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Self Organization of Organo fluorosilicates in the Nanometer Range

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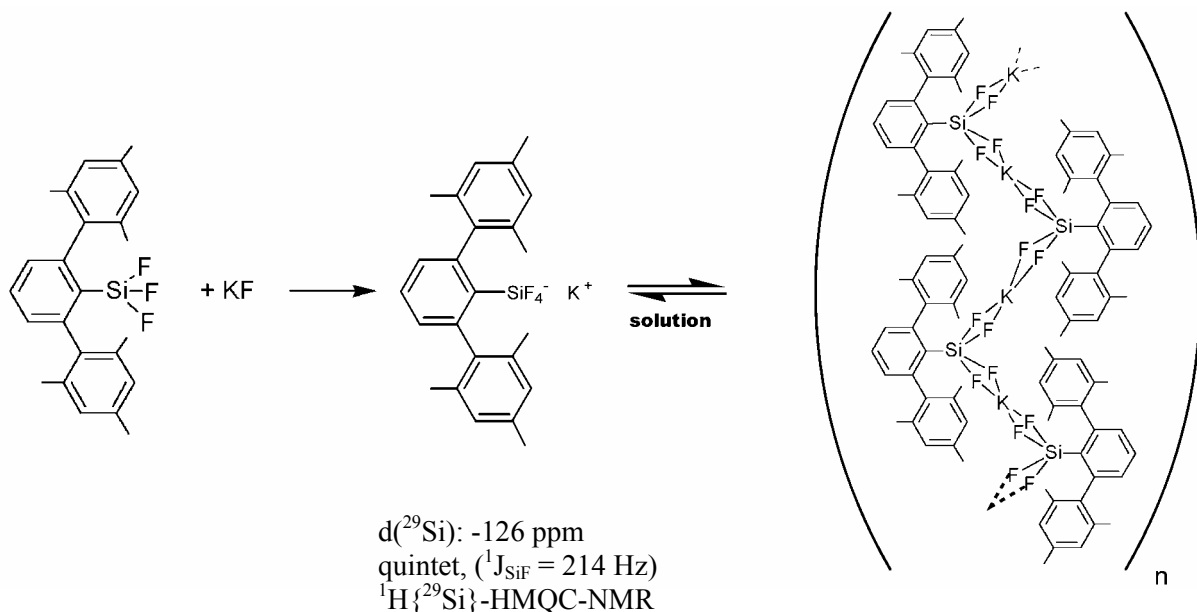
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Introduction

Over the last years coordination polymers have attracted considerable interest.¹ Besides their properties and potential application,² controlling the self organisation of the monomeric units to build one or higher dimensional frameworks has been a major achievement in this fascinating research area.³ Most of these inorganic-organic hybrid materials are constructed from metal cations connected by organic ligands, forming a hybridic inorganic-organic backbone.⁴ There are also examples of coordination polymers with a completely inorganic backbone showing a wealth of different coordination modes.⁵

Results and Discussion

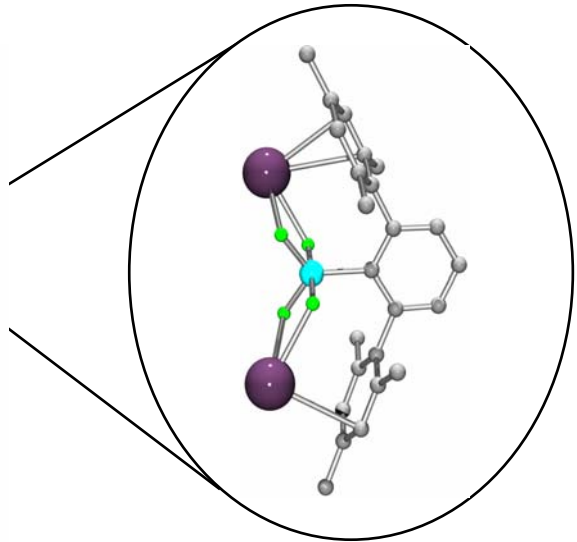
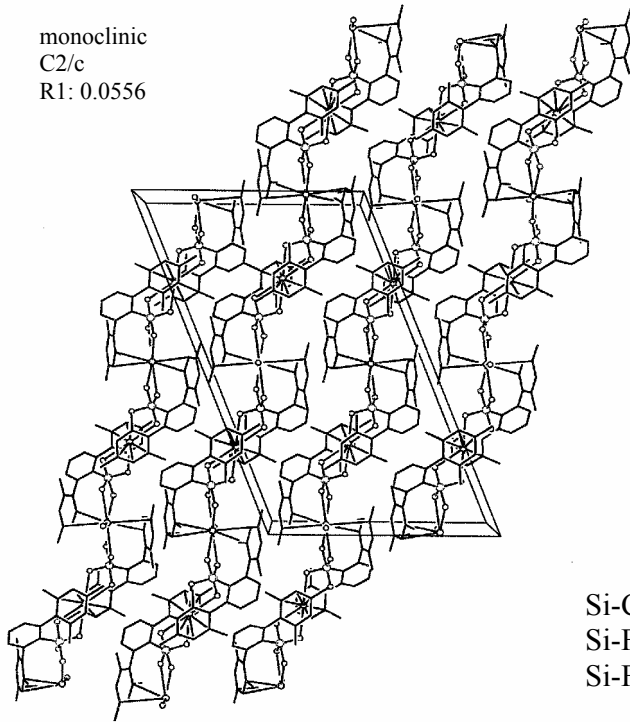
We investigated the reaction of 2,6-dimesitylphenyl trifluorosilane **1** with KF. Depending on the stoichiometry, we observed the formation of the terphenyl tetrafluorosilicate **2** which adopts a one dimensional polymeric structure in the solid state.⁶ To our knowledge this is the first structurally characterized potassium organo tetrafluorosilicate polymer and the interaction of the counter ions leads to association forming a K-F-Si-F-K type of a linear coordination polymer.



The polymeric structure of this one dimensional coordination polymer has been established by X-ray diffraction analysis. Polymer **2** is built by organo tetrafluorosilicate units of which each acts as a bidentate ligand towards two potassium ions. The potassium cations are surrounded by fluorine atoms forming a square planar coordination environment. The axial positions above and below the potassium are occupied by the mesityl substituent of the organic ligand. Additionally one molecule of acetone is present in the coordination sphere of every second potassium ion. The inorganic backbone consists of four membered SiF_2K rings which are spiro connected at the silicon and the potassium centres. The zig-zag arrangement of the inorganic backbone is shielded by the organic terphenyl ligands attached to each silicon atom. The bulky aryl ligands prevent extensive coordination of solvent to the potassium centres, which instead interact with the π -systems of the mesityl rings of the terphenyl system. This interaction of the cation with the organic shell seems to be crucial for the stability of the polymer, and despite some effort we have not been able to observe similar structures with smaller alkali metal ions.

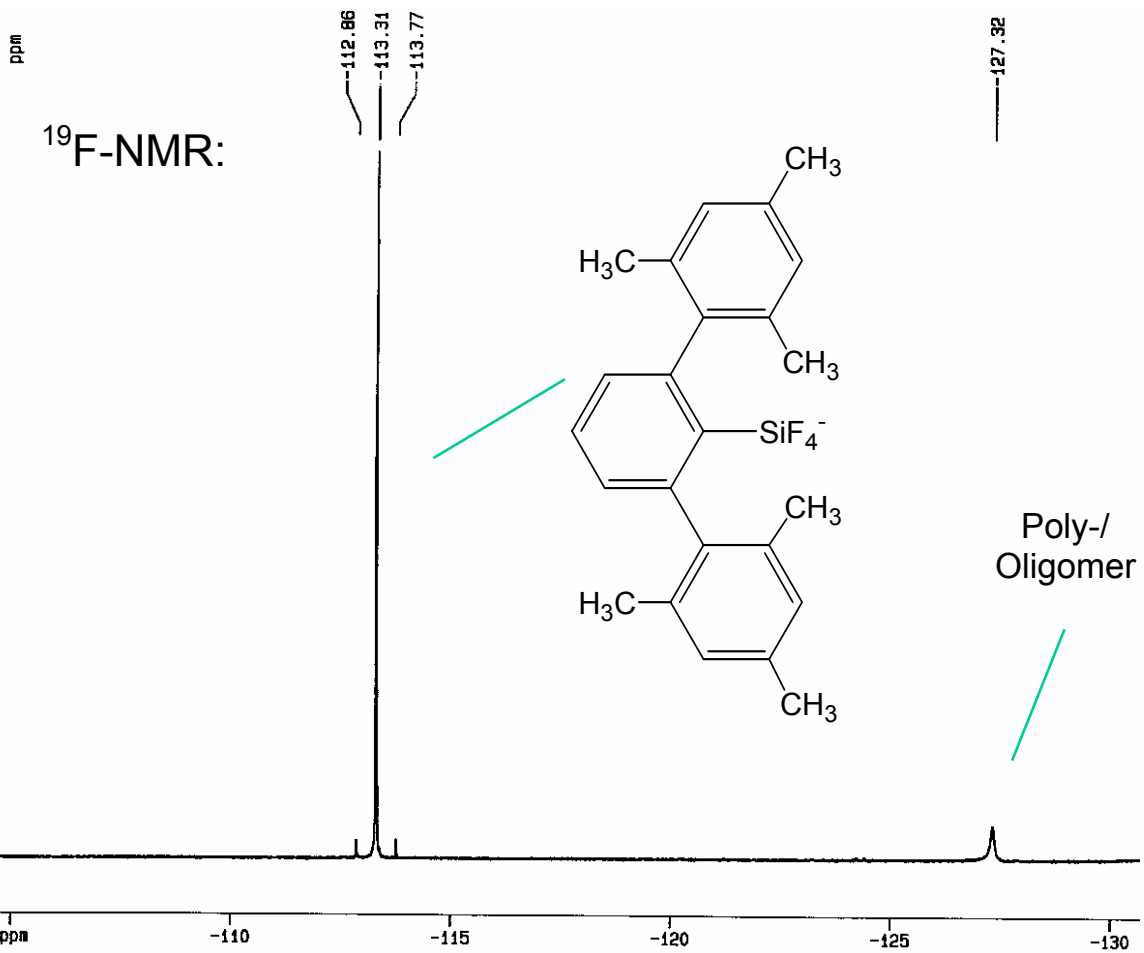
The self aggregation of terphenyl tetrafluorosilicate **2** is a reversible process and in solution the predominant species is the discrete monomeric tetrafluorosilicate according to ^{19}F NMR. However, at room temperature beginning aggregation is indicated by a signal at higher field which is broadened due to fast exchange on the NMR time scale.

monoclinic
C2/c
R1: 0.0556

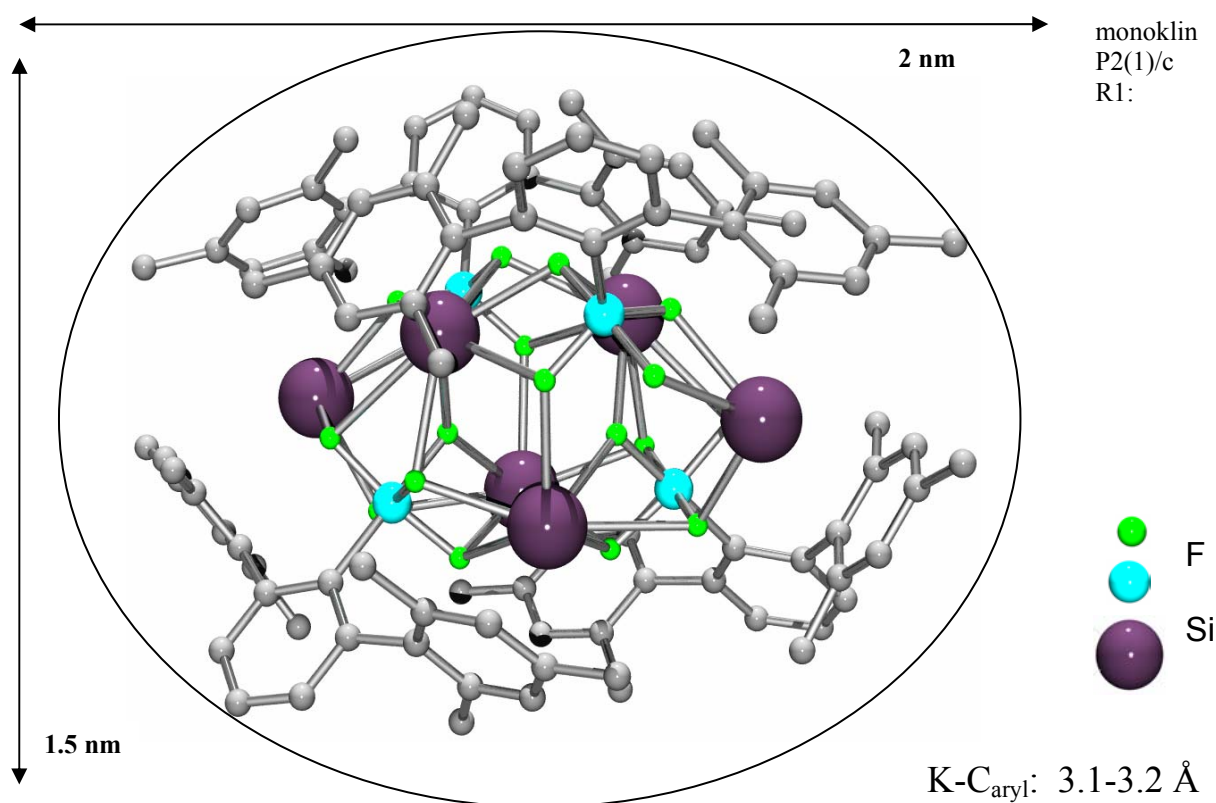
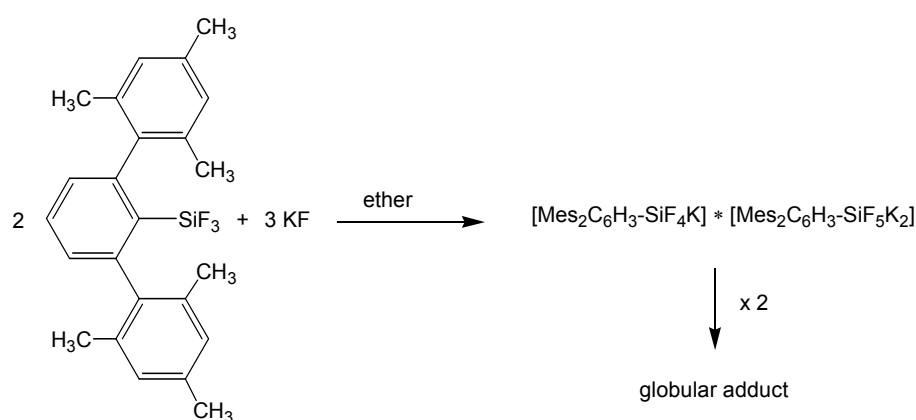


Si-C_{eq}: 1.891 Å
Si-F_{ax}: 1.672-1.694 Å
Si-F_{eq}: 1.623-1.625 Å

K-F_{ax}: 2.573-2.690 Å
K-F_{eq}: 2.705-2.740 Å



Employing a different stoichiometry not a polymeric structure is obtained, but a fluorosilicate network in which a globular inorganic core is covered by a shell of organic terphenyl ligands.⁷ Each of these aggregates contains two pentacoordinate and two hexacoordinate silicate centers per unit, bridged by potassium cations. The bond lengths of the axial positions of the hexacoordinate subunits are 177.1(2) pm (Si-F) and 196.9(3) pm (Si-C), unusually long compared to other known structures. Another interesting detail of the structure is the coordination environment of the potassium cations. For instance K(4) and K(6) are coordinated to five fluorine atoms on one hemisphere, while the other side is oriented toward the phenyl rings. The geometric dimensions of globular adduct **3** are in the nanometer range.



Acknowledgements

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