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Hydrolysis product of the [Na(15-crown-5)] salt of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion

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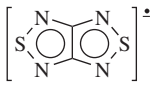
At ambient temperature, interaction of the solid radical anion salt [Na(15-crown-5)][$C_2N_4S_2$] with water vapour unexpectedly leads to the trithionate salt [Na(15-crown-5)]$_2$[$S(SO_3)_2$], whose coordination pattern is very different from the previously studied trithionate salts.

Heterocyclic thiazyl radicals and their Se congeners belong to the most promising building blocks for the design and synthesis of magnetic and conducting molecular materials.[1–5] In particular, they were successfully used in the preparation of low-temperature molecular ferromagnets, which also exhibited properties of molecular conductors.[1] While neutral and positively charged heterocyclic thiazyl radicals (radical cations) were subject of extensive studies, related negatively charged systems (radical anions) remained practically uninvestigated because they are much less accessible in the form of stable salts.[1–5]

Recently, the first salts of heterocyclic thiazyl radical anions, particularly those of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl ($C_2N_4S_2$, Scheme 1) were isolated in a crystalline state. At low temperatures, they revealed antiferromagnetic ordering of their spin systems. The salts were thermally stable up to ~100 °C but underwent decomposition (fast in solution and slow in the solid state) upon contact with the atmosphere. The decomposition products were not identified, and any other chemical properties of the salts were also not investigated.[6]

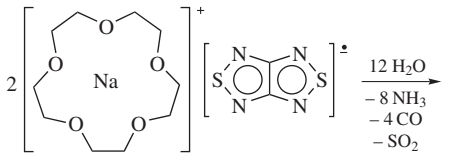


Scheme 1

The neutral heterocyclic precursor of the title radical anion, [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole ($C_2N_4S_2$), is air-stable,[6,7] but it is hydrolyzed by boiling water to give oxamide and elemental sulfur.[7]

We found that the ambient-temperature hydrolysis of solid radical anion salt [Na(15-crown-5)][$C_2N_4S_2$] **1** by water vapour[†] leads to a product identified by X-ray diffraction[‡] after crystallization from MeCN–THF as trithionate[8] salt [Na(15-crown-5)]$_2$-[$S(SO_3)_2$]·2MeCN **2**[†] (Figure 1). As a reaction by-product, ammonia was detected.[†] Due to these findings, the hydrolysis under discussion can be tentatively described by Scheme 2.

X-ray structure determinations of trithionate salts are rare;[9–13] there are only three reports on direct interactions of the anion with metal centers. In bis(2,2′-bipyridyl)trithionato copper(II), the trithionate anion acts as a bidentate bridging ligand connecting two Cu^{2+} centers under formation of polymer chains.[10] In $K_2[S(SO_3)_2]$, each anion interacts with eight K^+ centers (K···O distances of 264.6–324.4 pm) leading to a coordination number



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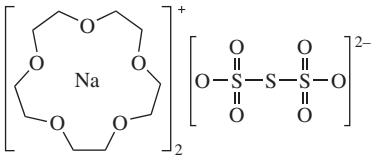

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Scheme 2

† *Hydrolysis of salt* **1**. Evacuated vessels containing 0.39 g (0.001 mol) of salt **1**[6(e)] and 50 ml of degassed water were connected to a vacuum line and left at ambient temperature (~25 °C). Over the course of two weeks, dark-red crystals of **1** were transformed into a yellow crystalline solid. This product was vacuum dried and then dissolved in a 1:1 mixture of THF and MeCN. The solution was filtered and cooled to –40 °C, whereupon the solvents were removed with a syringe, and the residue was vacuum dried. Compound **2** was obtained as transparent colourless crystals; yield, 0.33 g (0.00043 mol, 85%), mp (sealed capillary) 120–122 °C. Found (%): C, 38.11; H, 5.75; N, 3.72; S, 13.08. Calc. for $C_{24}H_{46}N_2Na_2O_{16}S_3$ (760.80) (%): C, 37.89; H, 6.09; N, 3.68; S, 12.64.

Both atmosphere above crude **2** (before vacuum drying) and the liquid water that was in a second vessel revealed a strong basic reaction, and a qualitative test of the water with Nessler's reagent indicated the presence of ammonia.

‡ *XRD data for salt* **2**: $C_{24}H_{46}N_2Na_2O_{16}S_3$, M = 760.79, triclinic, space group $P\bar{1}$, a = 875.6(3), b = 1275.4(6) and c = 1642.1(9) pm, α = 91.14(5)°, β = 99.04(3)°, γ = 94.05(3)°, V = 1.8056(14) nm^3, Z = 2, d_{calc} = 1.399 g cm^{-3}, μ(MoKα) = 0.298 mm^{-1}. The final indices are wR_2 = 0.1101, S = 1.023 for all 8235 F^2, R_1 = 0.0415 for 6797 $F_0 > 2\sigma F_0$ (488 parameters). The data were measured at 173(2) K on a Bruker P4 diffractometer using MoKα (λ = 71.073 pm) radiation with a graphite monochromator. The structure was solved by the direct methods using the SHELXS-97 program[14] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation by use of the SHELXL-97 program.[14]

CCDC 710550 contains 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

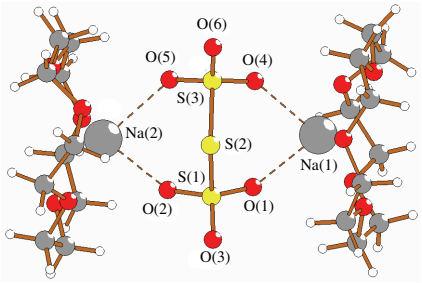

Figure 1 X-ray structure of salt **2** [MeCN molecules are omitted, and disorder of 15-crown-5 ether molecule coordinated to Na(1) atom is neglected]. Selected bond distances (pm) and bond angles (°): S(1)–O(1) 144.63(17), S(1)–O(2) 144.63(15), S(1)–O(3) 144.23(17), S(1)–S(2) 210.51(10), S(2)–S(3) 211.68(14), S(3)–O(4) 144.30(16), S(3)–O(5) 144.43(16), S(3)-O(6) 143.71(18), Na(1)···O(1) 236.19(18), Na(1)···O(4) 237.29(19), Na(2)···O(2) 235.87(18), Na(2)···O(5) 250.3(2); O(1)–S(1)–O(2) 112.84(10), O(1)–S(1)–S(2) 107.32(7), O(1)–S(1)–O(3) 114.01(10), O(2)–S(1)–O(3) 113.85(10), O(2)–S(1)–S(2) 106.29(7), O(3)–S(1)–S(2) 101.32(9), S(1)–S(2)–S(3) 102.49(4), S(2)–S(3)–O(4) 106.77(8), S(2)–S(3)–O(5) 106.07(8), S(2)–S(3)–O(6) 100.43(10), O(4)–S(3)–O(5) 113.20(10), O(4)–S(3)–O(6) 113.91(11), O(5)–S(3)–O(6) 114.93(11), S(1)–O(1)···Na(1) 134.85(9), S(1)–O(2)···Na(2) 129.41(9), S(3)–O(4)···Na(1) 135.31(9), S(3)–O(5)···Na(2) 127.06(9), O(1)···Na(1)···O(4) 79.61(16), O(2)···Na(2)···O(5) 80.33(6).

of 9 for each cation.[9] In $Cs_2[S(SO_3)_2]\cdot SO_2$, each anion interacts with seven Cs^+ centers (Cs···O distances of 301–353 pm), and the SO_2 ligand interacts end-on leading to a coordination number of 11 for each cation.[13]

In salt **2**, each Na^+ center is surrounded by seven oxygen atoms, five from the crown ethers and two from two different SO_3 groups of the same anion (Figure 1). The Na···O distances to the crown-ether oxygen atoms are in the range of 245.5–261.0 pm; they are significantly longer than the Na···O distances of 235.1–237.3 pm to the anion. The Na(2)···O(5) distance (Figure 1) is exceptionally longer. For this lengthening no convincing explanation can be given. It might be caused by steric interaction of O(5) atom (Figure 1) with a Me group from MeCN, which is situated between the crown ethers. While in the above K^+ and Cs^+ salts the interactions of the $[S(SO_3)]^{2-}$ with eight and nine metal centers, respectively, lead to three-dimensional polymeric structures, in **2** the interactions of the anion with only two Na^+ centers result in the formation of isolated ion pairs. Although all SO distances in **2** [143.71(18)–144.63(16) pm] are in the 3σ range and, therefore, not significantly different, the data obtained suggest, as expected, a slight lengthening of the SO bonds on interaction with the metal centers. The trithionate anion in **2** has *pseudo*-C_{2v} symmetry; the MeCN molecules are not coordinated to Na^+ cations; *i.e.*, in this context, **2** can be considered as an inclusion compound. One of the two 15-crown-5 ether molecules is disordered.

Thus, this work reports chemical properties of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion for the first time. Note that salt **2** can hardly be predicted *a priori* as the hydrolysis product of salt **1**. The coordination pattern of **2** is very different from the previously studied trithionate salts.

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