Complexes of the Bicyclic Multifunctional Sulfur-Nitrogen Ligand $F_3CCN_5S_3$ with Co^{2+}, Zn^{2+}, Cu^{2+}, and Cd[‡]

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Keywords: Bridging ligands / Heterocycles / N ligands / S ligands / Transition metals

The ability of the sulfur-nitrogen-carbon bicycle $F_3CCN_5S_3$ to act as a donor towards transition metal cations has been investigated. $F_3CCN_5S_3$ forms complexes with $[M(SO_2)_2](AsF_6)_2$ [M = Co, Cu, Zn, Cd] in the ratio 2:1 of the composition $[M(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ [M = Co (**1**), Zn (**3**)], $[Cu(F_3CCN_5S_3)_2(\mu\text{-}F)(\mu\text{-}F_2AsF_4)]_2$ (**4**), and $[Cd(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)(\eta^2\text{-}F_2AsF_4)_2]_2$ (**5**) in liquid sulfur dioxide. In the octahedral Co and Zn complexes $F_3CCN_5S_3$ coordinates as a monodentate ligand through the bridging nitrogen atom N5, which carries the highest negative charge according to theoretical calculations. With Cu^{2+} a dinuclear structure with a central planar, four-membered Cu_2F_2 ring is formed, which has the shortest Cu···Cu distance of all structurally characterized Cu_2F_2 units. Similar to the Co and Zn complexes, $F_3CCN_5S_3$ acts as a terminal monodentate ligand in the Cu compound. The reaction with the larger and softer Cd^{2+} cation results in a dinuclear complex that contains terminal and bridging $F_3CCN_5S_3$ ligands. The bridging ligands coordinate through N5 and a nitrogen atom neighboring the carbon atom. In addition, a third weak bonding interaction between one fluorine atom of the trifluoromethyl substituent and the Cd^{2+} center is observed. The formation of the different structures and the versatile coordination modes of the $F_3CCN_5S_3$ ligand are discussed.

Introduction

Recently, we reported the syntheses, crystal structures, and solid-state packing of $1\lambda^4,3\lambda^4,5\lambda^4$-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]nona-1(9),2,3,5,7-pentaenes (RCN_5S_3) with different alkyl and aryl substituents.[1] Based on quantum chemical calculations,[1a,2] these bicyclic sulfur-nitrogen heterocycles were proposed to act as versatile multifunctional ligands in coordination chemistry. The presence of several lone pairs and energetically low-lying orbitals of different symmetries should allow different coordination modes and a versatile chemistry. The calculations showed that the nitrogen atoms carry a high negative partial charge and the sulfur atoms a high positive one. The highest negative charge was found to be at the bridging nitrogen atom N5, independent of the substituent R.[1a] Thus, RCN_5S_3 might act as either a donor or an acceptor. Electrophiles exclusively attack the heterobicycle at the sulfur atom of the sulfurdiimide bridge, as was shown in reactions with EPh_3 (E = P, As)[3,4a] and in the structure determination of $[(Me_2N)_3S]^+[F_3CCN_5S_3NC(NH_2)CF_3]^-$.[4a] Reactions with Lewis acids, however, are more versatile. The Lewis acid AsF_5 attacks, as expected, at the bridging nitrogen atom N5 of $F_3CCN_5S_3$, while the proton, the simplest Lewis acid, interacts with a nitrogen atom neighboring the ring carbon atom.[4]

In this report we will focus on reactions of $F_3CCN_5S_3$ with $[M(SO_2)_x](AsF_6)_2$. The trifluoromethyl-substituted derivative $F_3CCN_5S_3$ is a representative example of this class of compounds. In addition, the sulfur-nitrogen heterocycle is stabilized by the F_3C group.[1a,5] Transition metal sulfur dioxide hexafluoroarsenates in liquid sulfur dioxide are an excellent system to introduce even very weak donor ligands into coordination chemistry.[6,7] Due to the weakly coordinating SO_2 ligands and AsF_6^- counteranions, the metal centers are almost “naked”. Thus, even very weak donors can be attached to the metal centers. Until now only two metal complexes of $F_3CCN_5S_3$ were known,[2] namely $[Ni(F_3CCN_5S_3)_2(SO_2)_2(AsF_6)_2]$, formed from $[Ni(SO_2)_6](AsF_6)_2$, where, similar to the AsF_5 adduct, the $F_3CCN_5S_3$ acts as an N-ligand and coordinates through the bridging nitrogen atom N5 to the metal center, and the silver complex $[Ag(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)]_2(AsF_6)_2$, which contains two differently coordinating $F_3CCN_5S_3$ molecules as terminal and bridging ligands, respectively. These two examples show that the coordination modes of the ligand depend on the metal center. Therefore it seemed worthwhile to extend our investigations to other metals.

In this paper reactions of the metal sulfur dioxide hexafluoroarsenates $[M(SO_2)_2](AsF_6)_2$ (M = Co, Cu, Zn, Cd) with $F_3CCN_5S_3$ are reported. The X-ray structures of the

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[‡] Part of this work was presented at the 10th International Symposium on Inorganic Ring Systems (Burlington, VT, USA, August 2003) and at the 14th European Symposium on Fluorine Chemistry (Poznan, Poland, July 2004).

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DOI: 10.1002/ejic.200500396

resulting complexes and the different coordination modes of the ligand $F_3CCN_5S_3$ are discussed.

Results and Discussion

The reaction of $F_3CCN_5S_3$ with the transition metal cations $Co^{2+}$and Zn^{2+} in liquid sulfur dioxide yielded orange crystals of $[M(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ [M = Co (**1**), Zn (**3**)], which are isostructural with the known Ni^{2+} complex **2**.[2] The presence of O-coordinated SO_2 in these complexes can be concluded from the S–O stretching mode in the IR spectra; O-coordination is preferred by hard metal centers.[6,8] The As–F stretching vibrations for the AsF_6^- counteranions are split and partly shifted to higher wavenumbers, in agreement with a distorted coordinated AsF_6^- (Scheme 1).

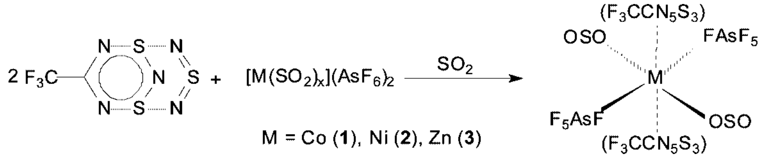
A different result is expected for the reaction with Cu^{2+}, because Cu^{2+} compounds (d^9) are strongly affected by the Jahn–Teller distortion. Very air-sensitive blue crystals were obtained from the reaction of $F_3CCN_5S_3$ with $[Cu(SO_2)_x](AsF_6)_2$ in liquid sulfur dioxide. The IR spectrum shows no absorptions in the region of S–O stretching vibrations, in agreement with the results of the X-ray structure determination (see below). The isolated dinuclear complex of the formula $[Cu(F_3CCN_5S_3)_2(\mu\text{-}F)(\mu\text{-}F_2AsF_4)]_2$ (**4**) contains a central four-membered Cu_2F_2 ring with two Cu^{2+} cations bridged by two fluoride and two AsF_6^- anions. In addition, each Cu^{2+} ion coordinates two $F_3CCN_5S_3$ ligands. The bridging fluoride ions result from the decomposition of AsF_6^- anions. It has been known for a long time that $[Cu(AsF_6)_2]$ readily loses AsF_5 with formation of $[CuF_n(AsF_6)_{2-n}]$ of ill-defined composition.[9] Recently, $[CuF(AsF_6)]$[10] has been structurally characterized[11] and might allow the straightforward preparation of **4** in the future (Scheme 2).

Cd^{2+} is a "softer" metal cation, due to its larger ionic radius than the cations of the first row transition metals discussed above, therefore a different behavior is observed: the reaction of $[Cd(SO_2)_x](AsF_6)_2$ with $F_3CCN_5S_3$ in liquid sulfur dioxide yields the dinuclear complex $[Cd(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)(\eta^2\text{-}F_2AsF_4)_2]_2$ (**5**), similar to the silver complex we described earlier (Scheme 3).[2]

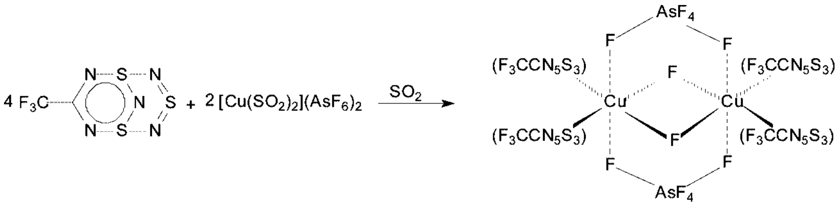
Structural Investigations

Structures of $[M(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ [M = Co (1), Zn (3)]

Single crystals of all compounds suitable for X-ray diffraction were obtained by slow evaporation of the solvent (liquid sulfur dioxide) at room temperature. Complexes **1** and **3** are isostructural and crystallize in the monoclinic space group $P2_1/n$ (Figure 1). The metal cation lies on an inversion center and is surrounded by two $F_3CCN_5S_3$ ligands. In addition, the two AsF_6^- counteranions are linked to the cation by bridging fluoride ions, with the remaining two free coordination sites being filled by sulfur dioxide solvent molecules to complete the octahedral coordination sphere (Figure 1). For comparison, selected average bond lengths are included in Table 1 together with the data for $F_3CCN_5S_3$ and $F_3CCN_5S_3{\cdot}AsF_5$.



Scheme 1.



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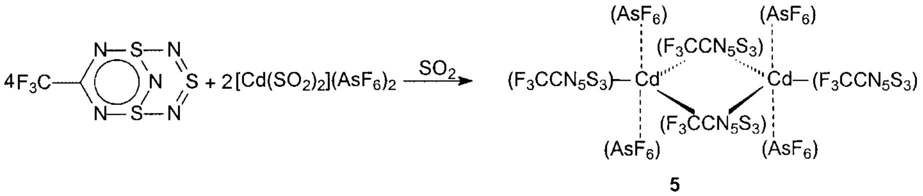
Scheme 2.



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Scheme 3.

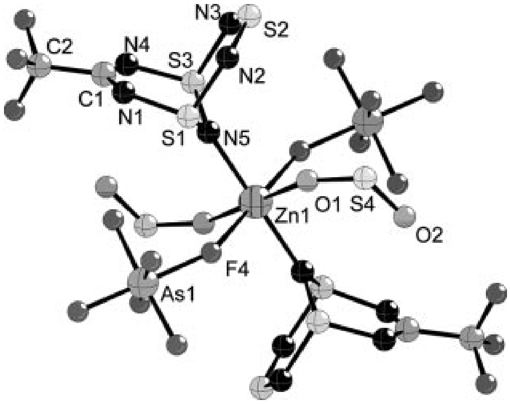


Figure 1. Structure of $[Co(F_3CCN_5S_3)_2(SO_2)_2(FAsF_5)_2]$ (**1**), which is isostructural to $[Zn(F_3CCN_5S_3)_2(SO_2)_2(FAsF_5)_2]$ (**3**). Selected bond lengths [pm] for **1**: Co(1)–N(5) 205.8(2), Co(1)–F(4) 209.53(16), Co(1)–O(1) 214.0(2), C(1)–N(1) 131.3(4), C(1)–N(4) 132.0(4), C(1)–C(2) 153.7(4), N(1)–S(1) 162.7(2), S(1)–N(5) 164.7(2), S(1)–N(2) 170.9(3), N(2)–S(2) 154.4(3), S(2)–N(3) 154.8(3), N(3)–S(3) 171.4(3), S(3)–N(4) 162.6(3), S(3)–N(5) 165.1(2), O(1)–S(4) 144.4(2), S(4)–O(2) 141.1(3), As(1)–F(4) 179.13(17), average As–F 169.9. Selected bond lengths [pm] for **3**: Zn(1)–N(5) 203.42(19), Zn(1)–F(4) 210.44(15), Zn(1)–O(1) 218.14(18), C(1)–N(1) 131.5(3), C(1)–N(4) 132.1(3), C(1)–C(2) 153.0(3), N(1)–S(1) 162.3(2), S(1)–N(5) 164.9(2), S(1)–N(2) 170.9(2), N(2)–S(2) 154.4(3), S(2)–N(3) 155.1(3), N(3)–S(3) 171.1(3), S(3)–N(4) 162.4(2), S(3)–N(5) 165.1(2), O(1)–S(5) 144.08(19), S(5)–O(2) 141.2(2), As(1)–F(4) 178.65(15), average As–F 169.8.

The $F_3CCN_5S_3$ ligand coordinates to the metal center through the bridging nitrogen atom N5, which carries the highest negative charge according to theoretical calculations.[4a] The M–N distance of about 205 pm in **1**, **2**, and **3** [203.42(19) pm in **1** and 206.3(4) in **2**] is in agreement with the similar ionic radii of the cations. The changes of the bond length within the sulfur-nitrogen heterocycle on coordination to a transition metal cation and on adduct formation with AsF_5 compared with the free ligand follow the same pattern as discussed previously.[4a]

The M···O distance increases from M = Zn to M = Ni by about 8 pm and is approximately 7 pm longer than in complexes containing only SO_2, such as $[Ni(OSO)_6](AsF_6)_2$ [203.3(3)–204.3(3) pm][13] and $[Co(OSO)_4(FAsF_5)_2]$ [205.9(4)–207.5(4) pm].[7]

In agreement with accepted bonding models,[14] the end-on coordination of the SO_2 ligand to the cation results in two different S–O bond lengths. Compared to the free SO_2 molecule (143 pm),[15] the M···O–S bond is slightly stretched (144 pm), whereas the terminal S–O bond is slightly shortened (140–141 pm). This distortion is a function of the Lewis acidity of the acceptor and decreases with the weakening of the M···O interaction from M = Zn to M = Ni.[2]

Similar to the M···O distances, the M···F distances [209.53(16) pm in **1**] are longer than in the complexes containing only SO_2 as additional ligands {e.g. $[Co(OSO)_4(FAsF_5)_2]$: 201.8(3)–202.6(3) pm}.[7] The counteranion acts as a monodentate ligand resulting in a distortion of the AsF_6^- octahedron. The As–F bond of the bridging fluoride F4 in **3** is about 10 pm longer than the average of the other As–F bond lengths.

Structure of $[Cu(F_3CCN_5S_3)_2(\mu\text{-}F)(\mu\text{-}F_2AsF_4)]_2$ (4)

Blue crystals suitable for X-ray diffraction were also obtained by slow evaporation of the liquid sulfur dioxide. Structure solution and refinement were realized in the triclinic space group $P\bar{1}$. The dinuclear complex contains a central planar, four-membered Cu_2F_2 ring (Figure 2). Two $F_3CCN_5S_3$ ligands coordinate through the bridging nitrogen atom N5 to each copper, completing a square-planar environment around the Cu^{2+} ion. In addition, the two metal centers are bridged by the AsF_6^- counteranions above and below the Cu_2F_2 unit. The contacts within the plane are much stronger than the Cu–F contacts perpendicular to the plane due to the Jahn–Teller effect. This view is supported by applying Brown's bond valence approach,[16] which assigns 0.28 v.u. (valency units) for the Cu–N contacts and 0.42 v.u. for the Cu–F bonds within the Cu_2F_2 ring, but only 0.13 v.u. for the Cu–F contacts to the bridging hexafluoroarsenate ions. Only a few compounds containing a Cu_2F_2 ring have been structurally characterized, and the Cu···Cu distance is normally in the range of 290–340 pm.[17] The title compound contains the shortest Cu···Cu distance of all Cu_2F_2 four-membered rings [287.5(2) pm], which might be a result of the AsF_6^- bridges. Since the Cu···F–AsF_4–F···Cu interactions are weak, the hexafluoroarsenate ions are less distorted than in the com-

Table 1. Selected average bond lengths [pm] for $[M(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ [M = Co (**1**), Ni (**2**), Zn (**3**)], $F_3CCN_5S_3{\cdot}AsF_5$, and $F_3CCN_5S_3$. The values in square brackets are valency units [v.u.] according to Brown's bond valence approach.[16]

	$F_3CCN_5S_3$[12]	**1**	**2**[2]	**3**	$F_3CCN_5S_3{\cdot}AsF_5$[4a]
M–N5		205.8(2) [0.33]	206.3(4) [0.33]	203.42(19) [0.43]	
M–O1		214.0(2) [0.29]	210.0(4) [0.30]	218.14(18) [0.28]	
M–F4		209.53(16) [0.29]	204.5(3) [0.31]	210.44(15) [0.27]	
F4–As1		179.13(17)	179.5(3)	178.65(15)	
average As–F		169.9	169.1	169.7	
C1–C2	152.4(4)	153.7(4)	153.9(8)	153.0(3)	153.2(8)
C1–N1	132.1	131.6	131.0	131.8	131.6
N1–S1	163.1	162.6	162.6	162.3	161.9
S1–N5	163.0	164.9	164.0	165.0	166.1
S1–N2	172.5	170.1	171.4	170.0	171.0
N2–S2	154.5	154.6	153.7	154.7	155.1

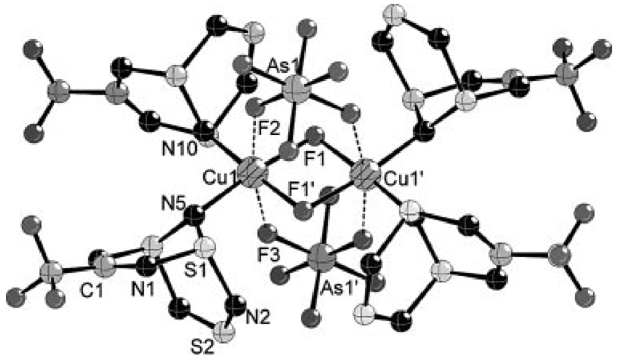


Figure 2. Structure of $[Cu(\mu\text{-}F)(\mu\text{-}F_3CCN_5S_3)(\mu\text{-}F_2AsF_4)]_2$ (**4**). Selected bond lengths [pm] and angles [°]: Cu(1)–F(1) 191.3(5), Cu(1)–F(1′) 191.9(5), Cu(1)–N(5) 197.4(7), Cu(1)–N(10) 199.4(8), Cu(1)–F(3) 235.3(5), Cu(1)–F(2′) 236.5(6), Cu(1)–Cu(1′) 287.5(2), C(1)–N(1) 131.0(12), C(1)–N(4) 133.5(12), C(1)–C(2) 151.9(13), N(1)–S(1) 163.2(7), S(1)–N(5) 165.4(7), S(1)–N(2) 170.8(8), N(2)–S(2) 154.3(8), S(2)–N(3) 154.4(8), N(3)–S(3) 171.1(8), S(3)–N(4) 162.5(8), S(3)–N(5) 165.1(7), C(3)–N(6) 131.2(12), C(3)–N(9) 132.4(12), C(3)–C(4) 154.5(13), N(6)–S(4) 160.3(8), S(4)–N(10) 165.7(8), S(4)–N(7) 172.5(9), N(7)–S(5) 153.6(9), S(5)–N(8) 154.8(9), N(8)–S(6) 171.1(9), S(6)–N(9) 161.6(9), S(6)–N(10) 163.4(8); F(1)–Cu(1)–F(1′) 82.8(2), F(1)–Cu(1)–N(5) 90.0(3), F(1′)–Cu(1)–N(5) 172.8(3), F(1)–Cu(1)–N(10) 175.2(3), F(1′)–Cu(1)–N(10) 93.0(3), N(5)–Cu(1)–N(10) 94.2(3). Symmetry transformation to generate primed atoms: $-x$, $-y + 2$, $-z + 1$.

plexes discussed above. The influence of the metal center on the average bond lengths of the $F_3CCN_5S_3$ ligands is small: the changes within the heterocycle are in the expected range for $F_3CCN_5S_3$ coordinated to an acceptor.[4a]

Magnetic measurements on **4** were not carried out but might be interesting as structural[17] and theoretical investigations[18] on Cu_2F_2 rings of similar geometry have shown antiferromagnetic coupling between the Cu^{2+} centers.

Structure of $[Cd(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)(\eta^2\text{-}F_2AsF_4)_2]$ *(5)*

Orange crystals suitable for X-ray diffraction were also obtained by slow evaporation of the liquid sulfur dioxide solvent. The structure solution and refinement were realized in the monoclinic space group $P2_1/n$. The complex has a structure similar to that of the corresponding silver compound $[Ag(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)]_2(AsF_6)_2$.[2] The dinuclear structure contains two different kinds of $F_3CCN_5S_3$ ligands – bridging and terminal (Figure 3). As usual, the terminal $F_3CCN_5S_3$ coordinates through the bridging nitrogen atom N5. The second $F_3CCN_5S_3$ acts as a bidentate ligand through the bridging nitrogen atom (here N10) and the nitrogen atom (N6) next to the trifluoromethyl substituent, and bridges the two metal cations to form an eight-membered $Cd_2N_4S_2$ metallacycle. The Cd–N6 distance [232.25(18) pm (M = Cd), 249.7(4) pm (M = Ag)] is much shorter, and the Cd–N10 distance [240.54(19) pm (M = Cd), 228.1(4) pm (M = Ag)] much longer, than in the corresponding silver compound, while the Cd–N5 distance to the terminal ligand is not influenced by the metal [225.79(19) pm (M = Cd), 222.3(5) pm (M = Ag)]. This is the result of an additional weak bonding interaction between one fluorine atom of the trifluoromethyl substituent and the cadmium center. Bidentate hexafluoroarsenate ions complete the coordination sphere around the metal center, to give a coordination number of eight. Bidentate hexafluoroarsenate ions are less common, but have been observed before in Ag^+ and Cd^{2+} complexes.[19] By applying the bond valence approach,[16] the relative strengths of the different contacts become obvious (Figure 4). The Cd–N contacts are the dominating interactions (0.30–0–45 v.u.), while the Cd–F contacts to the bidentate hexafluoroarsenate ions are weaker (0.13–0.20 v.u.). The additional bonding between

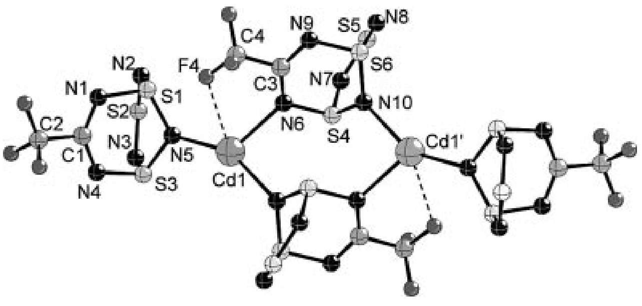


Figure 3. Structure of $[Cd(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)]_2^{4+}$. Anions have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Cd(1)–N(5) 225.79(19), Cd(1)–N(6) 232.25(18), Cd(1)–F(7) 240.07(13), Cd(1)–N(10′) 240.54(19), Cd(1)–F(14) 244.36(15), Cd(1)–F(13) 247.51(15), Cd(1)–F(8) 256.61(14), C(1)–N(1) 131.6(3), C(1)–N(4) 133.1(3), C(1)–C(2) 153.0(3), N(1)–S(1) 163.62(19), S(1)–N(5) 164.87(19), S(1)–N(2) 171.9(2), N(2)–S(2) 154.9(2), S(2)–N(3) 154.5(2), N(3)–S(3) 172.2(2), S(3)–N(4) 161.4(2), S(3)–N(5) 167.13(18), C(2)–F(3) 131.5(3), C(2)–F(1) 132.5(3), C(2)–F(2) 132.6(3), C(3)–N(9) 130.8(3), C(3)–N(6) 134.8(3), C(3)–C(4) 153.4(3), N(6)–S(4) 166.98(18), S(4)–N(10) 164.06(19), S(4)–N(7) 168.8(2), N(7)–S(5) 156.4(2), S(5)–N(8) 154.3(2), N(8)–S(6) 171.1(2), S(6)–N(9) 164.35(19), S(6)–N(10) 164.61(18), C(4)–F(6) 131.8(3), C(4)–F(5) 132.6(3), C(4)–F(4) 134.9(3); N(5)–Cd(1)–N(6) 122.82(6), N(5)–Cd(1)–N(10′) 152.02(6), N(6)–Cd(1)–N(10′) 84.68(6). Symmetry transformation to generate primed atoms: $-x$, $-y$, $-z$.

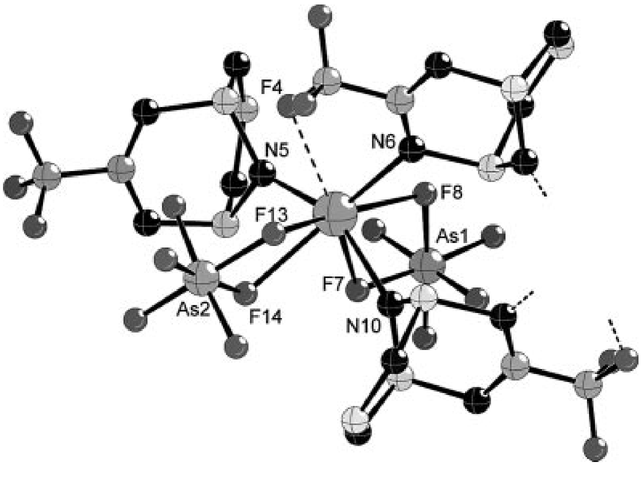
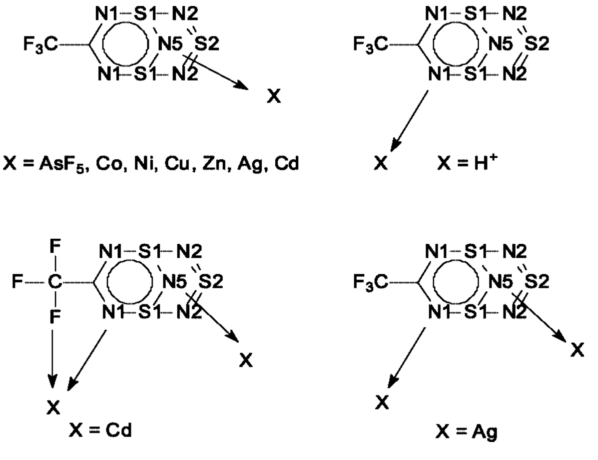


Figure 4. Part of the structure of $[Cd(F_3CCN_5S_3)(\mu\text{-}F_3CCN_5S_3)(\eta^2\text{-}F_2AsF_4)_2]_2$ showing the environment around the Cd^{2+} ion. For selected bond lengths and angles see caption to Figure 3. Selected valency units: Cd–N5 0.45, Cd–N6 0.38, Cd–N10 0.30, Cd–F4 0.10, F4–C4 0.92, average F–C4 1.00, Cd–F7 0.20, Cd–F8 0.13, Cd–F13 0.17, Cd–F14 0.18.

the trifluoromethyl group and the metal center is much weaker (0.10 v.u.), but strongly influences the structure.

Conclusions

The large number of different lone pairs and low-lying orbitals enables the versatile chemistry of $F_3CCN_5S_3$. It can act as a donor to Lewis acids in many different ways. Coordination through the bridging nitrogen atom N5, which, according to theoretical calculations, carries the highest negative charge, is preferred by hard transition metal cations. $F_3CCN_5S_3$ can coordinate as a terminal ligand, but is also able to bridge Lewis acid centers through the bridging nitrogen atom and a nitrogen atom next to the ring carbon. This allows the formation of eight-membered metallacycles. Surprisingly, even the fluorine atoms of the trifluoromethyl group are able to form an additional bond, which makes $F_3CCN_5S_3$ a tridentate ligand. A comparison of the different complexes shows that $F_3CCN_5S_3$ is a very flexible ligand, which can be seen as well in the possible angle between the S–N5–S plane and the N5–metal contact, which varies in a wide range between –13.1° (M = Cd) and +27.5° (M = Cu). The resulting structures depend on the ionic radii and the hardness of the metal cations. Scheme 4 shows the four possible coordination modes known so far. Together with the known reactions with Lewis bases, the chemistry of $F_3CCN_5S_3$ is very versatile and makes the bicycles of the type RCN_5S_3 an interesting class of compounds to investigate and understand the chemistry of sulfur-nitrogen compounds. Reactions with ligands containing other organic substituents and with other transition metals have been performed as well. They resulted in decomposition of the sulfur-nitrogen heterocycle, but in some cases, when decomposition products can be isolated, an interesting chemistry can be anticipated. These investigations, for example the formation of the eight-membered planar heterocycle $[RCN_4S_3]^+[AsF_6]^-$ from the reaction of RCN_5S_3 with $[Hg(SO_2)_x](AsF_6)_2$, will form part of a separate publication.[20]



Scheme 4. Observed coordination modes of $F_3CCN_5S_3$.

Experimental Section

General: All manipulations of the solid, air-sensitive materials were performed with the exclusion of oxygen and moisture under dry nitrogen. The reactions were carried out in lambda-type glass vessels with Teflon valves using liquid sulfur dioxide as solvent, which was transferred via a vacuum line. Sulfur dioxide was dried over P_4O_{10} and distilled prior to use. The starting materials $F_3CCN_5S_3$[1a] and $[M(SO_2)_x](AsF_6)_2$ (M = Co, Zn, Cu, Cd)[7] were prepared according to published procedures. IR spectra were obtained with a Perkin–Elmer Paragon 500 FT-IR spectrometer as Nujol or Kel-F mulls. ^{19}F NMR spectra were recorded with a Bruker DPX 200 spectrometer in CD_3CN (chemical shifts are given with respect to $CFCl_3$), and melting points with a Gallenkamp melting point apparatus in sealed melting point capillaries.

$[Co(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ (1): A 10 mL portion of SO_2 was condensed onto a mixture of $F_3CCN_5S_3$ (0.25 g, 1.0 mmol) and $[Co(SO_2)_4](AsF_6)_2$ (0.35 g, 0.5 mmol) at –196 °C via a vacuum line. The reaction mixture was allowed to warm slowly to room temperature, and a brown-black solution was formed. After slow removal of the solvent, a brown-black solid remained. Careful washing of the reaction mixture with cold (–40 °C) liquid sulfur dioxide yielded orange crystals of the title compound (0.35 g, 0.3 mmol, 60%), m.p. 100–110 °C (dec.). ^{19}F NMR (200 MHz, CD_3CN, 20 °C): δ = –67.1 (q, $^1J_{F,As}$ = 930 Hz, 12 F, AsF_6^-), –75.9 (s, 12 F, CF_3) ppm. IR: $\tilde{\nu}$ = 1335 w, 1313 m, 1290 sh, 2112 m, 1295 sh, 1181 m, 1133 m, 1030 m, 1018 m, 968 w, 895 w, 816 w, 796 w, 777 m, 750 sh, 719 s, 704 m, 670 m, 661 m, 586 m, 529 m, 518 m, 506 m, 491 w cm^{-1}.

$[Zn(F_3CCN_5S_3)_2(OSO)_2(FAsF_5)_2]$ (3): Similar to the preparation of **1**, an orange solution was formed from $F_3CCN_5S_3$ (0.20 g, 0.8 mmol) and $[Zn(SO_2)_2](AsF_6)_2$ (0.23 g, 0.4 mmol). After slow removal of the solvent, a red-black oil remained. Careful washing of the reaction mixture with cold (–40 °C) liquid sulfur dioxide yielded yellow crystals of the title compound (0.27 g, 0.25 mmol, 63%), m.p. 90 °C (dec.). ^{19}F NMR (200 MHz, CD_3CN, 20 °C): δ = –67.3 (q, $^1J_{F,As}$ = 930 Hz, 12 F, AsF_6^-), –75.9 (s, 12 F, CF_3) ppm. IR: $\tilde{\nu}$ = 1509 w, 1482 m, 1455 sh, 1145 m, 1396 m, 1362 m, 1313 s, 1213 s, 1182 s, 1139 s, 1023 m, 1019 m, 968 w, 891 w, 806 w, 788 m, 760 sh, 724 s, 704 m, 661 m, 586 m, 528 m, 517 m, 519 sh, 490 w cm^{-1}.

$[Cu(\mu-F)(F_3CCN_5S_3)_2(\mu-F_2AsF_4)]_2$ (4): $F_3CCN_5S_3$ (0.20 g, 0.8 mmol) and $[Cu(SO_2)_2](AsF_6)_2$ (0.23 g, 0.4 mmol) formed a brown-black solution. After slow removal of the solvent, a yellow-brown solid remained. Careful washing of the reaction mixture with cold (–40 °C) liquid sulfur dioxide yielded blue crystals of the title compound (0.20 g, 0.13 mmol, 65%), m.p. 110 °C (dec.). ^{19}F NMR (200 MHz, CD_3CN, 20 °C): δ = –67.1 (q, $^1J_{F,As}$ = 930 Hz, 12 F, AsF_6^-), –75.9 (s, 12 F, CF_3) ppm. IR: $\tilde{\nu}$ = 1344 w, 1300 w, 1246 m, 1218 m, 1199 m, 1178 m, 1146 m, 1023 sh, 1005 m, 979 sh, 957 sh, 894 w, 850 w, 818 w, 805 w, 783 m, 773 m, 754 m, 721 s, 698 m, 663 m, 588 m, 566 w, 552 w, 528 sh, 516 w, 504 w, 489 w, 454 w cm^{-1}.

$[Cd(F_3CCN_5S_3)(\mu-F_3CCN_5S_3)(\eta^2-F_2AsF_4)_2]_2$ (5): $F_3CCN_5S_3$ (0.20 g, 0.8 mmol) and $[Cd(SO_2)_2](AsF_6)_2$ (0.25 g, 0.4 mmol) formed an orange solution. After slow removal of the solvent, orange crystals of the title compound (0.39 g, 0.2 mmol, 100%) remained, m.p. 159 °C (dec.). ^{19}F NMR (200 MHz, CD_3CN, 20 °C): δ = –67.0 (q, $^1J_{F,As}$ = 932 Hz, 12 F, AsF_6^-), –75.9 (s, 12 F, CF_3) ppm. IR: $\tilde{\nu}$ = 1498 vs, 1474 s, 1446 s, 1391 w, 1368 s, 1343 m, 1299 w, 1228 m, 1197 m, 1168 m, 1106 sh, 1028 m, 1005 m, 956 w, 814 m, 790 m, 770 s, 750 sh, 725 vs, 710 vs, 666 s, 606 m, 585 m, 571 sh, 550 w, 542 w, 518 sh, 510 m, 490 w cm^{-1}.

Table 2. Crystal data and structure refinement for **1**, **3**, **4**, and **5**.

	1	**3**	**4**	**5**
Empirical formula	$C_4As_2CoF_{18}N_{10}O_4S_8$	$C_4As_2F_{18}N_{10}O_4S_8Zn$	$C_8As_2Cu_2F_{26}N_{20}S_{12}$	$C_8As_4Cd_2F_{36}N_{20}S_{12}$
Formula mass	1059.39	1065.83	1531.92	1969.48
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [pm]	944.9(2)	943.50(10)	947.7(3)	1464.2(3)
b [pm]	1361.7(2)	1361.7(2)	1043.7(3)	1016.6(2)
c [pm]	1073.3(2)	1078.10(10)	1206.7(3)	1667.6(3)
α [°]	90	90	66.28(2)	90
β [°]	97.680(10)	97.420(10)	68.70(3)	109.69(3)
γ [°]	90	90	84.27(2)	90
V [nm^3]	1.3686(4)	1.3735(3)	1.0144(5)	2.3371(8)
Z	2	2	1	2
$D_{calcd.}$ [Mg m^{-3}]	2.571	2.577	2.508	2.799
Crystal size [mm]	0.70 × 0.60 × 0.50	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.20	0.50 × 0.40 × 0.15
θ range	2.64–27.51	2.64–27.51	2.79–22.50	2.27–25.92
Reflections collected	4053	7340	3152	3195
Independent reflections	3132 [R(int) = 0.0181]	3154 [R(int) = 0.0254]	2544 [R(int) = 0.0389]	4496 [R(int) = 0.0465]
Goodnes-of-fit on F^2	1.089	1.028	0.990	1.018
Final R indices R_1, wR_2	0.0289, 0.0705	0.0255, 0.0602	0.0498, 0.1032	0.0182, 0.0446
R indices (all data)	0.0366, 0.0737	0.0329, 0.0632	0.0916, 0.1150	0.0214, 0.0456

Crystallographic Analysis: The single-crystal X-ray structure determinations were carried out with a Siemens P4 diffractometer or a Stoe IPDS using Mo-K_α (λ = 0.71073 Å) radiation with a graphite monochromator. The crystals were mounted onto a thin glass fiber using Kel-F oil. Details of the data collection and refinement are given in Table 2. The structures were solved by direct methods (SHELXS).[21] Subsequent least-squares refinement on F^2 (SHELXL 97-2) located the positions of the remaining atoms in the electron density maps.[21] All atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model and refined isotropically in blocks. The data were corrected for absorption (DIFABS).[22] Graphical representations of the structures were prepared with the program DIAMOND.[23] CCDC-265908 (**1**), -265907 (**3**), -265909 (**4**), and -265910 (**5**) 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.

Acknowledgments

We are grateful to the BFK NaWi, Universität Bremen, for financial support and Mr. Peter Brackmann for collecting the X-ray data.

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Received: May 3, 2005