product precipitated was filtered off and washed thoroughly with water to remove any remaining γ-cyclodextrin, then vacuum dried. Non-included **5** was removed by washing the residue with tetrahydrofuran and vauum drying. γ-CD-**5**: 1.31 g, pale brown powder.

The other inclusion compounds were prepared and isolated in the same manner, and their analytical and spectral data are summarized in Tables 1 and 2.

References

1 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry: a comprehensive text, 5th ed., Wiley-Interscience, New York, 1988, p. 1053.

2 A. Yamamoto, Organotransition Metal Chemistry—Fundamental Concepts and Applications, Wiley-Interscience, New York, 1986, p. 426.

3 F.R. Hartley (Ed.), The Chemistry of the Metal-Carbon Bond, Vol. 4, Wiley-Interscience, Chichester, 1987, p. 1163.

4 J. Szejtli, Cyclodextrins and Their Inclusion Complexes, Akademiai Kiado, Budapest, 1982; M.L. Bender and M. Komiyama, Cyclodextrin Chemistry, Springer Verlag, Berlin, 1978; W. Saenger, Angew. Chem., Int. Ed. Engl., 19 (1980) 344.

5 M. Colquhoun, J.F. Stoddart and D.J. Williams, J. Chem. Soc., Chem. Commun., (1981) 612; H.M. Colquhoun, S.M. Doughty, J.F. Stoddart and D.J. Williams, Angew. Chem., Int. Ed. Engl., 23 (1984) 235; L. Allwood, H.M. Colquhoun, J. Crosby, D. Pears, J.F. Stoddart and D.J. Williams, ibid., 23 (1984) 235; D.R. Alstone, A.M.Z. Slawin, J.F. Stoddart, D.J. Williams and R. Zarzycki, ibid., 26 (1987) 692; H.M. Colquhoun, S.M. Doughty, J.F. Stoddart, A.M.Z. Slawin and D.J. Williams, J. Chem. Soc., Dalton Trans., (1986) 1639.

6 B. Dietrich, M.W. Hosseini, J.-M. Lehn and R.B. Sessions, J. Am. Chem. Soc., 103 (1981) 1282; M.F. Manfrin, L. Moggi, V. Castelvetro, V. Balzani, M.W. Hosseini and J.-M. Lehn, ibid., 107 (1985) 6888.

7 L. Atwood, G. William Orr, F. Hamada, R.L. Vincent, S.G. Bott and K.D. Robinson, J. Am. Chem. Soc., 113 (1991) 2760; F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc., Chem. Commun., (1990) 1083.

8 M. Colquohoun, J.F. Stoddart and D.J. Williams, Angew. Chem., Int. Ed. Engl., 25 (1983) 487; D.R. Alstone, A.M.Z. Slawin, J.F. Stoddart and D.J. Williams, ibid., 24 (1985) 786; D.R. Alstone, A.M.Z. Slawin, J.F. Stoddart, D.J. Williams and R. Zarzycki, ibid., 27 (1988) 1184; J.F. Stoddart and R. Zarzycki, Recl. Trav. Chim. Pays-Bas, 107 (1988) 515; P.R. Ashton, J.F. Stoddart and R. Zarzycki, Tetrahedron Lett., (1988) 2103; V.I. Sokolov, Metalloorg. Khim., 4 (1988) 25; B. Klingert and G. Rhis, Organometallics, 9 (1990) 1135; Y. Kuroda, Y. Sasaki, Y. Shiroiwa and I. Tabushi, J. Am. Chem. Soc., 110 (1988) 4049; Y. Kuwajiri and N. Motohashi, J. Chem. Soc., Chem. Commun., (1989) 1336; M. Nango, M. Higuchi, H. Gondo and M. Hara, ibid., (1989) 1550; N. Kobayashi and M. Opallo, ibid., (1990) 477; R. Isnin, C. Salam and A.E. Kaifer, J. Org. Chem., 56 (1991) 35.

9 A. Harada and S. Takahashi, J. Chem. Soc., Chem. Commun., (1984) 645; A. Harada and S. Takahashi, ibid., (1984) 645; A. Harada and S. Takahashi, ibid., (1986) 1229; A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, J. Chem. Soc., Dalton Trans., (1988) 729; Y. Odagaki, K. Hirotsu, T. Higuti, A. Harada and S. Takahashi, J. Chem. Soc., Perkin Trans. 1, (1990) 1230; A. Harada, K. Saeki and S. Takahashi, Organometallics, 8 (1989) 730; A. Harada, S. Yamamoto and S. Takahashi, ibid., 8 (1989) 2560; A. Harada, K. Saeki and S. Takahashi, Chem. Lett., (1985) 1157; A. Harada, M. Takeuchi and S. Takahashi, ibid., (1986) 1893; A. Harada, Y. Hu and S. Takahashi, ibid., (1986) 2083.

10 M. Shimada, A. Harada and S. Takahashi, J. Chem. Soc., Chem. Commun., (1991) 263.

11 A preliminary report has been published; A Harada, M. Shimada and S. Takahashi, Chem. Lett., (1989) 275.

12 M. Shimada and S. Takahashi, unpublished results.

13 Y. Iwasita, Inorg. Chem., 8 (1969) 1179; G. Bor, Inorg. Chim. Acta, 18 (1976) L18; H. Greenfield, J. Am. Chem. Soc., 78 (1956) 120; G. Palyi, Inorg. Chim. Acta, Rev., 4 (1970) 109; I.V. Khaud, J. Chem. Soc., Perkin Trans. 1, (1973) 975.