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Carboranes as guests, counterions and linkers in coordination polymers and networks

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This review is dedicated to Russ Grimes, a true pioneer in carborane (carbaborane) cluster chemistry, on the occasion of his 80th birthday.

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ABSTRACT

Carborane clusters play a variety of roles in the assembly of 1D-coordination polymers and 2D- and 3D-networks. In this review, comments on coordination polymers in which neutral carborane guests are accommodated are followed by discussion of the incorporation of anionic carboranes into coordination polymers and networks, with critical comments concerning the classification of some 'coordination polymers' within the 2013 IUPAC guidelines. Functionalization of carborane clusters with carboxylato, phosphino, thiolato or 2,2′:6′,2″-terpyridinyl domains provides potential for their incorporation as covalently bound linkers into the backbones of coordination polymers and frameworks; in the case of phosphino- and thiolato-functionalized clusters, the carborane clusters are located on the periphery of the 1D-polymer chains.

Introduction

Russ Grimes has been active in the field of carborane chemistry since the 1960s and during this period, icosahedral C_2B_{10} and CB_{11}-clusters have progressed from something of a geometrical oddity to being components in a huge number of materials with wide-ranging applications [1]. In this article, the interface between icosahedral carboranes and coordination polymers including metal-organic frameworks, MOFs [2], is reviewed. The roles of carborane clusters in 1D-coordination polymers [3] and 2D- and 3D-networks varies from their capture as guest molecules, to their incorporation as weakly coordinating anions, and to their functionalizion so they can act as linkers in the backbones of coordination polymers and nets.

All searches of the Cambridge Structural Database (CSD) made for this review used the CSD version 5.36 with updates to November 2014 [4] and Conquest v. 1.17 [5] and figures have been drawn using original data.

Coordination polymers as hosts for carboranes

The bowl-shaped molecule cyclotriveratrylene (CTV) is dimensionally compatible with an icosahedral carborane cage. The transition from simple host-guest assembly with discrete domains [6] to coordination polymer [7] is made by replacing neutral 1,2-$C_2B_{10}H_{12}$ by a salt $M[CB_{11}H_{12}]$ (M = Na, K, Rb, Cs). However, the situation is not as straightforward as this statement suggests. A comparison of the structures of $\{[M(CTV)_2(OH)(H_2O)_2]\cdot DMF\cdot$1,2-$C_2B_{10}H_{12}\}_n$ (formed from CTV, 1,2-$C_2B_{10}H_{12}$ and MOH with M = Cs or Rb in DMF), $\{[Cs(CTV)_2(H_2O)_3][CB_{11}H_{12}]\cdot 2DMF\}_n$ (formed from CTV and $Cs[CB_{11}H_{12}]$) and $\{[Rb(CTV)_2(H_2O)_3][CB_{11}H_{12}]\cdot 2DMF\}_n$ (formed from CTV and $Rb[CB_{11}H_{12}]$ in the presence of MOH) reveals similar features (Fig. 1a); the structures are also similar to those of related systems containing K^+ and Na^+ ions. The authors [7] conclude that the carborane plays the same role whether it is neutral or anionic, and therefore steric factors are dominant. Functionalization of CTV with peripheral metal-binding domains (e.g. pyridyl groups, **1**, Scheme 1) provides a 3-connecting linker. When combined with $Cd(OAc)_2$, a 4.8^2 net assembles (Fig. 1b) which hosts 1,2-$C_2B_{10}H_{12}$ molecules within the bowl-shaped cavities of **1** (Fig. 1c). In the absence of the carborane, the

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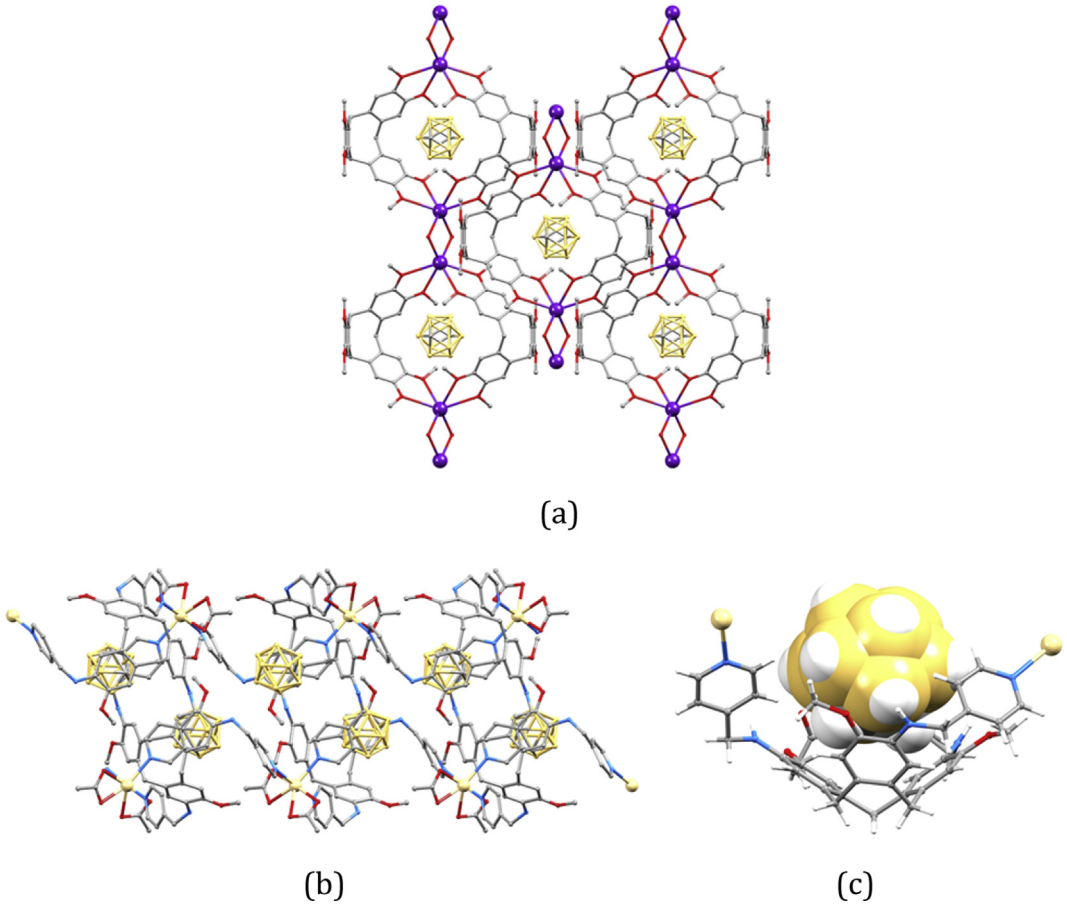
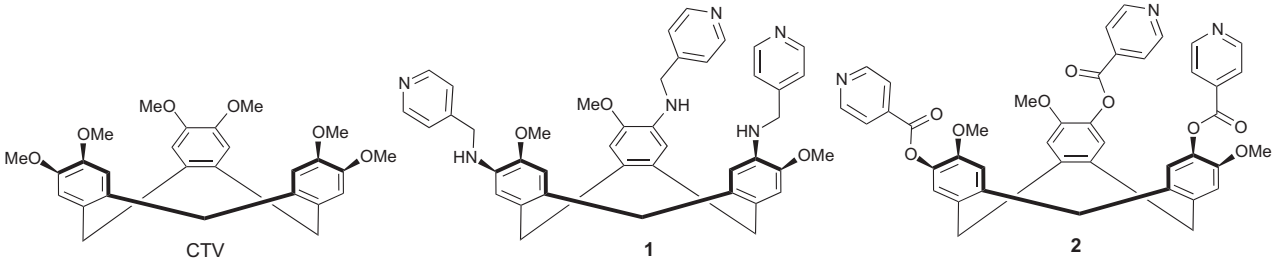


Fig. 1. Part of one sheet in (a) $\{[Rb(CTV)_2(OH)(H_2O)_2]\cdot DMF\cdot 1,2\text{-}C_2B_{10}H_{12}\}_n$ (CSD refcode XETTEV); H atoms and DMF molecules omitted, and (b) $\{[Cd(OAc)_2(\mathbf{1})]\cdot 2H_2O\cdot 1,2\text{-}C_2B_{10}H_{12}\}_n$ (refcode PUQKAO); H atoms and H_2O molecules omitted. (c) Accommodation of a $1,2\text{-}C_2B_{10}H_{12}$ molecule in the bowl-shaped host in $\{[Cd(OAc)_2(\mathbf{1})]\cdot 2H_2O\cdot 1,2\text{-}C_2B_{10}H_{12}\}_n$.



Scheme 1. Structures of cyclotriveratrylene (CTV), tris(4-pyridylmethylamino)cyclotriguaiacylene (**1**) and tris(isonicotinoyl)cyclotriguaiacylene (**2**).

2D-network is no longer formed. The authors [8] propose a discrete assembly for the cluster-free product, but crystallographic data are not available to confirm the structure. The templating ability of carboranes in coordination networks is reminiscent of the role that the fullerene C_{60} is known to play. However, templating cannot be guaranteed as is demonstrated in the reaction of **2** (Scheme 1) with $Ag[Co(C_2B_9H_{11})_2]$ in MeCN. Crystals isolated from this mixture have the composition $\{[Ag(\mathbf{2})_2][Co(C_2B_9H_{11})_2]\cdot 9MeCN\}_n$ and ligand **2** binds Ag^+ through only two of the three pyridyl domains generating a 1D-coordination polymer; chains are interwoven into 2D-sheets and the $[Co(C_2B_9H_{11})_2]^-$ anions reside in channels between the sheets rather than being hosted in the bowl-shaped cavities of **2**. In contrast to the templating effects of the neutral carborane in $\{[Cd(OAc)_2(\mathbf{1})]\cdot 2H_2O\cdot 1,2\text{-}C_2B_{10}H_{12}\}_n$, the bulky $[Co(C_2B_9H_{11})_2]^-$ anions in $\{[Ag(\mathbf{2})_2][Co(C_2B_9H_{11})_2]\cdot 9MeCN\}_n$ simply aid crystallization [9].

Carborane anions: weakly coordinating or coordinatively innocent?

The weakly coordinating nature of carborane anions allows them to act as putative linkers in coordination polymers. Many will argue that assemblies so formed are not true coordination polymers, the IUPAC definition of a coordination polymer being: '*a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions*' [10]. Nonetheless, the literature appears to have accepted the use of the term 'coordination polymer' where B–H ⋯ M interactions are the primary interactions directing polymer or network assembly [11], despite the fact that the M ⋯ B separations (more accurately determined than M ⋯ H distances) are typically longer than observed in metal tetrahydridoborato complexes in which $[BH_4]^-$ ions are ligands [12]. In this section, B–H⋯Ag interactions are considered, and two popular anions are