Preparation and Properties of Inclusion Complexes of 1,2-Dicarbadodecaborane(12) with Cyclodextrins

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One-to-one inclusion complexes were obtained in a crystalline state in high yields by treatment of β- and γ-cyclodextrin with 1,2-dicarbadodecaborane(12) (*o*-carborane), whereas α-cyclodextrin formed a 2 : 1 (cyclodextrin : guest) complex on sonication, and a 1 : 1 complex on crystallization from water–propan-2-ol.

Although cyclodextrins (α-, β-, and γ-CD) form inclusion complexes with a wide variety of organic compounds[1] and some organometallic complexes,[2] there are only a few reports on the preparation of inclusion complexes of inorganic compounds,[3] and none, to our knowledge, on inclusion complexes of main-group compounds. Carboranes have unique cage-type structures[4] and their dianions form complexes with transition metal complexes.[5] We have found that cyclodextrins form crystalline stoicheiometric inclusion complexes with 1,2-dicarbadodecaborane(12) (*o*-carborane) in high yields.

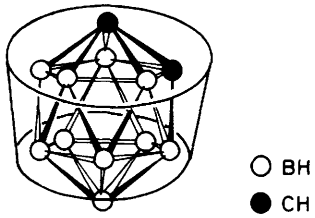
Inclusion complexes of *o*-carborane with cyclodextrins were obtained in good yield by sonication of an aqueous suspension of *o*-carborane in a saturated aqueous solution of the CD (method A), or by addition of a solution of *o*-carborane in propan-2-ol to an aqueous solution of the CD (method B). The precipitated product was washed with water to remove any remaining CD. Non-included *o*-carborane was removed by washing with benzene. During this process the guest was not liberated from the CD cavity. The products were recrystallized from water–propan-2-ol (4 : 1).

The results are summarised in Table 1; in particular β-CD gave inclusion complexes quantitatively by method B. The complexes were characterized by elemental analysis, i.r. and ^{1}H n.m.r. spectroscopy, and thermal analysis. They were all shown to be stoicheiometric compounds, with definite

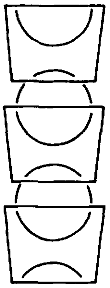
Table 1. Preparation of inclusion complexes.

		Product			
		Method A		Method B	
CD	Molar ratio CD : guest	Yield (%)	CD : guest	Yield (%)	CD : guest
α-CD	1 : 1	74[a]	2 : 1	88[b]	1 : 1
	2 : 1	58	2 : 1	88	1 : 1
β-CD	1 : 1	35	1 : 1	100[c]	1 : 1
	2 : 1			100	1 : 1
γ-CD	1 : 1	54	1 : 1	83	1 : 1
	2 : 1			92	1 : 1

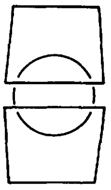
[a] Analysis: C, 42.2 (42.5), H, 6.5 (6.4), B, 5.35% (5.2%) (required values in parentheses); ^{1}H n.m.r. [360 MHz; $(CD_3)_2SO$] δ 4.70 (1H, s); i.r. (Nujol) ν_{B-H} 2600 cm^{-1} [*cf.* ν_{B-H} (free carborane) 2570 cm^{-1}]. [b] Analysis: C, 40.8 (40.85), H, 6.8 (6.5), B, 9.5% (9.7%); ^{1}H n.m.r. [360 MHz; $(CD_3)_2SO$] δ 4.70 (2H, s); i.r. (Nujol) ν_{B-H} 2600 cm^{-1}. [c] Analysis: C, 41.1 (41.3), H, 6.75 (6.5), B, 8.3% (8.45%); ^{1}H n.m.r. [360 MHz; $(CD_3)_2SO$] δ 4.70 (2H, s); i.r. (Nujol) ν_{B-H} 2580 cm^{-1}.



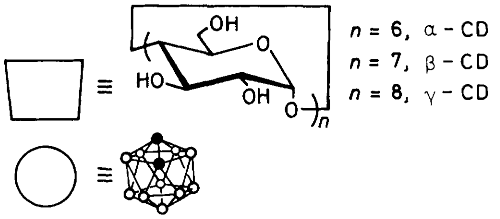
(1)



(2a)



(2b)



CD : guest ratios depending on the cyclodextrin and the preparation method. β-CD and γ-CD gave 1 : 1 inclusion complexes by both methods A and B, even when *o*-carborane was treated with a two molar excess of CD. α-CD formed a 2 : 1 (CD : guest) complex even when sonicated with an equimolar amount of *o*-carborane (method A), but gave a 1 : 1 complex by method B.

These inclusion complexes are sufficiently stable to be recrystallized from water–propan-2-ol. They are also thermally stable: they do not liberate *o*-carborane when heated to 200 °C *in vacuo*. Non-included *o*-carborane is completely sublimed below 80 °C under reduced pressure. Thermogravimetric analyses showed that stability of these complexes persists up to 250 °C; dissociation occurs around the m.p. of the CD component (about 270 °C). These results indicate that the *o*-carborane is tightly included in a CD cavity.

Included *o*-carborane could be recovered by refluxing an aqueous ethanolic solution of the inclusion complex or by heating *in vacuo* in a sublimation tube to the m.p. of the CD.

Computer simulations of the molecular structure indicate that *o*-carborane fits well into a β-CD cavity as shown in structure (**1**). However, it appears that the *o*-carborane molecule is too large to be completely included in a single α-CD cavity, but fits well into the cavity formed by two α-CD molecules.[6] Therefore, we propose structure (**2a**) for the 1 : 1 inclusion complexes obtained by crystallization from water–propanol and the structure (**2b**) for the 2 : 1 complexes obtained by sonication.

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