Crystal Structure of $CF_3SNSO-AsF_5$

Axel Brosius and Alois Haas*

Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum,
D-44780 Bochum

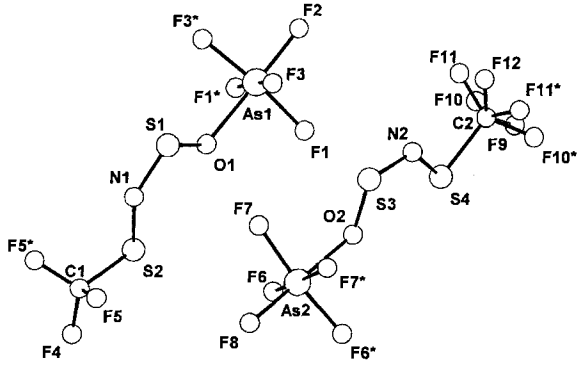
Received December 19, 1994

Key Words: (Trifluoromethyl)sulfanyl sulfinylimine / Arsenic pentafluoride, crystal structure

Reinvestigation of an earlier reported preliminary X-ray structure verifies the coordination of AsF_5 to the oxygen atom of CF_3SNSO. The resulting differences in bond lengths of the cumulene system SNSO via an attachment of the Lewis acid are mentioned.

Recently, we have reported on possible reaction paths of the hydrolysis of CF_3SNSO to $[NH_4^+][CF_3SSO_3^-]$[1]. They are based on a crystal structure determination of the adduct $CF_3SNSO-AsF_5$ and the resulting main resonance form $CF_3SN{=}S^+-\overline{O}|^-$. The determined space group $P2_1$ afforded no results that could be physically utilized. This was attributed to a dynamic disorder of the CF_3 group in the crystal[1]. Since the structure greatly affects the course of the hydrolysis and because of the fact that it is the first structure determination of a sulfinylimine adduct with arsenic pentafluoride we corrected the misinterpreted measuring data. Useful results were obtained with the space group $P2_1/m$. The reported distance d(S–O) deviates from the newly calculated one by 0.033 Å; the AsF_5 group is as described coordinated to the oxygen atom so that there are no consequences concerning the course of the hydrolysis.

Figure 1. Molecular structure and numbering of the atoms[a]



[a] Selected bond lengths [Å] and angles [°]: As1–F1 1.699(4), As1–F3 1.701(4), As2–F6 1.692(5), As2–F8 1.686(6), S1–O1 1.512(6), S2–N1 1.650(8), S3–O2 1.502(6), S4–N2 1.651(8), F4–C1 1.29(1), F5–C1 1.308(6), F11–C2 1.30(2), As1–F2 1.670(5), As1–O1 1.928(6), As2–F7 1.700(4), As2–O2 1.929(6), S1–N1 1.488(8), S2–C1 1.84(1), S3–N2 1.478(8), S4–C2 1.82(1), F9–C2 1.26(3), F10–C2 1.26(3), F12–C2 1.17(2); F3*–As1–F2 93.0(1), F1*–As1–F2 93.2(1), O1–As1–F3 87.4(1), O1–As1–F1 86.4(1), F3–As1–F1 90.0(2), F7*–As2–F7 88.5(2), F6*–As2–O2 86.8(1), F6*–As2–F7 173.8(2), O2–As2–F8 178.9(3), O2–As2–F6 86.8(1), F8–As2–F6 93.9(1), N1–S1–O1 112.3(4), C1–S2–N1 94.6(4), N2–S3–O2 111.0(4), C2–S4–N2 96.1(6), F3*–As1–F3 90.4(2), F3*–As1–F1 173.8(2), F1*–As1–F1 89.0(2), O1–As1–F2 179.4(3), F7*–As2–F6* 90.4(2), F7*–As2–F6 173.8(2), F6*–As2–F8 93.9(1), F6*–As2–F6 90.0(2), O2–As2–F7 87.1(1), F8–As2–F7 92.2(1), S1–O1–As1 122.0(4), S3–O2–As2 123.7(4), S2–N1–S1 128.5(5), S4–N2–S3 127.5(5), F5*–C1–F4 110.7(2), F5*–C1–F5 108.0(8), F5*–C1–S2 110.2(2), F4–C1–S2 107.2(7).

Molecular Structure of $CF_3SNSO-AsF_5$

As Figure 1 shows $CF_3SNSO-AsF_5$ contains two independent molecules with C_s symmetry on a mirror plane in the elementary cell, one of the CF_3 groups being disordered. Figure 1 confirms the interesting linkage of the Lewis base CF_3SNSO with the Lewis acid AsF_5 with the formation of an As–O single bond with an averaged length of 1.928(6) Å. Remarkable is the lack of a *trans* effect on the AsF bonding in *trans* position with respect to the As–O bond in the slightly distorted octahedral AsF_5O structural element. With an average value of 1.507(1) Å the S–O distance is by about 0.07 Å longer than d(S–O) [1.44(2) Å] in NSO compounds[2–4]. The S–N bond lengths are with 1.650(8) Å for the single bond and 1.483(1) Å for the double bond in the expected range for *N*-sulfinylimines. With respect to the S–N double bond the SNSO grouping is *cis*-configurated and the bond angle at the sulfur(IV) atom with 111.6(4)° is comparable to the value of 112.7(2)° determined for $S(NSO)_2$[5].

We are indebted of Prof. Dr. *Carl Krüger, Jörg Kuhnigk*, MPI Mülheim, and Prof. Dr. *Roland Boese*, Institut für Anorganische Chemie der Universität GH Essen, for the revision of the crystal structure analysis.

Experimental

The preparation and further characterization of $CF_3SNSO-AsF_5$ are described in ref[1].

Crystal Structure Analysis[6]: Size of colorless crystal obtained by sublimation: 0.20 × 0.30 × 0.40 mm; a = 9.507(1), b = 8.299(1), c = 11.434(1) Å; β = 90.77(1)°; V = 902.0 Å^3; space group: $P2_1/m$ (monoclinic); calcd. d = 2.45 g/cm^3; $AsCF_8NOS_2$ (333.1); Z = 4; radiation: Mo K_α, λ = 0.71069 Å; μ = 42.97 cm^{-1}; temperature: 20 °C; Enraf-Nonius CAD4 diffractometer; method: ω-20; $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}; total no. of measured reflections [$+h$ $+k$ $+l$], 1612 observed reflections [$F > 4.0\sigma(F)$]; structure solution by direct methods; empirical absorption correction; 145 refined parameters; R = 0.057, R_w 0.065 [$w^{-1} = \sigma^2(F) + 0.0001\,F^2$], maximum residual electron density: 1.07 eA^{-3}.

[1] A. Brosius, A. Haas, M. Pryka, *Chem. Ber.* **1994**, *127* 457–463.
[2] A. Haas, J. Kasprowski, *Chimia* **1987**, *41*, 340–340.
[3] A.Haas, R. Pohl, *Chimia* **1989**, *43*, 261–262.
[4] H. Oberhammer, *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1970**, *25A*, 1497–1501.
[5] G. S. H. Chen, J. Passmore, *J. Chem. Soc., Dalton Trans.* **1979**, 1257–1261.
[6] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59002.

[438/94]

  0009–2940/95/0606–0651 $ 10.00+.25/0