A sulfur nitrogen triple, double and single bond in one ligand: synthesis and structure of $[Co\{N{\equiv}SF_2{-}N{=}S(O)F_2\}_4][AsF_6]_2{\cdot}SO_2$

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$NSF_2NS(O)F_2$ reacts quantitatively with $[Co(SO_2)_n][AsF_6]_2$ to give $[Co\{N{\equiv}SF_2{-}N{=}S(O)F_2\}_4][AsF_6]_2{\cdot}SO_2$; X-ray structure analysis confirms the presence of a triple, double and single bond in the same ligand.

Sulfur nitrogen fluorine chemistry is one of the most fascinating fields in inorganic chemistry. Due to the possibilities of sulfur possessing different oxidation states and coordination numbers, forming single, double and triple bonds and being incorporated into acyclic and cyclic systems, an almost unprecedented variety of combination possibilities has been experimentally verified.[1] Although a large number of compounds have been reported, structural investigations on them are relatively rare. SN bond distances determined by electron diffraction on molecules in the gas phase range from 141.4 pm for $N{\equiv}SF_3$[2] to 169.8 pm in $SF_5{-}NF_2$[3] and in the solid state from 137–138 pm in coordination compounds of NSF_3 {*e.g.* $[M(NSF_3)_4(FAsF_5)_2]$,[4] $[Re(CO)_5(NSF_3)]^+$[5]} to 164–166 pm in $RSO_2{-}NR'_2$[6] and 169 pm in $SF_5N{=}CR_2$,[7] respectively, from X-ray structure determinations. The bond distances are dependent on the coordination number (hybridization) of sulfur and nitrogen[8] and on the oxidation state of sulfur. For $N{\equiv}SF_2{-}N{=}S(O)F_2$[9] the simple valence bond description suggests the presence of a triple, single and double bond between N and tetracoordinated S^{VI} centres. Coordination of this ligand to the 'naked' Co^{2+} centre[10] in pink $[Co(SO_2)_n][AsF_6]_2$[11] gives deep blue $[Co\{NSF_2NS(O)F_2\}_4][AsF_6]_2{\cdot}SO_2$ in quantitative yield.†

$$\underset{\mathbf{1}}{[Co(SO_2)_n][AsF_6]_2} + NSF_2NS(O)F_2\ (excess) \longrightarrow \underset{\mathbf{2}}{[Co\{NSF_2NS(O)F_2\}_4][AsF_6]_2{\cdot}SO_2}$$

At ambient temperature SO_2 is readily removed from **2** under dynamic vacuum. The structure of the cation of compound **2** is shown in Fig. 1.‡ The central Co^{2+} is surrounded by a regular tetrahedron [N–Co–N 108.0(2)–110.4(2)°] the Co–N distances being in the range 195.4(4)–197.4(5) pm. The bond distances in the ligand justify the description as containing an NS triple, single and double bond between isocoordinated N and S centres in the same ligand.

$$[Co\{N\overset{138.9\ pm}{\equiv\!\equiv\!\equiv}SF_2\underset{158.8\ pm}{-\!-\!-}N\overset{149.9\ pm}{=\!=\!=}S(O)F_2\}_4]^{2+}$$

So far, bond lengths for NS triple bonds have been documented only for coordination compounds of NSF_3[4,5] and NSF_2NMe_2[5] and lie in the range 137–139 pm, Exchange of one fluorine in NSF_3 by other substituents has little effect on the $N{\equiv}S$ bond length. From 170 structure determinations of organic $-\overset{\|}{\underset{|}{S}}=N-$systems reported in the CCDC an average of 154.4 pm for the NS double bond is found, while for $-\overset{\|}{\underset{\|}{S}}-N=$ single bonds (334 examples) an average of 160.5 pm is reported.[12] The average N=S and N–S bond distances in **2** are significantly shorter than this as a result of orbital contraction owing to the highly electronegative substituents in our ligand system.

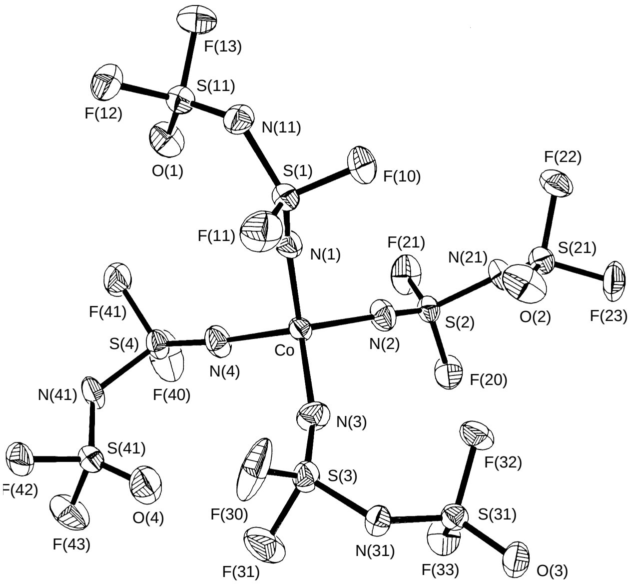

Fig. 1 Structure of the cation of **2** with selected bond distances (pm) and angles (°): Co–N 195.4(4)–197.4(5) (av. 196.9), $N^1{\equiv}S^1$ 138.3(4)–139.3(5) (138.9), $S^1{-}F^1$ 151.8(4) 153.1(4) (152.5), $S^1{-}N^2$ 157.6(4)–159.5(4) (158.8), $N^2{=}S^2$ 149.4(4)–150.6(5) (149.9), $S^2{-}O$ 137.3(4)–138.8(4) (138.2), $S^2{-}F^2$ 149.0(4)–151.6(4) (151.0), $N^1{-}Co{-}N^2$ 108.0(2)–110.5(2) (109.5), Co–$N^1{\equiv}S^1$ 159.6(3)–171.6(3) (166.4), $N^1{\equiv}S^1{-}N^2$ 123.6(3)–127.1(3) (125.2), $S^1{-}N^2{=}S^2$ 121.4(3)–125.7(3) (123.5). S^1=S(1), S(2), S(3), S(4); S^2=S(11), S(21), S(31), S(41); N^1=N(1), N(2), N(3), N(4); N^2=N(11), N(21), N(31),N(41); F^1=F(10), F(11), F(20), F(21), F(30), F(31), F(40), F(41); F^2=F(12), F(13), F(22), F(23), F(32), F(33), F(42), F(43); O=O(1), O(2) O(3), O(4).

In the non-coordinating SO_2 molecule of **2** [S(10)–O(11) 138.4(5) pm, S(10)–O(12) 141.2(5) pm, O–S–O 119.9(4)°] the O–S–O angle is identical to that of SO_2 in the gas phase (O–S–O 119.3°, S–O 143.3 pm).[13] The difference in the S–O bond lengths in **2** is due to the differing thermal motions of the sulfur and both of the oxygen atoms, which may also be the cause of the shortened S–O bonds in **2** compared to free SO_2.

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Footnotes and References

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† *Preparation* of **2**: SO_2 (10 ml) was condensed onto $[Co(SO_2)_2][AsF_6]_2$ (1.01 g, 1.78 mmol)[4] at −196 °C in a thick-walled Schlenck vessel, and an excess of $NSF_2NS(O)F_2$ (1.8 g, 8.15 mmol) was added. On warming to room temp. the solution changed from pink to deep blue. The solvent and excess of ligand were removed at ambient temperature in dynamic vacuum to give 2.09 g of **2** (quantitative), IR (Nujol, Kel-F mull): 1660w (sh),

1560m, 1452m, 1435m, 1255m (sh) 1220s, 940 (sh) 920m, 831s, 815m, 759m, 700vs, 580m, 533m, 525m, 497m, 480m, 399vs cm^{-1}. Elemental analysis. Calc.: F, 45.3; N, 9.55. Found: F, 44.9; N, 9.2%.

‡ *Crystal data* for $As_2CoF_{28}N_8O_4S_8 \cdot O_2S$: **2** crystallizes with one molecule of solvent per formula unit, monoclinic, space group $P2_1/c$, a = 1712.6(3), b = 1142.4(2), c = 1844.1(4) pm; β = 116.54(3)°, U = 3.2277(11) nm, Z = 4, D_c = 2.546 g cm^{-3}, μ = 3.350 mm^{-1}, F(000) 2372, crystal dimensions 0.5 × 0.4 × 0.2 mm, 8191 reflections collected with $2.66 < \theta < 27.51°$, 5256 unique used in structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation (λ = 71.073 pm) at 173 K. The structure was solved by direct methods.[14] All atoms were refined anisotropically. An empirical absorption correction using ψ-scans was applied. The refinement (487 parameters) converged with wR_2 = 0.0779 (R_1 = 0.0398) and final difference electron density maxima and minimina of 455 and −602 e nm^{-3}. CCDC 182/539.

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