

Diamagnetic π -Dimers of the [1,2,5]Thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl Radical Anion in the Crystalline State: Preparation and X-ray Crystal Structure of a $[(\text{Me}_2\text{N})_2\text{CC}(\text{NMe}_2)_2]^{2+}[(\text{C}_2\text{N}_4\text{S}_2)_2]^{2-}$ Salt

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Chemical reduction of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) with 1,1,2,2-tetrakis(dimethylamino)ethene (**3**) leads to the $[\mathbf{3}]^{2+}[\mathbf{1}_2]^{2-}$ salt (**4**) whose X-ray crystal structure reveals diamagnetic π -dimers of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**). The interplanar separation of 324.5 pm in the $[\mathbf{1}_2]^{2-}$ dimers is significantly shorter than the sum of the isotropic van der Waals radii of two S atoms of

348–358 pm. CASSCF calculations suggest that the largest contributor to the singlet ground state of these π -dimers is the closed-shell electronic configuration, although a noticeable contribution from a configuration with a singlet biradical character was also found.

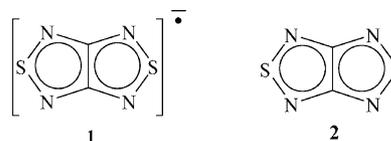
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Introduction

Currently, chalcogen–nitrogen chemistry^[1] plays an essential role in the design and synthesis of new molecular materials, especially conducting, superconducting and magnetic materials.^[2–8] In particular, numerous spin-carrying chalcogen–nitrogen compounds, consisting mostly of neutral and positively charged heterocyclic thiazyl radicals (radical cations), have been carefully explored as molecular magnets and/or conductors, while the rather rare negatively charged systems (radical anions) have been less studied.^[1–7]

Recently, we have described the preparation as well as X-ray diffraction and ESR characterization of thermally stable salts of heterocyclic thiazyl radical anions such as [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl, $[\text{C}_2\text{N}_4\text{S}_2]^-$ (**1**, Scheme 1), and its Se congener, $[\text{C}_2\text{N}_4\text{SSe}]^-$. Magnetic measurements performed on the salts with $[\text{K}(18\text{-crown-6})]^+$ and $[\text{Na}(15\text{-crown-5})]^+$ cations revealed low-temperature

antiferromagnetic ordering of their spins.^[9] The investigation of the electrical properties of these salts is in progress.



Scheme 1.

These salts were prepared by chemical reduction of the neutral $\text{C}_2\text{N}_4\text{S}_2$ (**2**, Scheme 1) and $\text{C}_2\text{N}_4\text{SSe}$ precursors with the PhS^- anion.^[9] A search for new reducing agents is of obvious interest since these might provide a pathway to radical anion salts with new cations, including paramagnetic ones. These paramagnetic species, especially multicharged cations, can enlarge the temperature range of the spin system ordering.

In this work, we report on the reduction of compound **2** with 1,1,2,2-tetrakis(dimethylamino)ethene (**3**), which gave the $[\mathbf{3}]^{2+}[\mathbf{1}_2]^{2-}$ salt (**4**). The X-ray crystal structure of **4** revealed diamagnetic π -dimers of the radical anion **1**. These dimers were not previously observed.

Results and Discussion

Compound **3** is a well known reducing agent.^[10a] In the HeI photoelectron spectrum, its vertical IE_1 and IE_2 are ca. 6.0 and 7.5 eV, respectively.^[10] That means that the IE_1 of **3** is only 1 eV higher than the IE_1 of the sodium atom. In redox processes, **3** forms monocationic salts (e.g., with C_{60} fullerene)^[11] as well as dicationic salts [e.g., with X_2 ($\text{X} =$

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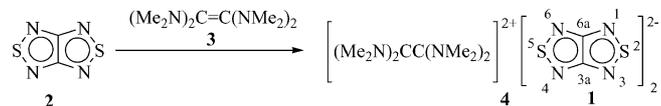
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Cl, Br)].^[10a] Interestingly, the salt **[3][C₆₀]** (where both the cation and anion are paramagnetic) reveals properties characteristic of an organic ferromagnet.^[11]

In this work, with **3/2** taken in a 1:1 molar ratio, the reduction gave the **[3]²⁺[1₂]²⁻** salt (**4**, Scheme 2), which was isolated in a yield of 90%.



Scheme 2.

According to the X-ray diffraction data (see Exp. Sect.), salt **4** contains π -dimers of the radical anion **1** (Figures 1 and 2). The dimers have an ideal parallel centrosymmetric structure. In this area of research, such an ideal arrangement is rather rare for π -stacked structures; usually some offset is observed.^[3,4] Since this ideal structure is crystallographically imposed in the $C2/c$ space group with $Z = 4$ in which salt **4** was refined, a comparative refinement in the acentric space group, Cc , was performed. However, for this space group the results are definitely worse. For example, for the Cc space group values of 0.0392 for R_1 and 0.1139 for wR_2 were obtained, while values of 0.0379 for R_1 and 0.0933 for wR_2 were obtained with the $C2/c$ space group. Additionally, for the Cc group the estimated standard deviations were almost three times larger than those for the $C2/c$ group.

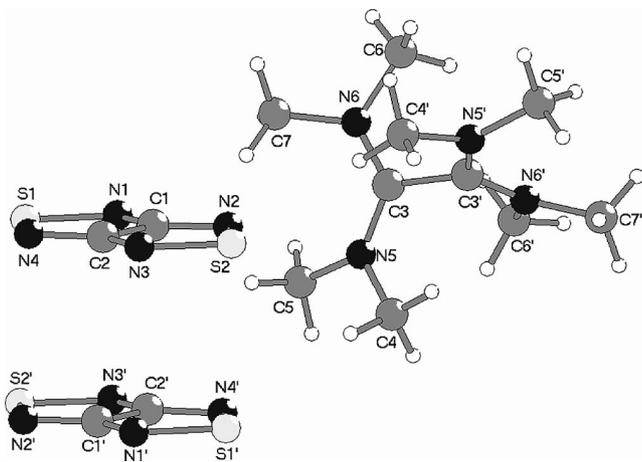


Figure 1. Structure of salt **4**. Crystallographic numbering is used. For selected bond lengths and bond angles of radical anion **1** in the **[1₂]²⁻** dimers, see Table 1. The shortened **S1...S2'** and **S2...S1'** contacts in the **[1₂]²⁻** dimers are 324.5 pm.

Another interesting structural feature of the dimers is a very short interplanar separation of 324.5 pm. This distance is significantly shorter than the sum of the isotropic van der Waals radii of two S atoms of 348–358 pm.^[12] The dication of **3** has a very long C–C bond of 152.2 pm; the two NCN planes are virtually orthogonal. This geometry is also typical of other structurally defined salts of the dication.^[10a] In the monocation of **3**, the C–C bond length is 140.8 pm.^[11b]

Salt **4** is ESR-silent in the solid state, and its magnetic susceptibility (χ) is constantly equal to zero in the 2–300 K

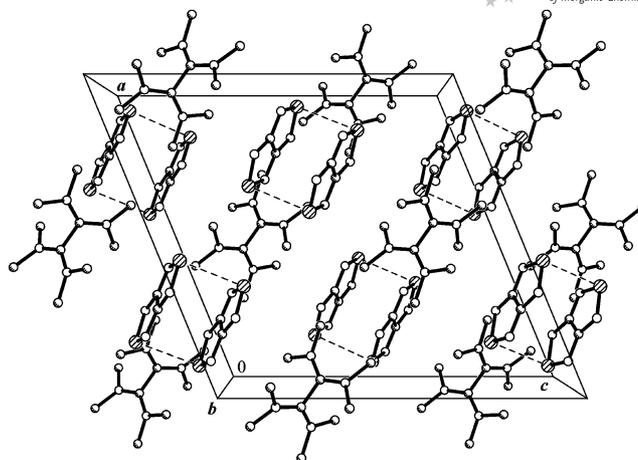


Figure 2. Crystal structure of salt **4**. The hydrogen atoms of the **3²⁺** cations are omitted for clarity. The shortened **S...S** contacts in the **[1₂]²⁻** dimers are shown by dashed lines.

temperature range. However, MeCN solutions of salt **4** display an intense ESR spectrum characteristic of radical anion **1** (nine-line pattern, $a_N = 0.314$ mT, $g = 2.0045$; cf. refs.^[9b,9c]). This indicates dissociation of the dimers in these solution. At ambient temperature and in sealed tubes, solutions of salt **4** are stable at least for a few months.

In all previously studied salts with **[Li(12-crown-4)₂]⁺**, **[Na(15-crown-5)⁺**, **[K(18-crown-6)⁺**, **[K(18-crown-6)(MeCN)⁺** and **[(Me₂N)₃S]⁺** cations, radical anion **1** is monomeric. In these salts **1** acts as a bridging or chelating ligand, or, with **[Li(12-crown-4)₂]⁺** and **[(Me₂N)₃S]⁺** (one of two crystallographically independent anions **1**), it is not coordinated to the cation.^[9b,9c] The coordination situation affects the X-ray molecular geometry of **1** only to a very minor extent.^[9b,9c] The comparison of the X-ray molecular geometries of radical anion **1** in the salts where it is monomeric with the geometry of salt **4** where it is dimeric leads to the conclusion that the π -dimerization practically does not affect the experimental geometry of **1**. Table 1 demonstrates, as an example, a comparison of the experimental geometry of the radical anion **1** in salts **4** and **[Li(12-crown-4)₂][1]**.^[9b]

The shortened **S...S** contact implies bonding interactions in the **[1₂]²⁻** dimer. According to (U)B3LYP/6-31+G(d) calculations, the **[1₂]²⁻** dimer has a closed-shell singlet ground state with a singlet-triplet (S-T) splitting of -9.4 kcal mol⁻¹. Figure 3 displays the frontier MOs of the **[1₂]²⁻** dimer in its ground state. With a simplified MO model, it is seen that the HOMO and LUMO of the dimer are respectively bonding and antibonding combinations of the π -SOMOs of radical anion **1**.

However, the bonding situation is not so simple since the restricted singlet ground state wavefunction of **[1₂]²⁻** is unstable. The unrestricted B3LYP calculations led to a lowering of the electronic energy of **[1₂]²⁻** by 0.22 kcal mol⁻¹ accompanied by the triplet contamination of a wavefunction ($\langle s^2 \rangle = 0.252, 0.006$ after annihilation of the triplet component). Hence, the **[1₂]²⁻** dimer has an unusual electronic

Table 1. Selected bond lengths [pm] and angles [°] of radical anion **1** in salts **4** and [Li(14-crown-4)₂][**1**] (**5**).^[a]

	4	5 ^[9b]
N1–S2	165.69(17)	165.95(16)
S2–N3	165.66(19)	166.35(15)
N3–C3a	133.7(2)	133.61(19)
C3a–N4	133.6(2)	133.8(2)
N4–S5	166.07(17)	165.97(14)
S5–N6	165.62(15)	166.30(16)
N6–C6a	133.6(2)	133.8(2)
C6a–N1	134.0(2)	133.5(2)
C3a–C6a	145.1(2)	145.39(18)
C6a–N1–S2	104.76(12)	104.84(10)
N1–S2–N3	101.35(8)	101.27(7)
S2–N3–C3a	104.78(12)	104.54(10)
C3a–N4–S5	104.67(12)	104.72(9)
N4–S5–N6	101.31(8)	101.30(7)
S5–N6–C6a	104.69(11)	104.70(10)
N1–C6a–C3a	114.45(16)	114.55(14)
C6a–C3a–N3	114.65(16)	114.81(13)
N4–C3a–C6a	114.52(16)	114.67(13)
N6–C6a–C3a	114.78(16)	114.60(14)

[a] For atom numbering see Scheme 2.

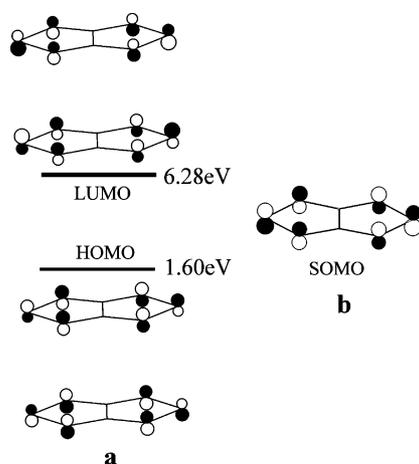


Figure 3. The frontier MOs of the [1₂]²⁻ dimer (HOMO 11b_{3u}, LUMO 11b_{1g}) (a) and the SOMO of radical anion **1** (b) from the HF/6-31G(d) and ROHF/6-31G(d) calculations, respectively.

structure which cannot be described in the framework of a single configuration approach.

To clarify the electronic structure of [1₂]²⁻, the more precise multiconfiguration CASSCF procedure was employed. The active space used in the CASSCF(14,12) calculations comprised seven bonding MOs and five antibonding MOs of the dimer occupied by 14 electrons. These bonding and antibonding MOs represent the positive and negative linear combinations of the π-MOs, π-SOMO and π*-MOs of radical anion **1**.

Similarly to the B3LYP calculations, the CASSCF ones predict a singlet ground state for the dimer with an S-T splitting of –10.9 kcal mol⁻¹. At the CASPT2 level of theory the S-T gap is equal to –8.5 kcal mol⁻¹. The ground state configuration makes the largest contribution of 71% to the wavefunction of the singlet ground state of [1₂]²⁻. The next

largest contribution of 12% comes from the doubly excited HOMO→LUMO configuration. Since the CASSCF natural orbital occupation numbers reveal significant deviation from 0 or 2 (at most 0.37 for the LUMO and 1.67 for the HOMO), one can conclude that the ground state of the [1₂]²⁻ dimer has noticeable singlet biradical character.

With the quantum chemical techniques employed, the energy difference between [1₂]²⁻ and two isolated radical anions **1** was always positive: the system of two isolated anions is more stable than [1₂]²⁻ because of the Coulombic repulsion of the negatively charged **1** species. The same repulsion leads to the dissociation of [1₂]²⁻ in solution (see above). In the crystal this repulsion is compensated for by the attraction of the radical anions **1** to the 3²⁺ cations. Under these conditions, i.e. in the presence of the electrostatic (packing) forces in the crystal lattice of salt **4**, the orbital overlap shown in Figure 2 is seemingly responsible for the observed π-dimeric state of the radical anions **1**.

Because of the π-dimerization of radical anion **1**, salt **4** is kinetically stabilized towards the action of atmospheric moisture and dioxygen, and can be kept without decomposition for a long time. Salt **4** can be considered as a suitable molecular reservoir for the radical anions **1** to be used in further experiments.

The crystal packing of neutral and positively charged thiazyl radicals is crucial for their macroscopic magnetic and conductive properties.^[2–5] Therefore, the reliable prediction and control of their crystal lattices is important for further progress in the field. The solid-state π-dimerization of neutral and positively charged thiazyl radicals was described previously.^[2–5] To the best of our knowledge, the solid-state dimerization of thiazyl radical anions is reported here for the first time. In the case of thiazyl species, dimerization is thought to be driven by packing forces which even overcome the Coulombic repulsion in the cases of charged radicals. In the context of crystal engineering of salts of the radical anion **1**, however, a specific question to be answered is as follows: will **1** always be π-dimerized in dicationic salts (salts of cations with even charge) and exist in a monomeric (paramagnetic) state only in monocationic salts (salts of cations with uneven charge)?

Recently, π-dimerization was also observed for radical anions of some hydrocarbon aromatics such as 1,3,5-trinitrobenzene.^[13] In the case of the radical anion of 1,3,5-trinitrobenzene (**5**), the properties of [5₂]²⁻ dimers are very different from those of [1₂]²⁻. The [Et₄N]₂[5₂] salt (**6**) is paramagnetic in the solid state,^[13] whereas salt **4** is diamagnetic. The X-ray analysis of salt **6** shows a π-stacked structure but the **5** moieties are not parallel to each other.^[13] Furthermore, [5₂]²⁻ is a triplet biradical (*S* = 1) in solution as evidenced by the ESR spectra of frozen DMF solutions (77 K). It is also thought that the tilted structure of the [5₂]²⁻ dimers observed for the solid salt **6** is maintained in solution until these π-dimers collapse into σ-dimers.^[13] In contrast, the [1₂]²⁻ dimers are unstable in solution and immediately dissociate to give the **1** monoradicals (*S* = 1/2). MeCN solutions of salt **4** frozen by immersion in liquid nitrogen reveal unresolved ESR spectra reminiscent of the

solid-state spectra of the previously studied salts of radical anion **1**.^[9b,9c] As mentioned above, in sealed tubes, solutions of salt **4** are stable for a minimum of a few months.

Conclusions

Under mild reaction conditions, 1,1,2,2-tetrakis(dimethylamino)ethene (**3**) smoothly reduces [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) to give the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**). The latter was isolated from the reaction mixture in the form of the thermally stable salt [3]²⁺[1]₂²⁻ (**4**). The salt is ESR-active in solution but, in contrast to previously studied salts of radical anion **1**, it is ESR-silent in the solid state, and its magnetic susceptibility is constantly equal to zero in the 2–300 K temperature range. The X-ray crystal structure of salt **4** reveals previously unknown diamagnetic π -dimers of radical anions **1**. The dimers have ideal parallel centrosymmetric structures. The interplanar separation of 324.5 pm in the dimers is significantly shorter than the sum of van der Waals radii of two S atoms. At the same time, the π -dimerization of radical anion **1** practically does not affect its molecular geometry. CASSCF calculations suggest that the largest contribution to the singlet ground state of the π -dimers is the closed-shell configuration, although a noticeable contribution from a configuration with a singlet biradical character was also found.

Because of the π -dimerization of radical anions **1**, salt **4** is kinetically stabilized towards the action of atmospheric moisture and dioxygen, and it can be considered as a suitable molecular reservoir for radical anions **1** to be used in further experiments.

Experimental Section

General: Compound **2** was prepared as described previously.^[9c] Compound **3** was used as received from Fluka. The synthesis described below was performed under argon in absolutely dried solvents.

The solid-state and solution ESR spectra of salt **4** were measured with a Bruker ESP-300 spectrometer (MW power 265 mW, modulation frequency 100 kHz, modulation amplitude 0.005 mT). Magnetic measurements were performed with an MPMS-XL Quantum Design SQUID magnetometer in a magnetic field of 5000 Oe.

Synthesis of Salt 4: At –30 °C, compound **3** (0.400 g, 0.002 mol) was added dropwise to a stirred solution of **2** (0.288 g, 0.002 mol) in MeCN (10 mL). The deep red reaction solution was slowly warmed to 20 °C. Then, Et₂O (10 mL) was condensed onto this solution at –196 °C, and the two-layered system was kept at 20 °C. When the mutual diffusion of the solvents ceased, the solvents were removed with a syringe. The solid was washed with THF and dried under vacuum. Salt **4** (0.440 g, 90% yield) was obtained as black plates (ruby in transmitted light). M.p. (sealed capillary) 105 °C (dec.). C₁₄H₂₄N₁₂S₄ (488.69): calcd. C 34.41, H 4.95, N 34.40, S 26.24; found C 34.59, H 4.74, N 34.29, S 26.40.

Crystallographic Analysis: The XRD data were collected with a Siemens P4 diffractometer using Mo-*K*_α ($\lambda = 71.073$ pm) radiation with a graphite monochromator. The structure of salt **4** 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] Salt **4**: C₁₄H₂₄N₁₂S₄; *M* = 488.69; monoclinic; *a* = 1543.6(3) pm; *b* = 926.8(2) pm; *c* = 1626.2(3) pm; β = 112.470(10)°; *V* = 2.1498(7) nm³; *T* = 173(2) K; space group, *C*2/*c*; *Z* = 4; $\rho_{\text{calcd.}}$ = 1.510 Mg m⁻³; $\mu(\text{Mo-}K_{\alpha})$ = 0.472 mm⁻¹; reflections measured, 5642; unique reflections, 2458 [*R*(int) = 0.0413]; no. of parameters, 141; *R*_{obs} = 0.0379; *wR*_{2obs} = 0.0933; $\Delta\rho_{\text{min,max}}$ = –0.242, 0.453; g.o.f. = 1.037.

CCDC-664270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Calculations: The electronic structure of the singlet and triplet states of the radical anion dimers was analyzed at the (U)B3LYP/6-31+G(d)^[15] and CASPT2/CASSCF/ANO-L^[16] levels of theory using the Gaussian03^[17] and MOLCAS^[18] programs, respectively. The experimental geometry of the radical anion dimers was used in both types of calculations. In the case of the CASSCF calculations, the geometry was slightly altered, so as to constrain the dimer to *D*_{2h} symmetry. The active space used in these calculations consisted of the 14 electrons on the 12 MOs.

Acknowledgments

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