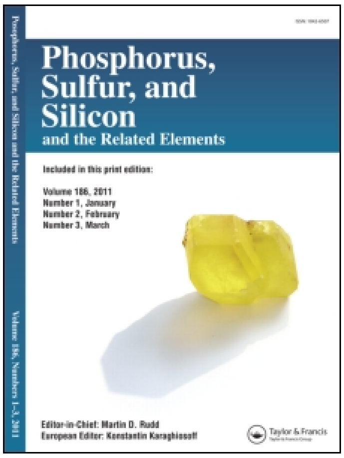

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$F_3CCN_5S_3$, A BICYCLIC MULTIFUNCTIONAL SULFUR-NITROGEN LIGAND

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*The bicyclic sulfur-nitrogen heterocycle $F_3CCN_5S_3$ (**1**) was investigated as a donor and acceptor toward H^+, metal cations, and F^-. Whereas the protonated species $F_3CCN_5S_3H^+$ AsF_6^- (**2**) can be isolated, the product of the reaction with F^- is unstable and decomposes among other products to TAS^+ $F_3CCN_5S_3NC(NH_2)CF_3^-$ (**3**), which is isolated from this reaction in small amounts.*

Keywords: Coordination chemistry; crystal structures; protonation; sulfur-nitrogen heterocyles; TASF

The bicyclic sulfur-nitrogen heterocycles of the type RCN_5S_3[1–3] are multifunctional systems, which we propose will have a versatile coordination chemistry. Within this series the trifluoromethyl-substituted compound $F_3CCN_5S_3$ (**1**) plays an important role due to its high stability. Recently we reported the syntheses, structures, and theoretical investigations of **1** and related compounds.[3] The NBO analyses show a highly negative and positive charge on the nitrogen and sulfur atoms respectively.[3] Therefore **1** contains a great number of different donor and acceptor positions. Up to now only two complexes of **1** with Ni and Ag have been reported.[4] With EPh_3 (E = P, As), similar to $PhCN_5S_3$,[5] **1** is transformed to the eight-membered imino derivatives $F_3CCN_4S_3NEPh_3$.[6]

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RESULTS AND DISCUSSION

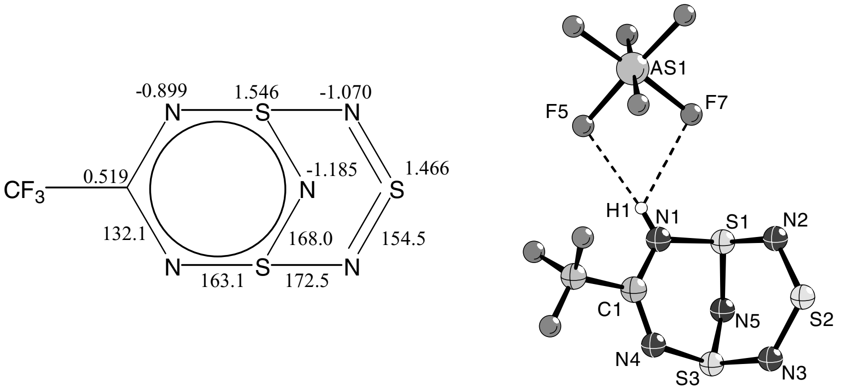
The reaction of **1** with $AgAsF_6$ in liquid SO_2 forms a silver complex, which is reacted *in situ* with HCl yielding AgCl and orange crystals of $F_3CCN_5S_3H^+$ AsF_6^- (**2**) in high yield.

$$\underset{\mathbf{1}}{F_3CCN_5S_3} \xrightarrow{AgAsF_6} [F_3CCN_5S_3Ag](AsF_6) \xrightarrow[-AgCI]{HCI} \underset{\mathbf{2}}{F_3CCN_5S_3H^+ \; AsP_6^-}$$

Surprisingly the H^+ doesn't attack the nitrogen atom with highest charge N5 but N1, neighbor to the F_3C-substituent. This is in agreement with theoretical calculations (RHF/6-311+G*), which prefer the protonation on N1 by 35.5 kJ/mol. Due to the electrophilic attack at N1 the bicyclic system in **2** is distorted in comparison to **1**. The anion AsF_6^- is weakly coordinated to the cation by H—F interactions.

Attempts to fluoridate **1** with TASF (tris(dimethylamino)sulfonium trimethylsilydifluoride), a well known fluorinating reagent, in CH_3CN at −40°C were not successful. The proposed fluorinated intermediate is unstable and decomposes to yellow crystals of TAS^+ $F_3CCN_5S_3NC(NH_2)CF_3^-$ (**3**), which were isolated and crystallographic characterized in addition to some unidentified compounds.

$$\underset{\mathbf{1}}{F_3CCN_5S_3} \xrightarrow[-Me_3SIF]{TASF} \underset{\mathbf{3}}{TAS^+F_3CCN_5S_3NC(NH_2)CF_3^-} + \cdots$$



a)

b)

FIGURE 1 a) Selected (average) bond length [pm][7] and NBO charges[3] for **1**. b) Crystal structure of **2**.[8] Selected bond length [pm] and angles [°]: C1–N1 134.8(3), C1–N4 128.7(3), N1–S1 168.6(2), N4–S3 167.18(19), S1–N5 161.0(2), S3–N5 163.0(2), S1–N2 168.2(2), S3–N3 171.3(2), N2–S2 155.2(2), N3–S2 154.6(2), N1–C1–N4 129.7(2), C1–N1–S1 122.14(17), C1–N4–S3 119.28(15).

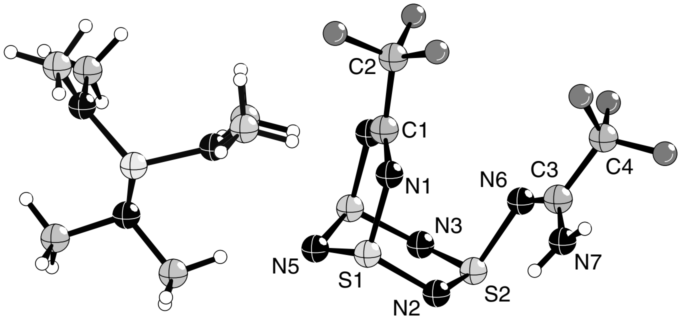


FIGURE 2 Crystal structure of **3**. Selected (average) bond length [pm] and angles [°]: C1–N1 132.0, N1–S1 167.0, S1–N5 163.9, S1–N2 164.1, N2–S2 163.1, S2–N6 170.54(18), N6–C3 129.1(3), C3–N7 133.3(3), N2–S2–N3 112.90(10). (The crystallographic data is deposited with the Cambridge Crystallographic Data Centre, UK.)

3 is the first product of a nuclephilic attack, whereby the bicyclic sulfur-nitrogen system is kept intact. With the attack of the anionic fragment $F_3CC(NH_2)N^-$ at S2, with rehybridization from sp^2 to sp^3, a negative charge is transferred to the heterocyclic ring. Therefore the bond length and angles change dramatically compared to **1**. The side chain is situated on the *endo* side, which corresponds to a *all-cis* configuration of the trithiatriazine ring (N5, S1, N2, S2) with a chair conformation.

CONCLUSIONS

1 is shown to act as a donor or acceptor respectively, which opens a wide field of new chemistry. Recent results show, that **1** yields a 1:1 adduct with AsF_5 and with different metal cations [M^{2+} = Co, Cu, Zn, Cd] coordination compounds are formed.[6] Whereas surprisingly with Hg^{2+} the bridging nitrogen atom N5 of **1** and similar systems (R = Me_2N, C_6H_5, 2,6-$F_2C_6H_3$) is removed and the planar eight-membered trithiatetrazocinium cations $RCN_4S_3^+$ AsF_6^- are formed.[6]

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