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Preliminary Communication

Preparation and properties of cyclodextrin–metal carbonyl inclusion compounds

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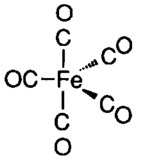
Abstract

One-to-one inclusion compounds were obtained in a crystalline state in high yields by treatment if ironpentacarbonyl and dimanganesedecacarbonyl with γ-cyclodextrin. These represent the first examples of cyclodextrin inclusion compounds with binary metal carbonyl complexes; the metal carbonyl complexes included in cyclodextrins are thermally more stable than the free complexes.

Cyclodextrins (CDs) comprise a series of cyclic molecules composed of six, seven or eight glucose units (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 complexes with a wide variety of guest compounds without any covalent bond being formed [1]. Recently we and Stoddart *et al.* have reported the preparation and properties of cyclodextrin inclusion compounds with organometallic complexes [2]. However, to date, the guest organotransition–metal complexes have been limited to those having a hydrophobic moiety such as cyclopentadienyl [3], arene [4], diene [5], alkyne [6] or phosphine [7] ligand on the metal, and there have been no reports, to our knowledge, on the interaction between cyclodextrins and the simple metal carbonyl complexes without such organic ligands. Our interest in this class of transition-metal complexes, which catalyze carbonylation of olefins or acetylenes, has led us to consider their potential as guest molecules for cyclodextrins, and the product inclusion compounds are potentially water-soluble catalysts. Now we have attempted to prepare the inclusion compounds of binary metal carbonyl complexes and a related nitrosyl carbonyl complex with cyclodextrins and have investigated the thermal stability of the complexes included in cyclodextrins. We report here the preparation and characterization of cyclodextrin inclusion compounds of ironpentacarbonyl, dimanganesedecacarbonyl and tricarbonylnitrosylcobalt [8].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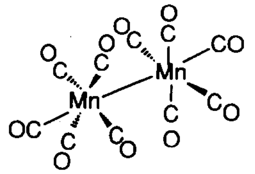
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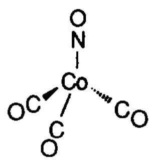
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Inclusion compounds of metal carbonyl complexes with cyclodextrins were prepared by adding fine crystals of the complexes to a stirred saturated aqueous solution of cyclodextrin at 40°C under a carbon monoxide atmosphere. The product which precipitated was collected and washed with water to remove remaining cyclodextrin, and dried *in vacuo*. Nonincluded metal complexes were removed by washing the residue with methylene chloride. During this process, the included guest complex was not liberated from the cyclodextrin cavity. Table 1 shows the results for the preparation of cyclodextrin inclusion compounds of metal carbonyl complexes and a related nitrosyl carbonyl complex. The inclusion compounds were characterized by elemental analyses and IR spectra as well as the thermal analyses. Stoichiometries were determined by elemental analyses and the metal contents measured by atomic absorption analyses. Dimanganesedecacarbonyl formed 1:1 inclusion compounds in a high yield with γ-CD having the largest cavity among three cyclodextrins, while α-CD and β-CD did not encapsulate the complex. In the case of ironpentacarbonyl and tricarbonylnitrosylcobalt, both formed 1:1 inclusion compounds with β- or γ-CD, while α-CD gave 2:1 (α-CD: guest) complexes even if α-CD was treated with excess ironpentacarbonyl or tricarbonylnitrosylcobalt.

Inclusion by CD increases thermal stability of metal carbonyl complexes. The thermogravimetric analysis revealed that the inclusion compound of dimanganesedecacarbonyl with γ-CD is stable up to 174°C under an argon atmosphere, though under the same

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TABLE 1. Preparation of inclusion compounds

Guest	CD	Yield (%)	Metal		CD:Guest
			Found (%)	Calcd (%)	
$Fe(CO)_5$	α	14[a]	2.47	2.46	2:1
	β	27[b]	3.15	3.74	1:1
	γ	40[c]	3.33	3.65	1:1
$Mn_2(CO)_{10}$	α	0	–	–	–
	β	0	–	–	–
	γ	85[d]	5.99	6.37	1:1
$CoNO(CO)_3$	α	25[e]	2.69	2.70	2:1
	β	28[f]	–	–	1:1
	γ	32[g]	3.61	4.01	1:1

[a] Analysis: C, 40.64 (40.78), H, 5.75 (5.95)%, (required values in parentheses, calculated as 2α-CD-**1**$\cdot 7H_2O$). IR (Nujol) ν(CO) 2027, 1999 cm^{-1} [*cf.* (free **1**) ν(CO) 2022, 1998, 1965 cm^{-1}].

[b] Analysis: C, 37.51 (37.81), H, 5.86 (5.94)%, (β-CD-**1**$\cdot 9H_2O$). IR ν(CO) 2027, 1999 cm^{-1}.

[c] Analysis: C, 41.43 (41.63), H, 5.76 (5.53)%, (γ-CD-**1**$\cdot 2H_2O$). IR ν(CO) 2025, 1985 cm^{-1}.

[d] Analysis: C, 40.21 (40.42), H, 5.18 (4.91)%, (γ-CD-**2**$\cdot 2H_2O$). IR ν(CO) 2045, 2020 cm^{-1} [*cf.* (free **2**) ν(CO) 2040, 2008, 1986 cm^{-1}.

[e] Analysis: C, 41.94 (42.16), H, 6.02 (5.76), N, 0.70 (0.66)%, (2α-CD-**3**$\cdot H_2O$). IR ν(CO) 2095, 2025 cm^{-1}, ν(NO) 1805 cm^{-1} [*cf.* (free **3**) ν(CO) 2095, 2033 cm^{-1}, ν(NO) 1805 cm^{-1}].

[f] Not obtained in an analytically pure form. Calculated for the 1:1 inclusion compound.

[g] Analysis: C, 41.43 (41.67), H, 5.70 (5.49), N, 1.00 (0.95)%, (γ-CD-**3**). IR ν(CO) 2095, 2025 cm^{-1}, ν(NO) 1795 cm^{-1}.

conditions the nonincluded manganese complex decomposes at 128°C (Fig. 1). This result was fully confirmed by the IR investigation. The IR spectrum of nonincluded dimanganesedecacarbonyl showed, after heating up to 140°C, no absorption bands in the carbonyl region, indicating complete decomposition. In contrast the γ-CD inclusion compound showed clear strong absorption bands due to the carbonyl ligands at 2020 and 2045 cm^{-1} after the same treatment. Dimanganesedecacarbonyl is stabilized by tight inclusion within a γ-CD cavity.

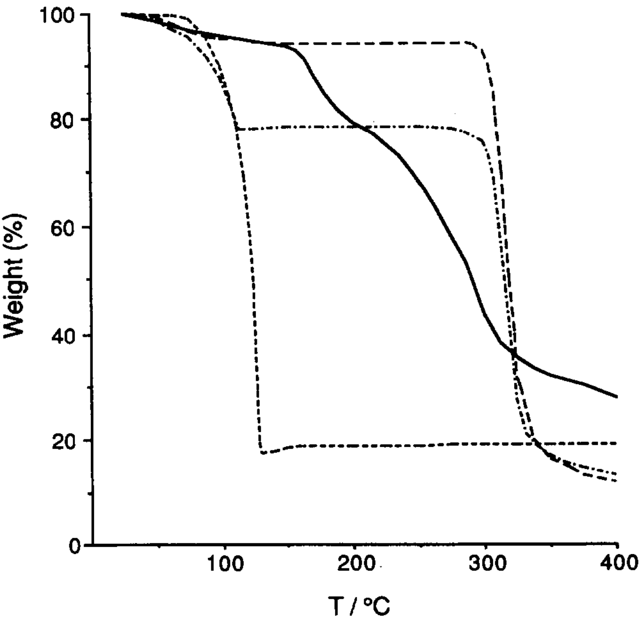

Fig. 1. Thermogravimetric analysis of $Mn_2(CO)_{10}$ (- - - - - -), its 1:1 γ-CD inclusion compound (————), γ-cyclodextrin (— — —), and a 1:1 mixture of $Mn_2(CO)_{10}$ and γ-cyclodextrin (·–·–·).

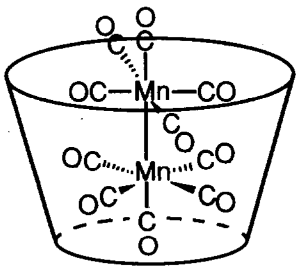

Fig. 2. Proposed structure of the inclusion compound of $Mn_2(CO)_{10}$ with γ-CD.

In the cases of ironpentacarbonyl and tricarbonylnitrosylcobalt the complexes in a free state evaporate or sublimate even at room temperature *in vacuo*, but their inclusion compounds are thermally stable and do not liberate the guest complexes on heating at 150°C *in vacuo*, indicating that the metal carbonyl complexes are tightly included in the cyclodextrin cavities.

According to a consideration with CPK structural models a molecule of dimanganesedecacarbonyl is too large to be included in an α-CD or a β-CD cavity, but γ-CD is large enough to accommodate the complex. Ironpentacarbonyl and tricarbonylnitrosylcobalt, which are more compact than dimanganesedecacarbonyl, fit well into a β-CD cavity, whereas it appears that they are too large to be completely encapsulated in a single α-CD cavity, but are accommodated within the cavity built up by two α-CD molecules. A proposed structure for the inclusion compound of dimanganesedecacarbonyl is shown in Fig. 2.

Acknowledgments

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