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Review

Anion receptor chemistry: Highlights from 2016

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Dedicated to Professor Paul D. Beer on the occasion of his 60th birthday.

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ABSTRACT

This review covers recent advances in anion receptor chemistry from 2016, including developments in self-assembly, sensing, anion separation, transport, catalysis and fundamental advances in anion recognition systems.

Contents

Abbreviations: AcO^-, acetate; CD, circular dichroism; CyD, cyclodextrin; CPP, cell penetrating peptide; DFT, density functional theory; DMF, dimethylformamide; DMSO, dimethylsulfoxide; EPR, electron paramagnetic resonance; G, guest; H, host; HPLC, high performance liquid chromatography; ITC, isothermal titration calorimetry; K_a, association constant; MD, molecular dynamics; MS, mass spectrometry; NMR, nuclear magnetic resonance; TBA, tetrabutylammonium.

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1. Introduction

This article marks the 20th year of coverage of anion receptor chemistry by this series of reviews. In the first review, published in Coordination Chemistry Reviews in 2000 (and covering highlights in anion coordination and anion directed assembly in 1997 and 1998) [1], it was noted that

> "Anion coordination has received little attention over the last 30 years when compared to that devoted to the coordination chemistry of cations."

Now as we look back over the last 50 years we see that this has changed and that many real world applications for anion complexation have emerged [2]. Although this review has moved between publications over the last two decades [1,3–11]; – it is appropriate for it return to Coordination Chemistry Reviews to mark both this milestone and the special issue devoted to Coordination Chemistry in Australia.

2. Fundamental studies

This section covers the development of new receptors and understanding the fundamentals of anion interactions, ranging from classic hydrogen-bond systems to more exotic halogen and chalcogen bond-based receptors. In 2016, we have seen examples of anion receptors that advance our understanding of aromatic, hydrophobic and ion-pair interactions, and the development of photo-switchable receptors and multivalent systems.

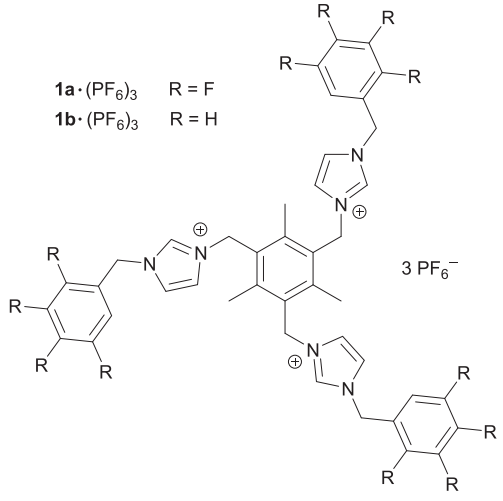

Fig. 1. Structure of tripodal CH hydrogen-bonding receptors **1a**·$(PF_6)_3$ and **1b**·$(PF_6)_3$.

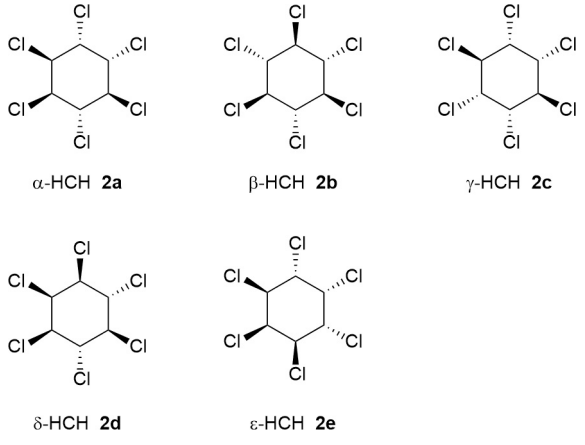

Fig. 2. Diastereomers of hexachlorocyclohexane (HCH) **2a–e**.

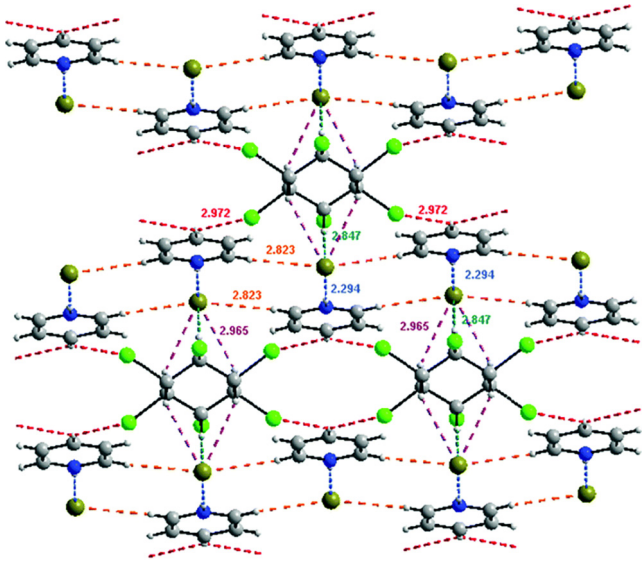

Fig. 3. Representation of the solid-state supramolecular network in the pyridine hydrochloride complex of β-HCH **2b** [the β-sheet like ribbons (contact in orange and blue) and the 2D structure are shown in detail, while the formation of the 3D aggregate is suggested by the contacts (in red) involving the hydrogen atom at the 4-position of the pyridine rings]. Atom colors: white, H; gray, C; blue, N; green, Cl; yellow, Br. Reproduced with permission from Grosu et al. [13]. Copyright 2016 The Royal Society of Chemistry.

2.1. Hydrogen-bond based receptors

A number of groups have exploited CH hydrogen bonds for the recognition of anions. Amendola and co-workers [12] reported the CH hydrogen bonding receptor **1a**·$(PF_6)_3$ based on a tripodal 1,3,5-trimethylbenzene scaffold and incorporating imidazolium and 2,3,4,5-tetrafluorobenzene moieties as CH hydrogen-bond donors (see Fig. 1). Proton NMR titrations in CD_3CN and CD_3CN/DMSO-d_6 9:1 demonstrated that the receptor possessed a strong affinity for chloride with $\log K_a \geq 6$ and in the more competitive CD_3CN/D_2O 4:1 binding chloride with a $\log K_a$ of 3.4. Analogous experiments using the non-fluorinated analog **1b**·$(PF_6)_3$ showed no shift in the *ortho*-benzyl protons and a much-reduced $\log K_a$ of 2.2. This, and upfield shifts of all signals in ^{19}F NMR titrations of $\mathbf{1a}^{3+}$ with TBACl in CD_3CN due to polarization of the aromatic C—F bonds, revealed the contribution of the CH hydrogen-bonds from the 2,3,4,5-tetrafluorobenzene motifs to anion complexation.

Grosu et al. [13] have investigated the anion recognition properties of the diastereomers of hexachlorocyclohexane (HCH) (Fig. 2). For example, in the solid state, β-HCH **2b** formed a 1:2 complex with pyridinium chloride and pyridinium bromide (Fig. 3). β-HCH was able to bind an anion on each face of the ring through six CH···anion contacts. The pyridine rings connect to three anions through two CH···X^- interactions and NH^+···X^- contacts, allowing the assembly of a 2D network of supramolecular ribbons. A second structure with pyridinium bromide was also observed (Fig. 4), comprising ~20% of crystals obtained. This 1:1:1 complex of β-HCH/Py·HBr/Py formed columns of β-HCH Br^- complexes, linked into 2D sheets by halogen-bonding between C—Cl bonds on the ring. CH interactions between the anion and pyridine–pyridinium units sharing a proton link these sheets in the greater 3D structure. Proton NMR titrations however, indicated a 1:1 binding mode in solution with binding constants ranging from 1400 M^{-1} for HSO_4^- to 2200 M^{-1} for Cl^- (CD_3CN).