

Encapsulation of Halocarbons in a Tetrahedral Anion Cage**

Dong Yang, Jie Zhao, Yanxia Zhao, Yibo Lei, Liping Cao, Xiao-Juan Yang, Martin Davi, Nader de Sousa Amadeu, Christoph Janiak, Zhibin Zhang, Yao-Yu Wang, and Biao Wu*

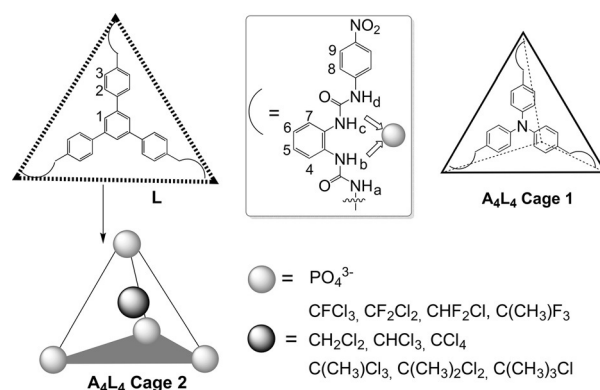
Abstract: Caged supramolecular systems are promising hosts for guest inclusion, separation, and stabilization. Well-studied examples are mainly metal-coordination-based or covalent architectures. An anion-coordination-based cage that is capable of encapsulating halocarbon guests is reported for the first time. This A_4L_4 -type (A = anion) tetrahedral cage, $[(PO_4)_4L_4]^{12-}$, assembled from a C_3 -symmetric tris(bisurea) ligand (**L**) and phosphate ion (PO_4^{3-}), readily accommodates a series of quasi-tetrahedral halocarbons, such as the Freon components $CFCl_3$, CF_2Cl_2 , $CHFCl_2$, and $C(CH_3)F_3$, and chlorocarbons CH_2Cl_2 , $CHCl_3$, CCl_4 , $C(CH_3)Cl_3$, $C(CH_3)_2Cl_2$, and $C(CH_3)_3Cl$. The guest encapsulation in the solid state is confirmed by crystal structures, while the host–guest interactions in solution were demonstrated by NMR techniques.

Chemistry in a confined space has attracted much interest in many applications, including recognition and separation of a guest, stabilization of reactive molecules or reaction intermediates, drug delivery, biomolecular sensing, and catalysis.^[1] Chemists have devoted much effort to create enforced cavities, such as the zeolite-like complexes, organic (covalent) cages, metal coordination complexes, and non-covalent organic frameworks.^[2] In particular, discrete molecular cages have been extensively studied in host–guest chemistry.^[3] Whereas the majority of caged structures are based on metal coordination, with a small portion of covalent systems, we demonstrate in the current work that guest inclusion can also be achieved by anion coordination cages.

Halocarbons are toxic chemicals that may cause severe problems to human health and to the environment. Some

chlorinated hydrocarbons are suspected carcinogens,^[4] while Freon compounds, which are useful refrigerants, can cause ozone depletion in the stratosphere and display strong and long-term greenhouse effects.^[5] Thus, the detection and capture of these species is imperative. Various synthetic host systems, including metal coordination compounds and organic hosts, can bind some halocarbon guests, such as the commonly used solvents, CH_2Cl_2 , $CHCl_3$, and CCl_4 , and halogenated aromatics.^[6–8] However, reports on the encapsulation of Freon components, many of which are gases at room temperature, are very rare. Atwood et al.^[6] reported Freon and methane storage in the lattice voids of calix[4]arene molecules. Very recently, Miljanić et al.^[9] reported a porous noncovalent organic framework for fluorocarbons and chlorofluorocarbons (CFCs). It is noteworthy that the encapsulation of Freon in a well-defined, discrete cage remains unknown.

We have been interested in anion coordination chemistry.^[10–13] Recently we reported the first anion-coordination tetrahedral cage (**1**, A_4L_4 -type, “A” denotes anion; Scheme 1)



Scheme 1. Assembly of the $[A_4L_4]^{12-}$ tetrahedral anion cage **2** from phosphate anion and ligand **L** and the encapsulation of halocarbons.

assembled by phosphate and a C_3 -symmetric tris(bisurea) ligand.^[10] However, this cage is too small to include a guest. To facilitate the guest-inclusion chemistry of such anion-based supramolecular systems, we designed the larger ligand **L** (Scheme 1; see Supporting Information for the synthesis). A DFT modulation of $[(PO_4)_4L_4]^{12-}$ performed at the HF/STO-3G level (Supporting Information) provided evidence for the formation of a tetrahedral cage. The targeted guests were (quasi)tetrahedral halocarbons (especially the highly challenging Freons) in consideration of the good match in shape (both are tetrahedral) and size (the internal cavity of cage **2** was estimated to be about 229 \AA^3 , while the volume of some halocarbons ranges from 71 to 134 \AA^3 ; Supporting Informa-

[*] D. Yang, J. Zhao, Dr. Y. Zhao, Prof. Y. Lei, Prof. L. Cao, Prof. X.-J. Yang, Prof. Y.-Y. Wang, Prof. B. Wu
Key Laboratory of Synthetic and Natural Functional Molecule
Chemistry of the Ministry of Education
College of Chemistry and Materials Science
Northwest University, Xi'an 710069 (China)
E-mail: wubiao@nwnu.edu.cn

Dr. M. Davi, Dr. N. d. S. Amadeu, Prof. Dr. C. Janiak
Institut für Anorganische Chemie und Strukturchemie
Universität Düsseldorf
Universitätsstrasse 1, 40225 Düsseldorf (Germany)

Dr. Z. Zhang
Division of Solid State Electronics, Department of Engineering
Sciences, Uppsala University
Uppsala 75237 (Sweden)

[**] This work was supported by the National Natural Science Foundation of China (21271149 and 21325102). We thank Prof. Sichun Zhang and Xingyu Si for their help in the ESI-MS measurements.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201502399>.

tion) between the guest and host. Furthermore, the triphenylbenzene spacer of ligand **L** may benefit C–X $\cdots\pi$ interactions with the halocarbon guest.

As expected, ligand **L** readily forms the tetrahedral cage **2**, which is capable of encapsulating a wide range of environmentally problematic halocarbons, including the Freon components CFC₁₁ (CFC-11), CF₂Cl₂ (CFC-12), CHF₂Cl (HCFC-22), and C(CH₃)F₃ (HFC-143a),^[14] the widely used solvents CH₂Cl₂, CHCl₃, and CCl₄, as well as chlorinated, “tetrahedral” hydrocarbons C(CH₃)Cl₃, C(CH₃)₂Cl₂, and C(CH₃)₃Cl (Scheme 1). X-ray crystal structures clearly show the inclusion and interaction of these guests with the tetrahedral cage, and solution studies also confirmed their binding by the host.

Treatment of **L** with 1 equiv of (TMA)₃PO₄ (generated from (TMA)OH and H₃PO₄; TMA = tetramethylammonium) afforded the expected A₄L₄-type tetrahedral cage [(PO₄)₄L₄]^{12–} (**2**). In contrast to the empty cage **1**, the crystal structure of complex (TMA)₁₂[(PO₄)₄L₄] (**2**⊃TMA⁺) clearly indicates the presence of a TMA⁺ guest inside the tetrahedral cavity (Figure 1). The main backbone of **2** is similar to cage

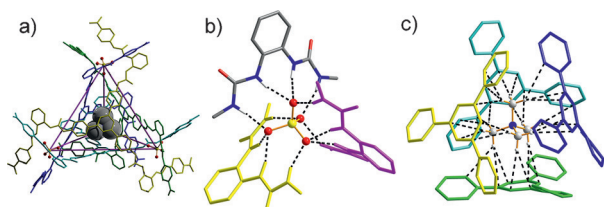


Figure 1. a) Crystal structure of the tetrahedral cage [(PO₄)₄L₄]^{12–} (**2**) with an encapsulated TMA⁺ ion; b) hydrogen bonds around the PO₄^{3–} ion; c) CH $\cdots\pi$ interactions around the TMA⁺ guest.^[17]

1,^[10] with four ligands lying on the triangular faces and phosphate ions on the vertices of the tetrahedron. Each PO₄^{3–} is coordinated by three bisurea arms through 12 strong N–H \cdots O hydrogen bonds to reach coordination saturation. The PO₄ \cdots PO₄ separations (16.3–17.6 Å) are longer than that in cage **1** (15 Å),^[10] corresponding to a larger cavity. The included TMA⁺ guest is located at the center of the cage, with the four methyl groups pointing to the four vertices, while the other eleven TMA⁺ ions are outside the cage. All of the hydrogen atoms of the encapsulated TMA⁺ are involved in CH $\cdots\pi$ interactions with the central aryl rings of the ligands,^[15] which, in combination with the size and geometry complementarity and electrostatic attraction, may provide sufficient stabilization of the inclusion complex.

To examine whether an “empty” cage **2** can exist without the encapsulated TMA⁺ cation, the assembly of **L** and PO₄^{3–} was performed in the presence of the large [K([18]crown-6)]⁺ counteranion in acetone or acetonitrile. Encouragingly, it appeared that cage **2** is quite stable and can be isolated as **2**⊃CH₃COCH₃ and **2**⊃CH₃CN, respectively, in which a solvent molecule is weakly bound (Supporting Information, Figures S7, S8). This established the desired ability of cage **2** to include a neutral guest without electrostatic interaction, which was then used in the capture of organics that are of more environmental impact.

First, treatment of **L** and [K([18]crown-6)]₃PO₄ in acetonitrile with an excess (ca. 40 equiv relative to cage **2**) of CFCl₃ (CFC-11) afforded complex **2**⊃CFCl₃, in which a CFCl₃ molecule is included (Figure 2). The CFCl₃ resides on the

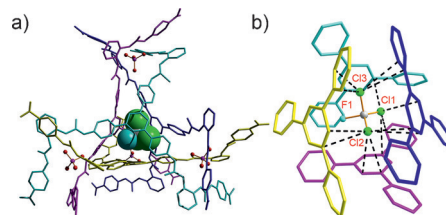


Figure 2. a) Crystal structure of the CFCl₃ inclusion complex, [**2**⊃CFCl₃]^{12–}; b) weak interactions around CFCl₃.^[17]

center of the tetrahedral cavity, forming extensive weak contacts with the host, including a C–H \cdots Cl hydrogen bond (C \cdots Cl 3.399 Å, \angle C–H \cdots Cl 105°) and multiple C–Cl $\cdots\pi$ interactions^[16] (Cl \cdots C(ar) 3.420 to 3.604 Å) with the central triphenylbenzene spacer. These interactions, though quite weak independently, make a significant contribution to the guest binding when organized together.

More remarkably, the CF₂Cl₂ (CFC-12) molecule, which is a gas at room temperature (b.p. –29.8°C), can be entrapped in the tetrahedral cage when bubbled (for about 0.5 h) through a mixture of phosphate and **L**. The structure of [K([18]crown-6)]₁₂[(PO₄)₄L₄]·CF₂Cl₂ (**2**⊃CF₂Cl₂, Figure 3a)

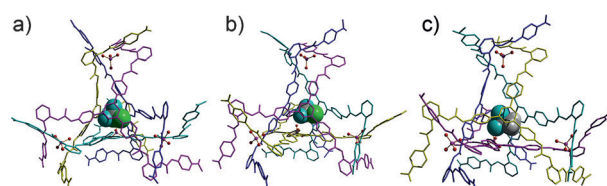


Figure 3. Crystal structures of the Freon inclusion complexes, **2**⊃CF₂Cl₂ (a), **2**⊃CHF₂Cl (b), and **2**⊃C(CH₃)F₃ (c).^[17]

resembles **2**⊃CFCl₃, with a similar host–guest binding mode including C–Cl $\cdots\pi$ and C–F $\cdots\pi$ interactions (Supporting Information, Figure S9). Another two gaseous Freon guests, CHF₂Cl (HCFC-22, b.p. –40.8°C) and C(CH₃)F₃ (HFC-143a, b.p. –47°C), can also be encapsulated within cage **2** as confirmed by the crystal structures of **2**⊃CHF₂Cl and **2**⊃C(CH₃)F₃ (both with [K([18]crown-6)]⁺ counteranions, Figure 3b,c; Supporting Information, Figures S10, S11). In these cases, multiple weak interactions between host and guest were also observed.

Next, we switched to the chlorinated hydrocarbon solvents. The inclusion complexes **2**⊃CH₂Cl₂, **2**⊃CHCl₃, and **2**⊃CCl₄ ([K([18]crown-6)]⁺ counteranion; Supporting Information, Figures S12–S14) are very similar to each other, and **2**⊃CCl₄ is discussed here (Figure S14). In the structure, the four Cl atoms of CCl₄ interact with the surrounding triphenylbenzene moieties of the ligands through two C–H \cdots Cl and fifteen C–Cl $\cdots\pi$ interactions (Figure S14b). Since the inclu-

sion complexes were obtained from acetonitrile with a small amount of the guest (ca. 0.3–3 % mol relative to solvent), it seems that the chloromethanes are bound more tightly than CH₃CN. This may result from both the favorable shape of CCl₄ and multiple interactions involving Cl atoms.

Furthermore, the tetrahedral host **2** can also capture a series of chlorinated and methylated methanes. The structures of the complexes [K([18]crown-6)]₁₂[(PO₄)₄L₄⊃G] (G = C(CH₃)Cl₃, C(CH₃)₂Cl₂, and C(CH₃)₃Cl) (Supporting Information, Figures S15–S17) are close to 2⊃CCl₄. The difference is that the number of weak interactions decreases significantly with decreasing number of Cl atoms on the guest (Figures S15, S16). As a result, only two C–H⋯Cl bonds and six C–Cl⋯π interactions can be identified in 2⊃C(CH₃)₃Cl (Figure S17). This trend is also reflected in the solution binding studies discussed below.

The guest inclusion behavior of cage **2** in solution was studied by NMR spectroscopy. All of the thirteen structurally characterized inclusion complexes display very large downfield shifts of the urea NH signals (Δδ = 2.75–3.58 ppm; Supporting Information, Figures S18–S31) in [D₆]DMSO compared to the free ligand, indicative of strong hydrogen bonding to PO₄^{3−} (Figure S32). Similar downfield shifts of the urea NH protons were observed when 1.0 equiv of PO₄^{3−} ions (as both the [K([18]crown-6)]⁺ and TBA⁺ salt) were added to **L** (5 × 10^{−3} M; Figure S33). Moreover, titration experiments proved the 1:1 (4:4) binding ratio of **L** and phosphate ion in solution (Figure S34).

When PO₄^{3−} ions (as TMA⁺ salt) were titrated to a solution of **L** (5 × 10^{−3} M), the ¹H NMR of TMA⁺ showed a signal in the normal range (δ = 2.99 ppm) and a peak in upfield (δ = 0.15 ppm) with an integral ratio of about 11:1, demonstrating the encapsulation of a TMA⁺ ion by the cage. An obvious upfield shift of the signal of H9 proton (Δδ = −0.53 ppm; see Scheme 1 for the numbering of protons) occurred because of the shielding effects (Supporting Information, Figure S34). Furthermore, H1 (Δδ = 0.15 ppm) and H2 (Δδ = 0.24 ppm) of the central aromatic backbone shifted downfield due to interaction with the trapped TMA⁺ (Figure S35). Titration of TMA⁺ into a solution of cage **2** (3.0 mM) in acetonitrile was carried out and the changes of integral area of trapped guest were plotted and fitted with a Hill function (Figure S44), giving an apparent association constant *K*_a of 588 M^{−1} for TMA⁺ ion.

The NOESY spectrum also revealed the formation of cage **2** (Supporting Information, Figure S37). Cross-peaks are formed between all adjacent NH protons as well as H7, H8/H9, H5/H6, H8, and H5/H6, H9, indicating the spatial proximity of the nitrophenyl and *o*-phenylene groups as was found in the crystal structure (Figure S38). Meanwhile, the H atoms of the trapped TMA⁺ guest show the expected through-space interactions with H1, H2, and H3 protons on the central triphenylbenzene fragment. The ³¹P NMR spectrum of complex 2⊃TMA⁺ in [D₆]DMSO (Figure S6) showed only one signal at 9.14 ppm (triphenylphosphine as external standard), suggesting the formation of a single complex.

High-resolution ESI-MS of 2⊃TMA⁺ exhibited intense signals for [(PO₄)₄L₄(TMA)₂H₄]^{6−} at *m/z* = 918.9258 (Supporting Information, Figure S46 and Table S1). The observed

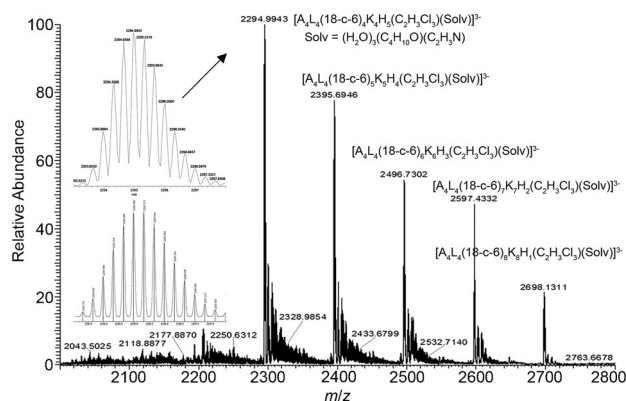


Figure 4. High-resolution ESI-MS spectrum of the inclusion complex 2⊃C(CH₃)Cl₃; inset: measured and simulated peaks at *m/z* = 2293.6530.

isotopic patterns are consistent with the simulated peaks. Meanwhile, the sample 2⊃C(CH₃)Cl₃ (Figure 4) displayed peaks for the [A₄L₄] species with the guest, [(PO₄)₄L₄(18-crown-6)_xK_xH_y(C₂H₅Cl₃)(H₂O)₃(C₄H₁₀O)(C₂H₅N)]^{3−} at *m/z* = 2293.6530 (*x* = 4, *y* = 5), 2394.3550 (*x* = 5, *y* = 4), 2495.0512 (*x* = 6, *y* = 3), 2596.0817 (*x* = 7, *y* = 2) and 2696.7741 (*x* = 8, *y* = 1) (Figure S47). These NMR and MS results imply the persistence of the tetrahedral cage in solution.

The guest inclusion was further confirmed by ¹⁹F NMR spectra of cage **2** with added CFCl₃ (ca. 40 equiv) or bubbled CF₂Cl₂ gas. For CFCl₃, a signal that is shifted substantially upfield to −3.05 ppm relative to the free CFCl₃ molecule (0 ppm, Figure 5) was observed, indicative of guest inclusion

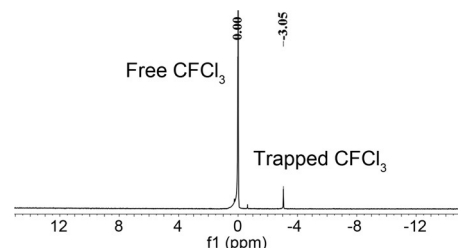


Figure 5. ¹⁹F NMR spectrum of cage **2** with added CFCl₃ (376 MHz, [D₆]DMSO, 20 °C).

within the cage. The ¹⁹F NMR spectrum of CF₂Cl₂-including cage also displayed an upfield signal (−10.68 ppm) compared to −7.36 ppm of free CF₂Cl₂ (Figure S39). Moreover, variable-temperature ¹⁹F NMR measurements have been done about free CFCl₃ (CFC-11) and complex 2⊃CFCl₃ in CDCl₃. To probe the stability of the inclusion complex, the solid-state sample of 2⊃CFCl₃ was stored under ambient conditions for three months before the NMR measurements. In the ¹⁹F NMR spectrum of free CFC-11, the signal observed at lower temperatures disappeared at the range 20–22 °C, slightly below its boiling point (24.5 °C) (Figure S40a). However, when caged, the guest CFC-11 started to lose at above 25 °C and disappeared completely at 40 °C (Figure S40b). These results demonstrate that, in the solid state, CFC-11 can be caged and kept reasonably stable for a long time.

To further understand the inclusion properties of cage **2**, competition experiments were carried out. First, we examined the inclusion/release process of guest by taking $\text{C}(\text{CH}_3)\text{Cl}_3$ as an example. ^1H NMR studies in $[\text{D}_6]\text{DMSO}$ revealed that the signal of trapped $\text{C}(\text{CH}_3)\text{Cl}_3$ (-0.51 ppm) decreased and the free $\text{C}(\text{CH}_3)\text{Cl}_3$ signal increased by time (Figure S41). Meanwhile, the downfield shifts of H1 and H2 moved back upon the release of $\text{C}(\text{CH}_3)\text{Cl}_3$. Through the change of the integral areas, the half-life period of the release of $\text{C}(\text{CH}_3)\text{Cl}_3$ was calculated to be 16.4 min (Figure S42). Moreover, the association constant K_a was estimated to be 7.4 M^{-1} for $\text{C}(\text{CH}_3)\text{Cl}_3$ (Figure S45). Furthermore, a mixture of equimolar CCl_4 , $\text{C}(\text{CH}_3)\text{Cl}_3$, $\text{C}(\text{CH}_3)_2\text{Cl}_2$, and $\text{C}(\text{CH}_3)_3\text{Cl}$ were added to a $[\text{D}_6]\text{DMSO}$ solution of cage **2**. The relative integral areas of signals corresponding to trapped $\text{C}(\text{CH}_3)\text{Cl}_3$ (-0.51 ppm), $\text{C}(\text{CH}_3)_2\text{Cl}_2$ (-0.93 ppm) and $\text{C}(\text{CH}_3)_3\text{Cl}$ (-1.41 ppm) revealed about 28% $\text{C}(\text{CH}_3)\text{Cl}_3$, 4.5% $\text{C}(\text{CH}_3)_2\text{Cl}_2$, and scarcely any $\text{C}(\text{CH}_3)_3\text{Cl}$ (Figure S43), leaving 66% for CCl_4 . The result implies an order of affinity of $\text{C}(\text{CH}_3)_3\text{Cl} < \text{C}(\text{CH}_3)_2\text{Cl}_2 < \text{C}(\text{CH}_3)\text{Cl}_3 < \text{CCl}_4$, which might be attributed to the increasing host-guest interactions with more Cl atoms.

In summary, we report the first examples of the inclusion chemistry of an anion-coordination-based cage structure. This tetrahedral cage shows very good size and shape complementarity to a wide range of quasi-tetrahedral halocarbons. The results represent a new concept for constructing confined space for the inclusion of specific guests. Construction of new caged structures and exploration of the inclusion of other guests are currently underway.

Keywords: anion coordination · anion-based tetrahedral cages · Freon · halocarbons · inclusion compounds

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 8658–8661
Angew. Chem. **2015**, *127*, 8782–8785

- [1] a) N. Ahmad, H. A. Younus, A. H. Chughtai, F. Verpoort, *Chem. Soc. Rev.* **2015**, *44*, 9–25; b) S. H. A. M. Leenders, R. Gramage-Doria, B. de Bruin, J. N. H. Reek, *Chem. Soc. Rev.* **2015**, *44*, 433–448; c) A. I. Joseph, S. H. Lapidus, C. M. Kane, K. T. Holman, *Angew. Chem. Int. Ed.* **2015**, *54*, 1471–1475; *Angew. Chem.* **2015**, *127*, 1491–1495; d) C. Zhang, Q. Wang, H. Long, W. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 20995–21001; e) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Science* **2007**, *316*, 85–88.
- [2] a) Y. Li, J. Yu, *Chem. Rev.* **2014**, *114*, 7268–7316; b) G. Zhang, M. Mastalerz, *Chem. Soc. Rev.* **2014**, *43*, 1934–1947; c) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734–777.
- [3] a) I. M. Oppel (née Müller), K. Föcker, *Angew. Chem. Int. Ed.* **2008**, *47*, 402–405; *Angew. Chem.* **2008**, *120*, 408–411; b) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144–1147; c) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015–2041; d) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; e) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841; f) R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851–853; *Angew. Chem.* **1988**, *100*, 878–880; g) D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem. Int. Ed.* **1998**, *37*, 1840–1843; *Angew. Chem.* **1998**, *110*, 1940–1943.
- [4] a) J. F. Ferguson, J. M. H. Pietari, *Environ. Pollut.* **2000**, *107*, 209–215; b) W. J. Brattin, S. D. Pencil, R. L. Waller, E. A. Glende, Jr., R. O. Recknagel, *Environ. Health Perspect.* **1984**, *57*, 321–323.
- [5] a) L. A. Barrie, J. W. Bottenheim, R. C. Schnell, P. I. Crutzen, R. A. Rasmussen, *Nature* **1988**, *334*, 138–141; b) T. R. Karl, K. E. Trenberth, *Science* **2003**, *302*, 1719–1723.
- [6] J. L. Atwood, L. J. Barbour, A. Jerga, *Science* **2002**, *296*, 2367–2369.
- [7] a) R. A. Bilbeisi, J. K. Clegg, N. Elgrishi, X. de Hatten, M. Devillard, B. Breiner, P. Mal, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 5110–5119; b) M. M. J. Smulders, S. Zarra, J. R. Nitschke, *J. Am. Chem. Soc.* **2013**, *135*, 7039–7046; c) Y.-B. Dong, Q. Zhang, L.-L. Liu, J.-P. Ma, B. Tang, R.-Q. Huang, *J. Am. Chem. Soc.* **2007**, *129*, 1514–1515; d) T. K. Ronson, C. Giri, N. K. Beyeh, A. Minkinen, F. Topić, J. J. Holstein, K. Rissanen, J. R. Nitschke, *Chem. Eur. J.* **2013**, *19*, 3374–3382; e) I. A. Riddell, M. M. J. Smulders, J. K. Clegg, J. R. Nitschke, *Chem. Commun.* **2011**, *47*, 457–459.
- [8] a) H. Takezawa, T. Murase, G. Resnati, P. Metrangolo, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 1786–1788; b) M. G. Sarwar, D. Ajami, G. Theodorakopoulos, I. D. Petsalakis, J. Rebek, Jr., *J. Am. Chem. Soc.* **2013**, *135*, 13672–13675.
- [9] T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, O. Daugulis, A. J. Jacobson, O. Š. Miljanić, *Nat. Commun.* **2014**, *5*, 5131.
- [10] B. Wu, F. Cui, Y. Lei, S. Li, N. D. S. Amadeu, C. Janiak, Y.-J. Lin, L.-H. Weng, Y.-Y. Wang, X.-J. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 5096–5100; *Angew. Chem.* **2013**, *125*, 5200–5204.
- [11] a) J. M. Lehn, *Acc. Chem. Res.* **1978**, *11*, 49–57; b) *Anion Coordination Chemistry* (Eds.: K. Bowman-James, A. Bianchi, E. García-España), Wiley-VCH, Weinheim, **2011**; c) P. D. Beer, P. A. Gale, *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516; *Angew. Chem.* **2001**, *113*, 502–532; d) E. A. Katayev, Y. A. Ustynyuk, J. L. Sessler, *Coord. Chem. Rev.* **2006**, *250*, 3004–3037.
- [12] C. Jia, B. Wu, S. Li, Z. Yang, Q. Zhao, J. Liang, Q.-S. Li, X.-J. Yang, *Chem. Commun.* **2010**, *46*, 5376–5378.
- [13] a) S. Li, C. Jia, B. Wu, Q. Luo, X. Huang, Z. Yang, Q.-S. Li, X.-J. Yang, *Angew. Chem. Int. Ed.* **2011**, *50*, 5721–5724; *Angew. Chem.* **2011**, *123*, 5839–5842; b) J. Zhao, D. Yang, Y. Zhao, X.-J. Yang, Y.-Y. Wang, B. Wu, *Angew. Chem. Int. Ed.* **2014**, *53*, 6632–6636; *Angew. Chem.* **2014**, *126*, 6750–6754.
- [14] Freon can be classified as CFC (chlorofluorocarbon), HCFC (chlorodifluoromethane), and HFC (hydrofluorocarbon) and named as CFC-xyz (or Freon-xyz, R-xyz). *z* represents the number of fluorine atoms, *y* is the number of hydrogen atoms plus one, and *x* is the number of carbon atom minus one (which is omitted when *x* = 0). J. M. Hamilton, Jr., *Adv. Fluorine Chem.* **1963**, *3*, 117.
- [15] Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawat, M. Nishiot, *Tetrahedron* **1999**, *55*, 10047–10056.
- [16] a) M. D. Prasanna, T. N. G. Row, *Cryst. Eng.* **2000**, *3*, 135–154; b) T. V. Rybalova, I. Y. Bagryanskaya, *J. Struct. Chem.* **2009**, *50*, 741–744.
- [17] CCDC 1052762–1052774 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: March 14, 2015

Revised: April 20, 2015

Published online: June 5, 2015