Encapsulation of molecular Na$_2$SiF$_6$ by two metallacrown complexes

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A complex of molecular Na$_2$SiF$_6$, stabilised by two 12-metallacrown-3 host complexes, has been synthesised and characterised by single crystal X-ray diffraction.

The salt Na$_2$SiF$_6$ shows a very low solubility in common solvents.[1] This fact is used in analytical chemistry for the qualitative determination of SiF$_6$$^{2-}$ in aqueous solutions: upon addition of Na$^+$ a crystalline precipitate is rapidly formed.[2] In industrial chemistry, a related reaction is used to separate SiF$_6$$^{2-}$ during the production of phosphoric acid.[3] Due to the high thermodynamic stability of the crystalline form, complexes of *molecular* Na$_2$SiF$_6$ are intrinsically difficult to stabilise and to best of our knowledge, complexes of this kind have not been described so far.

Recently, we have reported the trinuclear ruthenium complex **1**, which represents an organometallic analogue of 12-crown-3.[4,5] This complex is able to bind lithium and sodium salts with high affinity and selectivity. In organic solvents such as chloroform, the affinity of **1** towards NaCl is comparable to that of cryptands, with the guest molecule being bound as an ion pair. This characteristic prompted us to investigate the possibility to use the receptor **1** for the stabilisation of the molecular form of Na$_2$SiF$_6$.
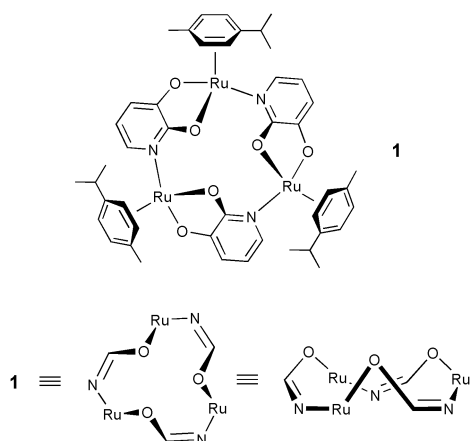
Because of the low solubility of Na$_2$SiF$_6$, we have first prepared the NaBF$_4$ adduct **2** by reaction of **1** with an excess of NaBF$_4$ in methanol and subsequent extraction with benzene. Complex **2** with a weakly bound BF$_4$$^-$ anion was expected to be a suited starting material for the generation of a Na$_2$SiF$_6$ complex using a salt metathesis reaction.

The NaBF$_4$ adduct **2** was characterised by NMR spectroscopy (^{1}H, ^{13}C, ^{19}F), elemental analysis and single crystal X-ray analysis.† It can clearly be distinguished from the free receptor **1** by ^{1}H NMR spectroscopy. Especially for the aromatic CH protons of the cymene π-ligand pronounced differences of the chemical shifts are found: for complex **2** four signals at 4.38, 5.45, 5.67 and 6.14 ppm are observed whereas the corresponding signals of **1** appear at 4.65, 5.19, 5.26 and 6.66 pm, respectively (toluene-d$_8$). This indicates that the NaBF$_4$ guest molecule is in close contact to the cymene ligands.

The structure of **2** in the crystal (Fig. 1) shows a pseudo C_3-symmetric metallacrown complex[6] with a sodium ion co-ordinated to the three adjacent O-atoms of the macrocyclic ring (Na1–O1 2.271(3) Å, Na1–O3 2.260(3) Å, Na1–O5 2.257(3) Å). The BF$_4$$^-$ anion is coordinated in a slightly asymmetric fashion *via* two fluoro bridges to the Na$^+$ ion (Na1–F1 2.449(3) Å, Na1–F2 2.366(4) Å). A pentanuclear metallacrown copper complex that contains a Na(μ-F)BF$_3$ guest molecule was reported by Saalfrank *et al.*[7] BF$_4$$^-$ anions coordinated *via* one fluoro bridge to a sodium ion were found for an 1-aza-18-crown-6 derivative with a [F$_3$B(μ-F)Na(μ-F)BF$_3$]$^-$ guest molecule.[8]
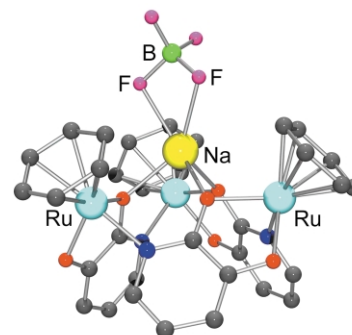

Fig. 1 Ball-and-stick representation of the molecular structure of **2** in the crystal. The hydrogen atoms and the side chains of the aromatic π-ligand are not shown for clarity.

On average, the three ruthenium atoms in **2** are 5.43 Å apart from each other. This distance is longer than that found for the free receptor **1** (5.36 Å).[4] Apparently, the guest molecule is able to slightly enlarge the metallamacrocyclic framework. Some of the aromatic cymene CH protons can be found in close proximity to the bridging fluorine atoms (CH⋯F ≥ 2.37 Å). This could explain the pronounced differences in chemical shifts observed in the proton NMR spectrum upon complexation of NaBF$_4$.

When complex **2** is treated with (Et$_4$N)$_2$SiF$_6$ in benzene, anion exchange rapidly occurs (Scheme 1). The analytically pure Na$_2$SiF$_6$ complex **3** can subsequently be obtained in 25%
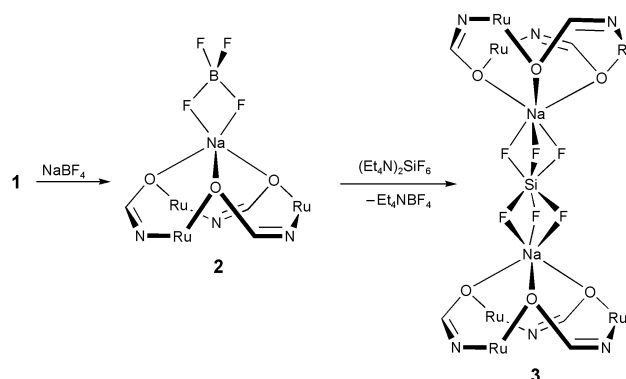
Scheme 1 Synthesis of the Na$_2$SiF$_6$ complex **3** by anion exchange.

yield by crystallisation from toluene–acetonitrile–pentane. Complex **3** was comprehensively characterised including single crystal X-ray analysis.† In the NMR spectra (^{1}H, ^{13}C, ^{19}F), two sets of signals can be observed (C_6D_6, 70 °C).[9] They correspond to the two diastereoisomers formed upon guest mediated dimerisation of two chiral metallacrown complexes.[10] The relative ratio of these isomers is 7:3, which shows that there is chiral recognition between the two adjacent host compounds. Complex **3** is stable in solutions of benzene and chloroform. In methanol, on the other hand, the formation of the free receptor **1** and precipitation of Na_2SiF_6 is observed after several hours.

The structure of complex **3** in the crystal is shown in Fig. 2. As observed for the $NaBF_4$ adduct **2**, the sodium ions are coordinated to the three adjacent O-atoms of the macrocyclic ruthenium receptors. The SiF_6^{2-} anion is bound *via* three fluoro-bridges to each of the Na^+ ions thereby connecting the two metallacrown complexes. The Si-atom represents a crystallographic inversion centre. Consequently, the two chiral host compounds have the opposite relative configuration. Complex **3** co-crystallises with two molecules of water both of which interact with O-atoms of the pyridonate ligand forming a polymeric hydrogen-bond network. The sodium atoms display a distorted trigonal prismatic geometry and are coordinated to the bridging fluorine atoms in an asymmetric fashion (Na–F 2.358(8), 2.419(8) and 2.489(8) Å). The Na–O distances, on the other hand, are similar to each other (2.27 ± 0.02 Å). In crystalline Na_2SiF_6, for comparison, the octahedral surrounding of the sodium atom has a mean Na–F distance of 2.32 Å.[11] Structural data on *molecular* complexes in which sodium atoms are coordinated to SiF groups are rare. The Na(μ-F)Si arrangement has been observed for [$^tBu_3Si(ONa)OSi^tBu_2F$]$_3$ (Na–F 2.30–2.37 Å),[12] for [$^tBu_3SiFNa(THF)_2PC_6H_2Me_3$]$_2$ (Na–F 2.383(2) Å),[13] and for a dimeric sodium phosphanide (Na–F 2.262(5) Å).[14]

The Na(μ-F)$_3$Si(μ-F)$_3$Na molecule is well shielded by the sterically demanding cymene π-ligands (Fig. 2). As for the $NaBF_4$ complex **2**, there are several close contacts between the cymene protons and the bridging fluorine atoms (CH$\cdots$F $\geqslant$ 2.25

Å). This tight encapsulation contributes to the kinetic and thermodynamic stabilisation of the host-guest complex.

In summary, we have synthesised a complex of molecular Na_2SiF_6 using organometallic crown complexes as stabilising hosts. Na_2SiF_6 is a molecule intrinsically difficult to isolate due to the high lattice energy of the corresponding crystalline form.

The resulting host–guest complex shows an unusual sandwich-type structure[15] with an ion-paired Na(μ-F)$_3$Si(μ-F)$_3$Na guest molecule.

Notes and references

† *Crystal data*: for **2**·2C_6H_6·0.5C_5H_{12}: $C_{59.5}H_{69}BF_4N_3NaO_6Ru_3$, M = 1335.19, triclinic, space group $P\bar{1}$, a = 10.6792(5), b = 14.5923(8), c = 19.1853(11) Å, α = 104.577(5), β = 90.350(4), γ = 93.685(4)°, V = 2886.7(3) Å^3, T = 143(2) K, Z = 2, μ = 0.847 mm^{-1}, λ = 0.71073 Å, 17183 measured reflections, 8932 independent reflections, R_{int} = 0.0277, R_1 [$I > 2\sigma(I)$] = 0.0382, wR_2 (all data) = 0.1173. The half pentane molecule is disordered over an inversion centre and was refined as isotropic with geometrical contraints. For **3**·2H_2O: $C_{90}H_{106}F_6N_6Na_2O_{14}Ru_6Si$, M = 2290.30, monoclinic, space group $P2_1/n$, a = 12.5292(10), b = 29.415(3), c = 13.0113(14) Å, β = 109.567(9)°, V = 4518.4(7) Å^3, T = 140(2) K, Z = 2, μ = 1.078 mm^{-1}, λ = 0.71073 Å, 26357 measured reflections, 7286 independent reflections, R_{int} = 0.1487, R_1 [$I > 2\sigma(I)$] = 0.0717, wR_2 (all data) = 0.1219. CCDC reference numbers 193869 and 193870. See http://www.rsc.org/suppdata/cc/b2/b208996c/ for crystallographic data in CIF or other electronic format.

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9 At room temperature, broad signals are observed.

10 The Ru-atoms of receptor **1** are chiral and have the same configuration: $R_{Ru}R_{Ru}R_{Ru}$ or $S_{Ru}S_{Ru}S_{Ru}$. For the sandwich complex **3**, the following stereoisomers are expected: $R_{Ru}R_{Ru}R_{Ru}R_{Ru}R_{Ru}R_{Ru}$, $S_{Ru}S_{Ru}S_{Ru}S_{Ru}S_{Ru}S_{Ru}$ and the *meso* form $S_{Ru}S_{Ru}S_{Ru}R_{Ru}R_{Ru}R_{Ru}$.

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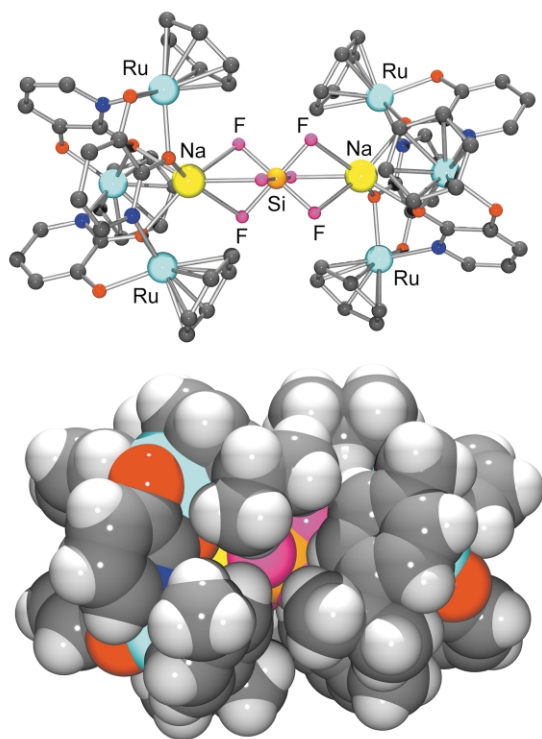

Fig. 2 Top: Ball-and-stick representation of the molecular structure of **3** in the crystal. The hydrogen atoms and the side chains of the aromatic π-ligand are not shown. Bottom: CPK representation including hydrogen atoms and side chains.