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Resolution of Racemic 1,2-Dibromohexafluoropropane through Halogen-Bonded Supramolecular Helices[**]

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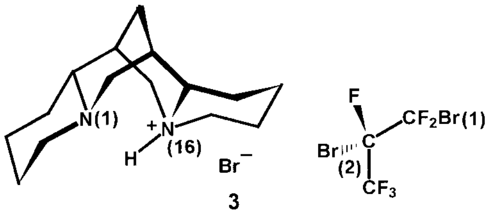
Giuseppe Resnati,[*] and Giuseppe Vecchio

The chemical and physical properties of functionalized perfluorocarbons (PFCs) differ substantially from those of corresponding hydrocarbons (HCs).[1] The unique combination of properties expected for enantiopure PFC derivatives is likely to present unprecedented applications and to yield important information,[3] but this anticipation can hardly be verified as enantiopure PFCs are a virtually unknown class.[6]

As a consequence of the unique features of PFC derivatives, specifically tailored methodologies have to be developed to make enantiopure PFC derivatives available. The approach to obtain optically pure compounds by resolving their racemic forms through formation of diastereoisomeric and noncovalent adducts is well established in the HC series. This procedure could be applied to the resolution of racemic PFC derivatives by means of enantiopure HC resolving agents if an adequate PFC–HC interaction is identified. Here we describe the first example of a pairing that proves effective in the case of dibromoperfluoroalkanes. We report that the electron donor–acceptor interaction between enantiopure trialkylammonium hydrobromides (electron donor) and racemic perfluoroalkyl bromides (electron acceptor) is robust and selective enough to allow the resolution of the latter compounds through PFC–HC cocrystal formation.

We have already described the attractive intermolecular interaction between perfluoroalkyl iodides and trialkylamines.[7, 8] The term "halogen bond" has been proposed[9] for this interaction owing to its similarities with the hydrogen bond. The halogen bond is specific, directional, and strong enough to overcome the low affinity existing between PFC and HC derivatives, driving the self-assembly of the two motifs into solid and crystalline noncovalent copolymers starting from individual components which are liquid at room temperature. An electron donor–acceptor interaction occurs also between perfluoroalkyl bromides and nitrogen, oxygen, and sulfur atoms present in HC compounds, but this interaction is weaker that that with perfluoroalkyl iodides.[10] Thus it is not surprising that no solid copolymer was obtained starting from racemic 1,2-dibromohexafluoropropane and various chiral and enantiopure diamines (e.g. (−)-1,2-diaminocyclohexane, (+)-Tröger's base, (−)-sparteine).[11]

In contrast, when enantiopure (−)-sparteine hydrobromide (**1**) and racemic 1,2-dibromohexafluoropropane (**2**) were mixed in chloroform, the yellow cocrystal **3**, made up of **1** and (*S*)-**2** exclusively, was isolated (Figure 1). The architecture of **3** (Figure 2), as determined by single-crystal X-ray diffraction,[14] clearly evidences the propensity towards segregation of the functionalized PFC and HC motifs.[18] On the other hand, the high cohesion of the cocrystal **3** is demonstrated by its thermal stability (m.p. 105 °C, decomp.), when compared to the low melting point of racemic **2** (−95 °C), and by the 4% molar volume reduction with respect to the pure components (24 Å^3) on cocrystal formation.



3

Figure 1. Schematic representation of the interaction between units of **1** and **2** in the cocrystal **3** through halogen bonds. Selected bond distances [Å] and angles [°]: Br(1)···Br$^-$ 3.369(1), Br(2)···Br$^-$ 3.260(1), C–Br(1) 1.910(12), C–Br(2) 1.959(8), N(16)···Br$^-$ 3.548(6), N(1)···Br$^-$ 3.622(6); C–Br(1)···Br$^-$ 173.6(4), C–Br(2)···Br$^-$ 178.4(3), Br(1)···Br$^-$···Br(2) 143.01(4). The two bromine atoms bound to a given Br$^-$ ion belong to distinct PFC molecules. Standard sparteinium atom numbering is adopted.

The driving force towards cocrystallization is the Br$^-$··· Br–C intermolecular interaction between bromide ions, working as electron donors (i.e. bases), and carbon-bound bromine atoms, working as electron acceptors (i.e. acids).[20] Each bromide ion bridges a primary and a secondary bromine of two distinct PFC units **2**, each of which is well ordered through bonding to two bromide ions. Thus enantiopure, infinite twofold helices parallel to the *b* axis develop (Figure 3). The resolution of **2** is the result of a highly specific inclusion in a chiral crystal with a halogen-bonded helical arrangement. This process maximizes the transfer of information from the HC to the PFC units.

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[**] Perfluorocarbon-Hydrocarbon Self-Assembly, Part 5. Part 4: reference [7].

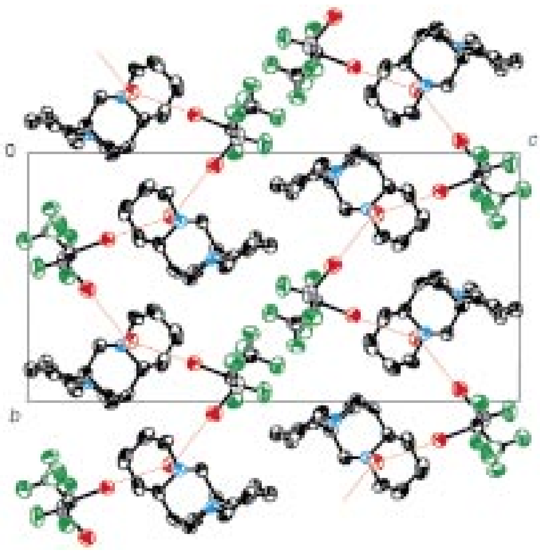

Figure 2. Projected view of **3** along the crystallographic *a* axis. Infinite twofold helices of the PFC units joined through bromide ions (red) extend along the *b* direction.

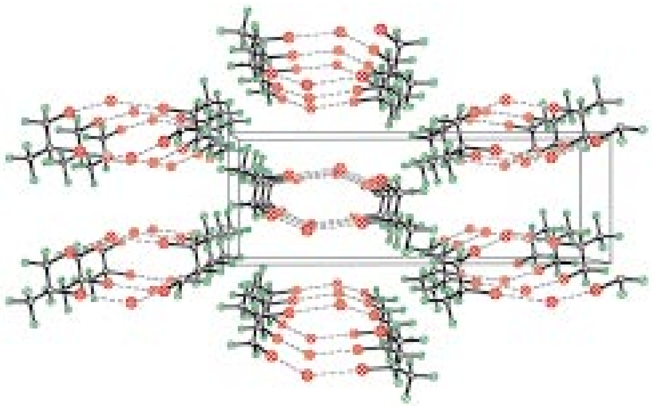

Figure 3. Perspective view of **3** along the crystallographic *b* direction: Sparteinium ions are omitted to better evidence the PFC halogen-bonded helices.

The $\mathrm{Br^-\cdots Br{-}C}$ distances in **3** (see Figure 1) are close to 3.3 Å, that is, approximately 20% shorter than the sum of the van der Waals radii, but substantially longer than Br–Br covalent bond lengths (2.3–2.5 Å). Rather extensive literature exists on attractive and noncovalent halogen–halogen interactions.[23] Several cases of stabilizing $\mathrm{Br^-\cdots Br{-}X}$ interactions[24] (e.g. $\mathrm{X = (CH_2CO)_2N}$) are documented in the literature, proving definitively the general ability of carbon-bound bromine atoms to act as electron acceptors with respect to bromide ions. The well-known anions $\mathrm{Br_3^-}$ and $\mathrm{I_3^-}$ can also be understood as the result of a halide–halogen interaction[25] that is so strong as to become nondistinguishable from a full covalent bond. In our case, the PFC skeleton of **2** withdraws electrons from the bromine atoms by an inductive effect, thus increasing the electron-acceptor ability of these carbon-bound bromine atoms and making the $\mathrm{Br^-\cdots Br{-}C}$ intermolecular interaction robust enough to drive the PFC–HC self-assembly.[26] Consistent with a significant $n\rightarrow\sigma^*$ character in this interaction[27] and with literature reports,[24, 25] the bromine atoms involved in the longer $\mathrm{Br^-\cdots Br{-}C}$ contacts show a shorter C–Br bond length.[28]

It is not surprising that the self-assembly of PFC derivatives which are inherently electron-acceptor species (i.e. acids) has been achieved through an anion-driven process. In general, the use of anions as templates for the formation of supramolecular entities is quite unexplored.[30]

The sparteinium hydrobromide forms a three-dimensional matrix interconnected by dispersion forces. Infinite columns of the PFC unit run through the crystal parallel to the crystallographic *a* axis, in pairs related by twofold screw axes. The rigid sparteinium unit in the adduct **3** is practically superimposable on the corresponding unit in single crystals of pure **1**,[31] and its spatial relationship to the bromide ion is only slightly perturbed by the presence of the functionalized PFC motif **2**, which clearly alters the packing of **1**.[32]

In conclusion, the implications of the described interaction are far reaching and extend to quite different fields. The ability of halide anions to act as electron donors to carbon-bound halogens may develop as a general protocol for halide-centered supramolecular chemistry. Any dibromo- or diiodoperfluoroalkane may become a suitable candidate for resolution through the processes described here. The $\mathrm{Br^-\cdots Br{-}C}$ interaction can be general enough to become also an economical approach for the separation of mixtures of PFC halides, a class of compounds of high technological relevance.[33] The approach of cocrystal formation followed by X-ray analyses might also be a reliable strategy for determining the absolute configuration of functionalized PFCs, a challenging, largely unresolved problem.[34] Implications of the results reported here can also be envisaged in all the fields where design and manipulation of chiral PFC aggregation processes play a key role.[38]

Experimental Section

3: Compounds **1** (1.576 g, 5.0 mmol) and **2** (0.714 mL, 5 mmol) were dissolved in chloroform (2.0 mL) at room temperature in a 10-mL vial of clear borosolicate glass. The open vial was placed in a closed cylindrical wide-mouth bottle (50 mL) containing **2** (5.0 mL). Chloroform and **2** were allowed to diffuse in slowly at −20 °C. After five days, yellow crystals of **3** (1.211 g) were filtered, washed with *n*-pentane, and analyzed. ^{13}C NMR ($\mathrm{CDCl_3}$; selected signals): $\delta = 25.82, 27.21, 29.50, 31.99, 35.54, 56.14, 58.55, 63.10, 63.93, 68.46$; ^{19}F NMR ($\mathrm{CDCl_3}$): $\delta = -133.53$ (CF), -74.35 ($\mathrm{CF_3}$), -59.26 and -57.42 ($\mathrm{CF_2}$); IR (KBr): $\tilde{\nu} = 2939, 2861, 1467, 1267, 1220, 1127, 917, 816, 704\ \mathrm{cm^{-1}}$; elemental analysis calcd for $\mathrm{C_{18}H_{27}Br_3F_6N_2}$ (625.12): C 34.89, H 4.88, Br 38.49, F 16.92, N 4.79; found: C 34.58, H 4.35, Br 38.35, F 18.23, N 4.48. X-ray analysis proves the optical purity of both HC and PFC units in the single crystal. The same prismatic morphology is shown by crystals from different crystallization batches, and powder diffraction patterns from microcrystalline material correspond with powder patterns simulated for the crystal structure of **3**. Moreover, circular dichroism spectra of (*S*)-**2** from crystallized and recrystallized batches were identical. Vacuum distillation of **3** (3 mmHg) allowed the **2** to be recovered as the distillate in pure form (liquid nitrogen trap,; circular dichroism: $[\Theta]^{20}_{193} = +2.59\times10^3$ ($c = 10.6\ \mathrm{mg\,mL^{-1}}$, $(n\text{-}\mathrm{C_3F_7})_3\mathrm{N}$); **1**, remaining unchanged, was ready for further use in the resolution of racemic **2**.

Received: December 21, 1998
Revised version: February 25, 1999 [Z12805IE]
German version: *Angew. Chem.* **1999**, *111*, 2585–2588

Keywords: chiral resolution · crystal engineering · fluorine · noncovalent interactions · supramolecular chemistry

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the *R* absolute configuration,[36] but after X-ray analyses it was revised as *S*.[37]

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A Germanium Zeotype Containing Intratunnel Transition Metal Complexes**

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Crystalline microporous materials are widely used in the fields of catalysis, ion exchange, and adsorption. Since the first discovery of zeolite, numerous natural and synthetic zeolites,[1–4] silica polymorphs, aluminophosphate-based molecular sieves, and microporous compounds built from MO_4 units ($M \neq Al, Si$)[5–8] have been synthesized.

Like silicon, germanium tends to be surrounded by a tetrahedron of oxygen atoms, which may join with other tetrahedra through shared corners to form larger units; in fact, some compounds of the two elements are isomorphous. However, in Ge zeotypes the structure of the framework can be formed by GeO_4 tetrahedra, GeO_6 octahedra, and sometimes GeO_5 trigonal bipyramids. Therefore, it is surprising that there are so few reports on microporous germanates. To our knowledge, the only fully characterized systems are those based on the pharmacosiderite structure[8–16] and those in which some of the Ge atoms are five-coordinate.[17, 18] Nevertheless, during the last year the interest in these materials seems to be increasing. We reported the new $(NH_4)_2Ge_7O_{15}$ (ICMM-1),[19] which is the first microporous material containing nine-rings. More recently, papers on new microporous germanates[20, 21] and gallogermanates[22–24] have appeared. All these new compounds have a framework structure and show many of the properties of zeolites.

We followed our synthesis strategy for preparing novel zeolite-like germanates by changing the ratio of GeO_6 octahedra to GeO_4 tetrahedra to obtain differently charged frameworks without introducing a trivalent cation. Here we report the novel $(NH_4)^+[M(NH_3)_2]^+(Ge_9O_{19})^{2-}$ (M = Cu, Ag; ICMM-2). These compounds are, to our knowledge, the first microporous germanates containing a transition metal complex in their channels. Furthermore, they are the result of our attempts to incorporate metals during the hydrothermal synthesis of the zeotype. As in the case of ICMM-1, a new group of zeolite-type structures arises since compounds of type ICMM-2 had not yet been prepared, neither as a silicate nor as a phosphate.

The relative stabilities of copper(I) and copper(II) in aqueous solution depend very strongly on the nature of the anions and other ligands present, and vary considerably with solvent or identity of the neighboring atoms in the crystal. In the following synthesis, the amines present in the reaction media reduce Cu^{II} to Cu^{I} and the ammonia simultaneously prevents disproportionation to Cu^0 and Cu^{II}. Thus the $[Cu(NH_3)_2]^+$ cation is stabilized and incorporated into the crystal to partially compensate for the charge of the anionic framework.

Both the Cu and Ag compounds were synthesized hydrothermally from reaction mixtures containing GeO_2, $Cu(NO_3)_2 \cdot 3H_2O$ or $Ag(NO_3)$, ammonia, water, and, in order to obtain larger crystals, ethylene glycol in a molar ratio of 1:0.1:2:2:0.1; in the case of the Cu compound propylamine and pyridine (0.3:1) were also added. The mixtures were heated at 180 °C for six days. Variations of the procedure were explored, in particular the effects of changing the temperature and duration of the reaction. The cubic and platelike crystals observed in the resulting solid product were identified as the title compound (approximate yield 70%) and the known cubic phase whit pharmacosiderite-type structure; the latter compound was easily eliminated upon heating at 250 °C for three hours.

A suitable single crystal of each compound with platelike features was selected and mounted in a diffractometer equipped with a CCD detector. According to the crystal structure determination[25] the composition is $(NH_4)^+$-$[M(NH_3)_2]^+(Ge_9O_{19})^{2-}$ (M = Cu, Ag), in which eight Ge atoms are tetrahedrically coordinated by oxygen and the remaining Ge atom forms a GeO_6 octahedron (Table 1).

The framework structure of ICMM-2 (Figure 1) is constructed from a secondary structural building unit denoted 4 = 1, which is present in several natural zeolites such as edingtonite, natrolite, and thomsonite. These 4 = 1 units are joined by three-tetrahedra rings into an infinite sheet of composition $[Ge_4O_9]^{2-}_{\infty}$ containing nine-tetrahedra rings. This arrangement has recently been reported in the gallogermanate UCSB-9[23] and is also present in ICMM-1;[19] in the latter GeO_6 octahedra were involved in both three- and nine-rings.

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[**] This work has been supported by the Spanish CICYT MAT98-1735-E and DGESIC PB97-1200. The authors acknowledge Prof. I. Rasines for his helpful comments.

1433-7851/99/3816-2436 $ 17.50+.50/0