DOI: 10.1002/ejic.200600220

Early Alkali Metal (Li, Na, K) and Tris(dimethylamino)sulfonium (TAS) Salts of [1,2,5]Thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl Radical Anion: Rational Syntheses, Structures and Magnetic Properties

Vladimir N. Ikorskii,[c] Irina G. Irtegova,[a] Enno Lork,[b] Alexander Yu. Makarov,[a] Ruediger Mews,*[b] Victor I. Ovcharenko,*[c] and Andrey V. Zibarev*[a,d]

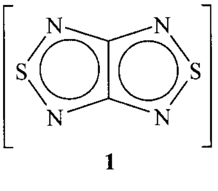
Keywords: Magnetic properties / Nitrogen heterocycles / Radical anions / Sulfur heterocycles

Salts of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**) and the early alkali metals, [Li(12-crown-4)$_2$][**1**] (**3**), [Na(15-crown-5)][**1**] (**4**), and [K(18-crown-6)][**1**] (**5**) as well as the salt [(Me$_2$N)$_3$S][**1**] (**6**) can be prepared by reduction of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) with PhS$^-$ anion followed by XRD and ESR characterization. These salts are thermally stable and soluble in MeCN. Low-temperature crystallization of salt **5** from MeCN or storage of **5** under MeCN for a few days at ambient temperature gives the solvate **5**·MeCN (**7**). The radical anion **1** acts as bridging ligand in salts **4** and **5** and as chelating ligand in salt **7**. In salt **3**, the radical anion **1** is not coordinated to the cation and can be considered as "naked" anion. In salt **6**, one of the two crystallographically independent **1** acts as bridging ligand, whilst the other is not coordinated to the cation. Magnetic susceptibility data obtained for salts **4** and **5** in the temperature range of 2–300 K revealed antiferromagnetic exchange interactions between paramagnetic centers: **4**, $J = -3.42$, $\alpha J = -1.12$ cm^{-1}; **5**, $J = -1.22$ cm^{-1}.

Introduction

The design, synthesis and investigation of new molecular materials, especially of conducting, superconducting, and magnetic materials, belong to the topical fields of current scientific and technological progress. Over the past two decades, there has been considerable interest in the syntheses, molecular and electronic structures, and physical properties of heterocyclic thiazyl radicals, neutral and charged, recognized as promising building blocks for new molecular magnets and/or molecular conductors.[1] Numerous neutral and positively charged heterocyclic thiazyl radicals (radical cations) have been carefully explored, while rather rare negatively charged systems (radical anions) have been less studied.[1] In this context, new preparative approaches to heterocyclic thiazyl radical anions are of obvious interest.

Recently, we have described the [K(18-crown-6)]$^+$ salt of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**, Scheme 1) and its solvate with MeCN that was unexpectedly isolated in low yield as a result of spontaneous decomposition of the [K(18-crown-6)] [PhXNSN] (X = S, Se) salts in MeCN solution.[2] Since the radical anion **1** might be of interest to material science as a building block for molecular ion-based conductors and/or magnets,[1] in this work we report on the rational preparation of the early alkali metal (Li, Na, K) and tris(dimethylamino)sulfonium (TAS) salts of the radical ion **1** based on the reduction of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) with the PhS$^-$ anion. The salts were isolated in high yields, in the case of the alkali metals as complexes with the corresponding crown ethers (12-crown-4, 15-crown-5, and 18-crown-6), followed by XRD and ESR characterization as well as measurements of magnetic susceptibility in the temperature range of 2–300 K.


1

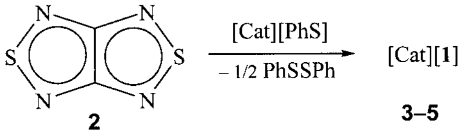
Scheme 1.

---

[a] Institute of Organic Chemistry, Russian Academy of Sciences,
630090 Novosibirsk, Russia
Fax: +7-383-330-9752
E-mail: zibarev@nioch.nsc.ru
[b] Institute for Inorganic and Physical Chemistry, University of Bremen,
28334 Bremen, Germany
Fax: +49-421-218-4267
E-mail: mews@chemie.uni-bremen.de
[c] International Tomography Center, Russian Academy of Sciences,
630090 Novosibirsk, Russia
Fax: +7-383-333-1399
E-mail: Victor.Ovcharenko@tomo.nsc.ru
[d] Department of Physics, Novosibirsk State University,
630090 Novosibirsk, Russia

Results and Discussion

In this work, salts of the radical anion **1** and the early alkali metals, [Li(12-crown-4)$_2$][**1**] (**3**), [Na(15-crown-5)][**1**] (**4**), and [K(18-crown-6)][**1**] (**5**), were prepared in a rational way by reduction of compound **2** with the PhS$^-$ anion in MeCN solution (Scheme 2). The corresponding PhSM thiolates (M = Li, Na, K) were used as a source of the PhS$^-$ anion.



2

3–5

[Cat] = [Li(12-crown-4)$_2$]$^+$ (**3**), [Na(15-crown-5)]$^+$ (**4**), [K(18-crown-6)]$^+$ (**5**)

Scheme 2.

For the in situ generation of the PhS$^-$ anion the desilylation of the Ph–S–SiMe$_3$ precursor was employed (Scheme 3). This approach allows to prepare salts of **1** not only with alkali metal cations, for example [K(18-crown-6)], but also with other cations including organic ones, for example the tris(dimethylamino)sulfonium (TAS) salt **6**.

The salts obtained were characterized by XRD (Table 3, Figure 1) and ESR (Figure 2) (for **5** XRD and ESR data were published before).[2] In MeCN solution for all salts the hfc constant $a(^{14}\mathrm{N}\times 4)$ = 0.314 mT, and g = 2.0045, are in accordance with previous measurements.[2]

Low-temperature crystallization of salt **5** from MeCN, or storage of **5** under MeCN for a few days at ambient temperature, gives the solvate **5**·MeCN (**7**, XRD and ESR data were published earlier).[2] In the case of **3** and **4**, under the same conditions only the initial salts are recovered, no inclusion of the MeCN solvent into the crystal lattices is observed. Transformation of **5** into **7** is reversible, and crystallization of **7** from boiling MeCN leads to **5**. The procedure can be repeated at least 3 times.

The salts **3**–**7** are thermally stable and soluble in MeCN. When protected from air, the salts **3**–**7** are stable in the crystalline state for several months, and in MeCN solution for several weeks, at least (under electrochemical conditions, a half-life time of **1** in MeCN solution was estimated as 74.5 s on the basis of the ESR data).[2] Upon contact with air, salts **3**–**7** decompose in both solid state and in solution. Among **3**–**7**, salt **3** is the most sensitive towards atmosphere.

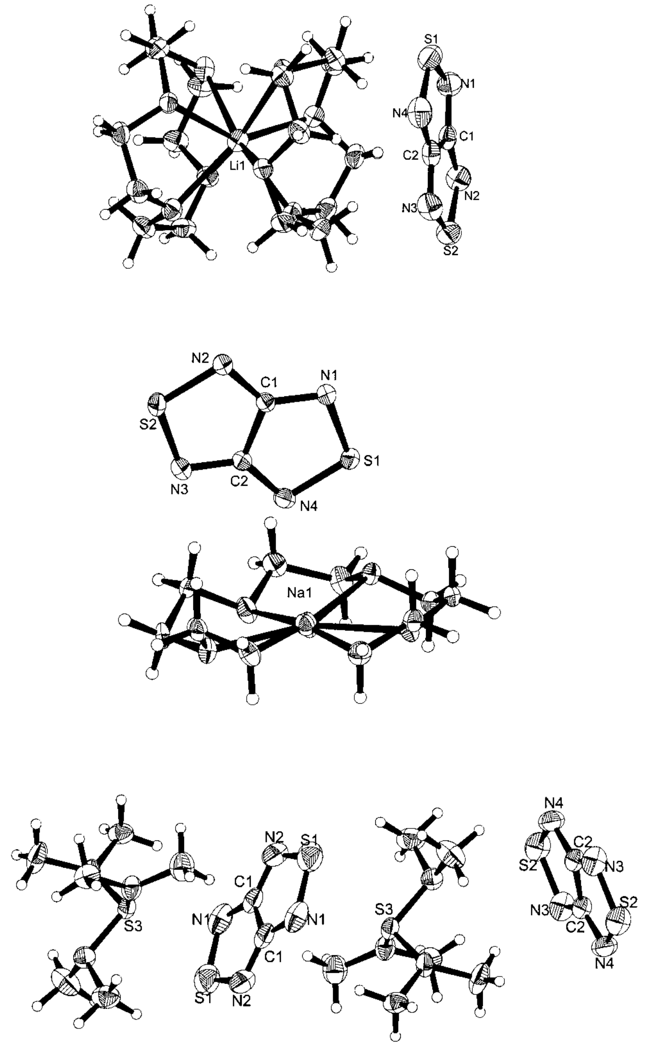
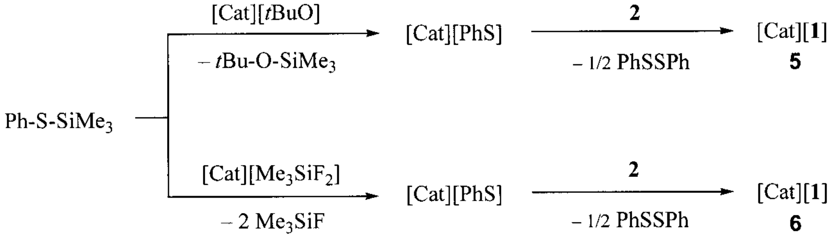


Figure 1. Structure of salts **3** (top), **4** (middle), and **6** (bottom). Crystallographic atom numbering is used; for selected bond lengths and bond angles, see Table 1.

It is known that the crystal packing of neutral thiazyl radicals (revealed general tendency to polymorphism)[1b,3] is crucial for their macroscopic magnetic properties.[1b] The crystal packing of salts **3**–**7** is different. The radical anion **1** acts as bridging ligand in salts **4** (Figure 3) and **5**,[2] and



[Cat] = [K(18-crown-6)]$^+$ (**5**); [(Me$_2$N)$_3$S]$^+$ (**6**)

Scheme 3.

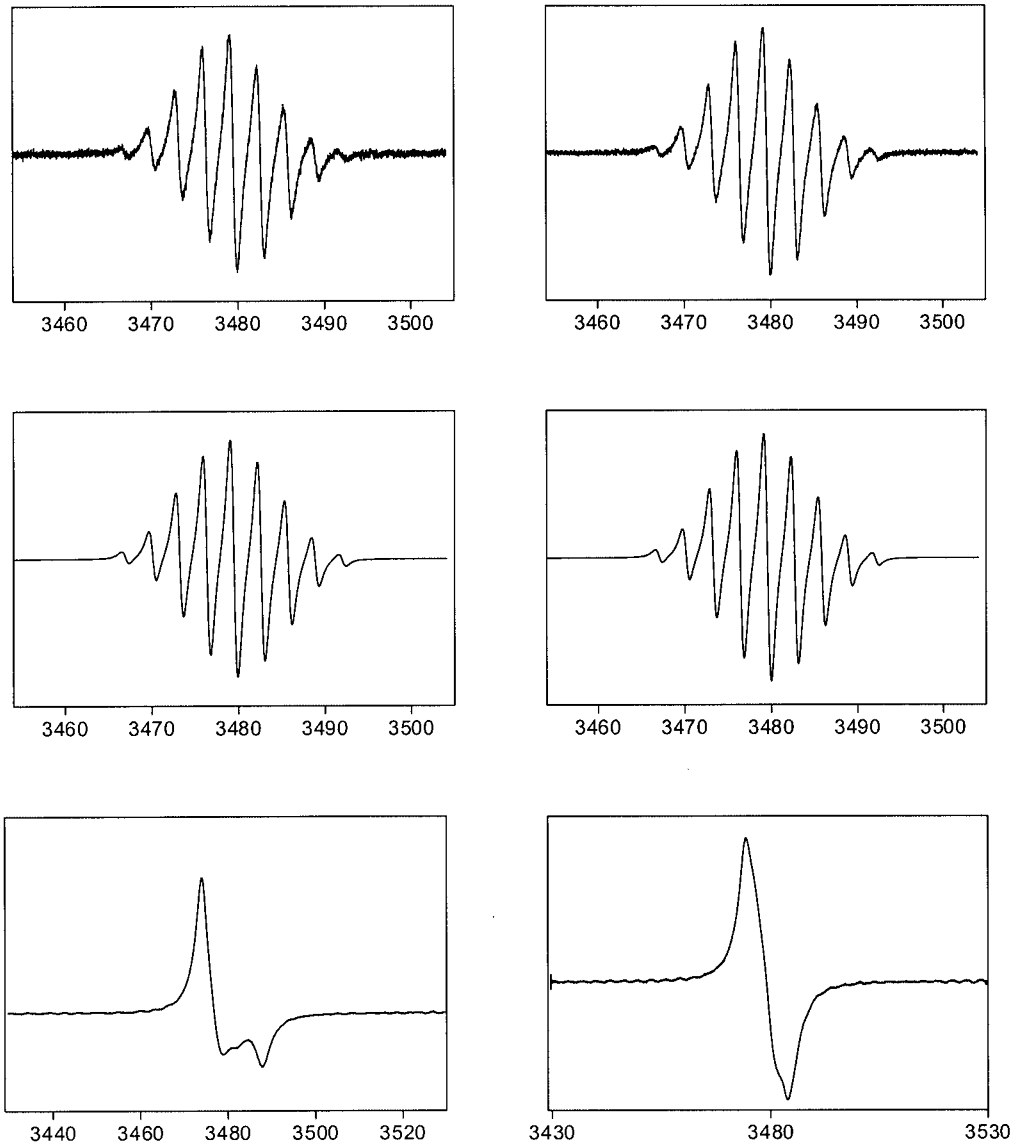


Figure 2. ESR spectra (|H| 10^4 T^{-1}). Salt **4** (left column): experimental in MeCN solution (top), simulated for solution (middle), and experimental in crystalline state (bottom). Salt **6** (right column): experimental in MeCN solution (top), simulated for solution (middle), and experimental in crystalline state (bottom).

as chelating ligand in salt **7**.[2] In contrast to salt **5** where **1** coordinates two cations symmetrically with N···K contacts of 288.5 pm, in salt **4** the bridging anion **1** coordinates the cations non-symmetrically via N···Na contacts of 251.1 and 283.7 pm, respectively. By these alternating contacts chains are formed along the crystallographic axis *b* (Figure 3).

In salt **3** the radical anion **1** is not coordinated to the Li cation (encapsulated in 2 crown ether molecules, Figure 4) and can be considered as "naked" anion. In salt **6** one of the two crystallographycally independent radical anions **1** acts as bridging ligand via S···S contacts of 361.2 pm, whilst the other is not coordinated to the cation (Figure 5).

Probably, the lack of stabilizing anion-cation interaction leads to the enhanced instability of salt **3** towards atmo-

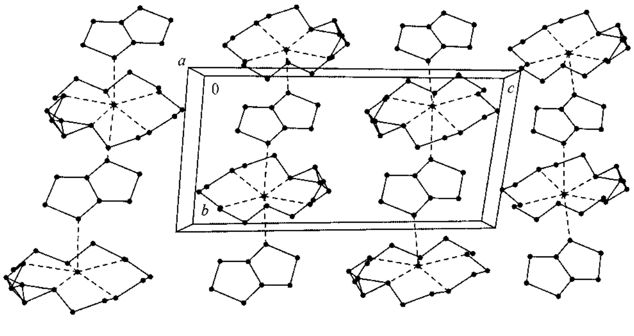


Figure 3. Crystal packing of salt **4** (dashed lines indicate shortened contacts).

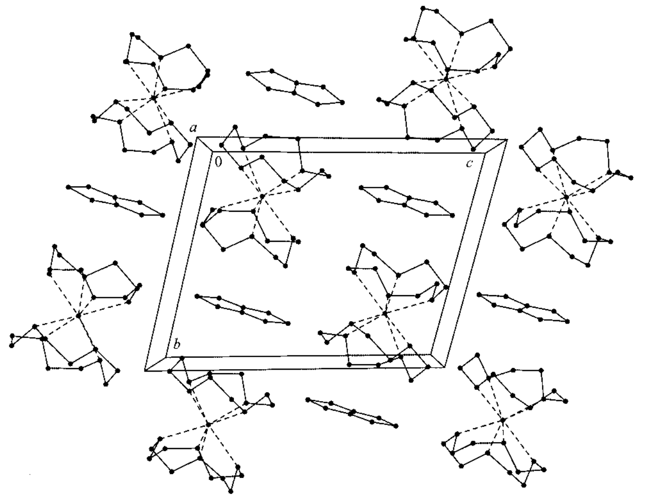


Figure 4. Crystal packing of salt **3** (dashed lines indicate shortened contacts).

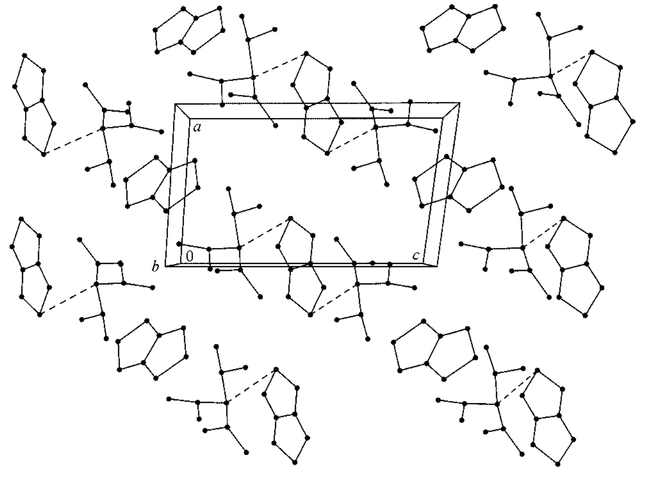


Figure 5. Crystal packing of salt **6** (dashed lines indicate shortened contacts).

sphere as compared with the other alkali metal salts **4**, **5**, and **7**. It should be noted, that the coordination chemistry of thiazyl radicals, both neutral and charged, is still in its infancy.[4]

Molecular geometry data of the radical anion **1** in salts **3**, **4**, and **6** are presented in Table 1 (data for salts **5** and **7** were published earlier).[2] Effects of the coordination of the radical anion **1** to the different cations on its geometry are rather minor.

Attempts to prepare salts with enlarged spin (negative charge) delocalization, for instance [Na(15-crown-5)][**1**][**2**] and [K(18-crown-6)][**1**][**2**], by low-temperature 1:1 co-crystallizations of salts **4** and **5** with the neutral precursor **2** were unsuccessful. The initial compounds were recovered.

The data of magnetic measurements for **4** and **5** are presented in Figure 6. For **4**, temperature dependence of magnetic susceptibility χ shows the maximum at 8 K. This is indicative of exchange coupling of radical anion clusters with even number of paramagnetic centers. For **5**, χ increases steadily with temperature lowering.

Table 1. Molecular geometry of **1** in salts **3**, **4**, and **6**.[a]

Bond [pm]/angle [°]	**3**	**4**	**6**[b]
N1–S2	165.95(16)	165.99(2)	164.6(10), 166.1(9)
S2–N3	166.35(15)	166.5(2)	166.0(10), 166.3(9)
N3–C3a	133.61(19)	134.3(2)	132.6(12), 133.7(11)
C3a–N4	133.8(2)	134.2(2)	130.7(13), 134.8(11)
N4–S5	165.97(14)	166.1(2)	164.6(10), 166.1(9)
S5–N6	166.30(16)	166.73(19)	166.0(10), 166.3(9)
N6–C6a	133.8(2)	134.4(3)	132.6(12), 133.7(11)
C6a–N1	133.5(2)	134.4(3)	130.7(13), 134.8(11)
C3a–C6a	145.39(18)	145.6(3)	145.5(18), 144.2(17)
C6a–N1–S2	104.84(10)	104.96(14)	106.3(7), 103.8(6)
N1–S2–N3	101.27(7)	101.43(9)	99.8(5), 102.1(4)
S2–N3–C3a	104.54(10)	104.47(14)	105.6(7), 103.3(6)
C3a–N4–S5	104.72(9)	104.98(15)	106.3(7), 103.8(6)
N4–S5–N6	101.30(7)	101.28(10)	99.8(5), 102.1(4)
S5–N6–C6a	104.70(10)	104.56(14)	105.6(7), 103.6(6)
N1–C6a–C3a	114.55(14)	114.23(18)	114.5(12), 114.7(10)
C6a–C3a–N3	114.81(13)	114.91(18)	113.7(14), 115.6(10)
N4–C3a–C6a	114.67(13)	114.47(18)	114.5(12), 114.7(10)
N6–C6a–C3a	114.60(14)	114.70(18)	113.7(12), 115.6(10)

[a] Systematic atom numbering is used. [b] Two crystallographically independent molecules.

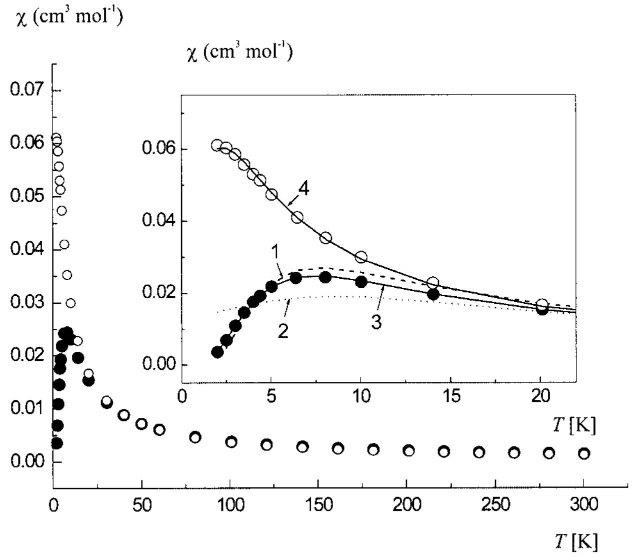


Figure 6. Dependence χ(T) in the temperature ranges of 2–300 K and 2–20 K (insert) for **4** (black circles) and **5** (white circles). Theoretical curves (models) 1 (i), 2 (ii), 3 (iii) and 4 (ii) described in the text.

As mentioned above, crystal packing of **4** and **5** reveals linear chains formed by the N···M (**4**, M = Na; **5**, M = K) contacts, alternating for **4** (251.1 and 283.7 pm) and non-alternating for **5** (288.5 pm). To estimate the energy of exchange interaction J between paramagnetic centers, analytical and numerical expressions of three different models were used, namely: i) the model of dimers,[5] $H = -2JS_1S_2$; ii) the Bonner–Fisher uniform chain model[6] with exchange parameters J equal along the chain, $H = -2J\Sigma S_iS_{i+1}$; and iii) the alternating chain model[6] with exchange parameters J and αJ alternated along the chain, $H = -2J\Sigma(S_{2i}S_{2i-1} + \alpha \cdot S_{2i}S_{2i+1})$. The optimized model parameters are given in Table 2. It is seen that the experimental data (Figure 6, insert) are best fitted by the alternating chain model (iii) in the case of **4**, and by the Bonner–Fisher model (ii) in the case of **5** (Table 2), in both cases in accordance with the discussed features of the crystal packing. Corresponding theoretical curves are shown in Figure 6 (insert). Thus, despite long distances between radical anions **1** in the crystal lattices of salts **4** and **5**, weak antiferromagnetic exchange interactions are observed.

Table 2. Optimal parameters in modeling exchange interactions.

Compound	Model	*g* factor	*J* [cm^{-1}]	–*aJ* [cm^{-1}]	R^2
	i	2.0(1)	4.06(3)		0.9929
4	ii	2.2(2)	4.9(8)		0.8159
	iii	2.003(7)	3.46(2)	1.12(2)	0.9991
5	ii	1.98(1)	1.22(2)		0.9997

One can conclude that even minor changes in the packing observed in going from **4** (this work) to **5**[2] affect the macroscopic magnetic properties of these salts. Overall, the crystal packing of the salts of the radical anion **1** seems to be important for their magnetic behavior.

Conclusions

Early alkali metal (Li, Na, K) and tris(dimethylamino)-sulfonium (TAS) salts of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]-thiadiazolidyl radical anion are prepared in a rational way by chemical reduction of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole with the PhS$^-$ anion. The salts, in the case of the alkali metals isolated in the form of complexes with the corresponding crown ethers (12-crown-4, 15-crown-5, and 18-crown-6), are characterized by XRD and ESR. Magnetic measurements confirmed the presence of unpaired electrons in the solids. The temperature dependence of the magnetic susceptibility χ indicates antiferromagnetic interactions in the solid state.

The salts prepared, which are thermally stable and soluble in MeCN, might be suitable starting materials (sources of the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion) in the synthesis of new molecular magnets and/or molecular conductors. The synthetic route based on Ph–S–SiMe$_3$ can obviously be generalized to preparation of salts of **1** with transition metal cations (including paramagnetic ones) since the chemistry of metal alkoxides (especially *tert*-butoxides) is well-developed.[7] On the other hand this approach can be expanded to many other π-heterocycles, especially nitrogen ones, possessing high electron affinity and forming stable radical anions.[1g]

Experimental Section

General: Compound **2** was prepared as described earlier.[2] The syntheses described below were performed with exclusion of oxygen in absolutely dry solvents by using a glove box and standard vacuum line techniques. The pressure was normalized with argon where necessary. The GC-MS measurements were performed with a Hewlett–Packard G1800A GCD device for solutions in CH$_2$Cl$_2$. The ESR measurements were carried out with a Bruker ESP-300 spectrometer (MW power 265 mW, modulation frequency 100 kHz, modulation amplitude 0.005 mT), under anaerobic conditions. The spectral integration and simulation were performed with the Winsim 32 program. The *g* factors were measured using an MnO standard with an accuracy of ±0.0002. Magnetic measurements were carried out on an MPMS-5S Quantum Design SQUID magnetometer in the temperature range of 2–300 K in a magnetic field of 5000 Oe. The molar magnetic susceptibility χ was calculated using corrections for the diamagnetism equal to $-207 \cdot 10^{-6}$ cm^3 mol^{-1} (for **4**) and $-243 \cdot 10^{-6}$ cm^3 mol^{-1} (for **5**).

Crystallographic Analysis: The data collection for the single-crystal structure determinations (Table 3) were carried out on a Bruker P4 diffractometer with graphite-monochromated Mo-K_α (71.073 pm) radiation. The structures were solved by direct methods by use of the SHELXS-97 program[8] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation by use of the SHELXL-97 program.[8]

CCDC-293646 (for **3**), -293645 (for **4**), and -293647 (for **6**) 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. For **5** and **7**, the data obtained in this work are in full agreement with those published previously.[2]

Syntheses of Salts 3–5: At –30 °C, a mixture of 0.144 g (0.001 mol) of **2**, 0.001 mol of PhSM (M = Li, Na, or K) and 0.001 mol (0.002 mol in the case of Li) of the corresponding crown ether was dissolved in 10 mL of MeCN. The wine-red solutions were warmed to 20 °C, stirred for 1 h, and filtered. The solvent was distilled off under reduced pressure, the residue washed with 10 mL of Et$_2$O, and dissolved in 5 mL of boiling MeCN under normal pressure. The solution was filtered and cooled to 20 °C in the case of salt **5**, or to –10 °C in the case of salt **4**. In the case of salt **3**, 10 mL of Et$_2$O were recondensed onto the filtrate at –196 °C and the two-layered system was placed into cryostat at –40 °C. The solvent was removed with a syringe, and the crystals were washed with 10 mL of Et$_2$O and dried in vacuo.

Salt **3** forms transparent red plates, yield 0.327 g (65%), m.p. (sealed capillary) 98 °C (dec.).

Salt **4** forms transparent red plates, yield 0.310 g (80%), m.p. (sealed capillary) 100 °C (dec.). $C_{12}H_{20}N_4NaO_5S_2$ (387.44): calcd. C 37.20, H 5.20, N 14.46, S 16.55; found C 37.37, H 5.12, N 14.38, S 16.36.

Salt **5** forms transparent ruby plates, yield 0.335 g (75%), m.p. (sealed capillary) 135 °C (dec.). $C_{14}H_{24}KN_4O_6S_2$ (447.64): calcd. C 37.57, H 5.40, N 12.52, S 14.33; found C 37.42, H 5.28, N 12.61, S 14.22.

In each case evaporation of the initially obtained Et$_2$O solutions gave PhSSPh (95–98%) identified by GC-MS technique via comparison with an authentic sample.

At –30 °C, a solution of 0.182 g (0.001 mol) of Ph–S–SiMe$_3$[9] in 2 mL of THF was added to a solution of 0.376 g (0.001 mol) of [K(18-crown-6)][*t*BuO][10] in 5 mL of the same solvent. The solution was warmed to 20 °C, stirred for 1 h, and the solvent was distilled off under vacuum to give a white crystalline residue. Compound **2** (0.144 g; 0.001 mol) and 10 mL of MeCN were added at –30 °C, and the wine-red solution obtained was warmed to 20 °C, stirred for 1 h, filtered and the solvents evaporated under vacuum. The residue was washed with 10 mL of Et$_2$O, dissolved in 5 mL of boiling MeCN under normal pressure, and the solution was cooled to 20 °C. The solvent was removed with a syringe, and the crystals were washed with 10 mL of Et$_2$O and dried in vacuo.

Table 3. Crystal data and structure refinement for salts **3**, **4**, and **6**.

Compound	3	4	6
Empirical formula	$C_{18}H_{32}LiN_4O_8S_2$	$C_{12}H_{20}N_4NaO_5S_2$	$C_8H_{18}N_7S_3$
Formula weight	503.54	387.43	308.47
Temperature [K]	173(2)	173(2)	173(2)
Wavelength [pm]	71.073	71.073	71.073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions *a* [pm]	837.20(10)	750.7(2)	785.6(12)
b [pm]	1088.7(2)	808.6(2)	804.2(9)
c [pm]	1370.2(2)	1536.2(6)	1253.3(12)
α [°]	102.370(10)	92.17(2)	87.51(5)
β [°]	96.120(10)	101.13(3)	83.68(8)
γ [°]	102.370(10)	112.05(2)	67.52(10)
Volume [nm^3]	1.1762(3)	0.8418(4)	0.7272(15)
Z	2	2	2
Density (calcd.) [Mg·m^{-3}]	1.422	1.529	1.409
Abs. coefficient [mm^{-1}]	0.277	0.373	0.505
F(000)	534	406	326
Crystal size [mm^3]	0.90×0.70×0.40	0.80×0.30×0.15	0.50×0.20×0.10
θ range for data collection [°]	2.52 to 27.50	2.72 to 27.50	2.82 to 22.51
Index range	$-10 \le h \le 1$, $-13 \le k \le 13$, $-17 \le l \le 17$	$-1 \le h \le 9$, $-10 \le k \le 10$, $-19 \le l \le 19$	$-1 \le h \le 8$, $-8 \le k \le 8$, $-13 \le l \le 13$
Reflections collected	6527	4829	2417
Independent reflections	5336 [*R*(int) = 0.0370]	3870 [*R*(int) = 0.0281]	1880 [*R*(int) = 0.0399]
Completeness to θ° [%]	98.9	99.9	98.4
Absorption correction	nNone	none	none
Max. and min. transmission	0.8971 and 0.7883	0.9461 and 0.7544	0.9512 and 0.7863
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5336/0/300	3870/7/227	1880/0/170
Goodness-of-fit on F^2	1.043	1.032	1.168
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0383$, $wR2 = 0.1010$	$R1 = 0.0423$, $wR2 = 0.0979$	$R1 = 0.0776$, $wR2 = 0.2067$
R indices (all data)	$R1 = 0.0432$, $wR2 = 0.1051$	$R1 = 0.0619$, $wR2 = 0.1070$	$R1 = 0.1240$, $wR2 = 0.2303$
Largest diff. peak/hole [eÅ^3]	0.396/–0.426	0.421/–0.471	0.483/–0.448

Salt **5** forms transparent ruby plates, yield 0.402 g (90%), m.p. (sealed capillary) 135 °C (dec.).

Evaporation of the initially obtained Et_2O solution gave PhSSPh (97%) identified by GC-MS technique via comparison with an authentic sample.

Synthesis of Salt 6: At –30 °C, a solution of 0.182 g (0.001 mol) of Ph–S–$SiMe_3$[9] in 1 mL of MeCN was added to a solution of 0.275 g (0.001 mol) of $[(Me_2N)_3S][Me_3SiF_2]$ (TASF)[11] in 5 mL of the same solvent. The solution was warmed to 20 °C, stirred for 1 h, and the solvent was distilled off under vacuum to give a white crystalline residue. A solution of 0.144 g (0.001 mol) of **2** in 10 mL of MeCN was added at –30 °C, the wine-red reaction mixture was warmed to 20 °C, stirred for 1 h, filtered and the solvents evaporated under vacuum. The residue was washed with 10 mL of Et_2O and dissolved in 5 mL of MeCN. Then 10 mL of Et_2O were recondensed onto the solution at –196 °C and the two-layered system was placed into cryostat at –40 °C. The solvent was removed with a syringe, and the crystals were washed with 10 mL of Et_2O and dried in vacuo.

Salt **6** forms transparent red needles, yield 0.230 g (75%), m.p. (sealed capillary) 92 °C (dec.). $C_8H_{18}N_7S_3$ (308.48): calcd. C 31.15, H 5.88, N 31.78, S 31.18; found C 31.30, H 5.74, N 31.85, S 31.06.

The PhSSPh by-product (95%) was identified as described above.

Preparation of Salt 7: Upon storage under mother liquor for a few days at ambient temperature, salt **5**, crystallized as described above, transformed slowly into salt **6** (ruby crystals turned to dark-brown). The solvent was removed with a syringe, and the crystals were washed with 10 mL of Et_2O and dried under vacuum for a short time.

Salt **7** forms dark-brown prisms (orange in transmitting light), yield 0.333 g (65%), m.p. (sealed capillary) 125 °C (dec.).

At –196 °C, 10 mL of Et_2O were recondensed onto a solution of 0.224 g (0.5 mmol) of salt **5** into 5 mL of MeCN and the system was placed into a cryostat at –40 °C. The solvent was removed with a syringe, and the crystals of salt **7** (0.243 g, 95%) were washed with 10 mL of Et_2O and dried under vacuum for a short time.

Acknowledgments

The authors are grateful to Prof. Yuri V. Gatilov for valuable discussions, to Mr. Peter Brackmann for his assistance in the XRD experiments, and to the Deutsche Forschungsgemeinschaft, Germany (grant 436 RUS 113/486/0-3 R), the Russian Foundation for Basic Research, Russia (grants 02-03-04001 and 06-03-32742), and the Siberian Division of the Russian Academy of Sciences (interdisciplinary project N 25) for financial support of this work. A. M. and A. Z. thank the Council for the President of Russian Federation's Grants for Young Scientists and Their Supervisors (grant MK-3178.2005.3), and A. M. thanks the National Science Support Foundation, Russia, for a postdoctoral scholarship.

---

[1] a) T. Chivers, *A Guide to Chalcogen-Nitrogen Chemistry*, World Scientific: New Jersey e. a., **2005**, pp. 318; b) J. M. Rawson, J. Luzon, F. Palacio, *Coord. Chem. Rev.* **2005**, *249*, 2631–2641; c)

L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, R. T. Oakley, R. W. Reed, J. F. Richardson, R. A. Secco, X. Yu, *Chem. Commun.* **2005**, 5745–5747; d) T. S. Cameron, M. L. Lemaire, J. Passmore, J. M. Rawson, K. V. Shuvaev, L. T. Thompson, *Inorg. Chem.* **2005**, *44*, 2576–2578; e) L. Beer, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, R. T. Oakley, R. W. Reed, *Chem. Commun.* **2002**, 2562–2563; f) J. M. Rawson, F. Palacio, *Struct. Bonding (Berlin)* **2001**, *100*, 93–128; g) R. T. Boere, T. L. Roemmele, *Coord. Chem. Rev.* **2000**, *210*, 369–445; h) J. M. Rawson, G. D. McManus, *Coord. Chem. Rev.* **1999**, *189*, 135–168.

[2] A. Yu. Makarov, I. G. Irtegova, N. V. Vasilieva, I. Yu. Bagryanskaya, T. Borrmann, Yu. V. Gatilov, E. Lork, R. Mews, W.-D. Stohrer, A. V. Zibarev, *Inorg. Chem.* **2005**, *44*, 7194–7199.

[3] a) C. Knapp, E. Lork, K. Gupta, R. Mews, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1640–1644; b) A. Alberola, C. S. Clarke, D. A. Haynes, S. I. Pascu, J. M. Rawson, *Chem. Commun.* **2005**, 4726–4728.

[4] a) M. Jennings, K. E. Preuss, J. Wu, *Chem. Commun.* **2006**, 341–342; b) A. J. Banister, I. May, J. M. Rawson, J. N. B. Smith, *J. Organomet. Chem.* **1998**, *550*, 241–253; c) H. Bock, P. Haenel, R. Neidlein, *Phosphorus Sulfur* **1988**, *39*, 235–252.

[5] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**.

[6] W. E. Hatfield, *J. Appl. Phys.* **1981**, *52*, 1985–1990.

[7] D. C. Bradley, *Chem. Rev.* **1989**, *89*, 1317–1322.

[8] G. M. Sheldrick, *SHELX-97 – Programs for Crystal Structure Analysis (Release 97-2)*, Institute for Inorganic Chemistry, University of Göttingen, Göttingen, Germany.

[9] I. Ojima, M. Nihonyangi, T. Nagai, *J. Organomet. Chem.* **1973**, *50*, C26–28.

[10] T. Borrmann, E. Lork, R. Mews, M. M. Shakirov, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2004**, 2452–2458.

[11] W. J. Middleton, *Org. Synth.* **1985**, *64*, 221–224.

Received: March 10, 2006