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Reviews

Chalcogen-nitrogen π-heterocyclic radical anion salts: the synthesis and properties*

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The review concerns methods of synthesis, as well as the molecular, electronic, and crystal structures and the magnetic properties of a novel class of paramagnetic compounds, namely, chalcogen-nitrogen π-heterocyclic radical anion salts derived from 1,2,5-chalcogenadiazole.

Key words: nitrogen, radical anions, antiferromagnetic compounds, heterocycles, paramagnetic compounds, synthesis, salts, structure, chalcogens.

The design, synthesis, and research on the functional (conducting, superconducting, and magnetic) properties of novel molecular materials to a great extent underlie modern progress in electronics and spintronics. Neutral radicals and radical ions (the spin and (or) charge carriers) are often used as building blocks for such materials; interactions between them in solids form the desired macroscopic electrical and (or) magnetic properties.[1—14] The search for new types of building blocks is an important avenue of further research.

Interesting prospects are offered by chalcogen-nitrogen chemistry.[15,16] Recently, a variety of chalcogen-nitrogen π-heterocyclic radicals and radical cations (in the individual state or as ligands in coordination compounds) have been successfully used in the design of molecular conductors and magnets.[2,5,9,15—28] Chalcogen-nitrogen π-heterocyclic radical anions detected[29—34] by ESR spectroscopy since the mid-1960s were not used in the synthesis of functional materials because of the lack of methods for their isolation as stable salts. Recently, such methods have been reported.[35—42]

In this review, we briefly outline the methods of synthesis and the properties of a novel class of paramagnetic

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* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

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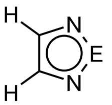
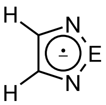
chemical compounds, namely, chalcogen-nitrogen π-heterocyclic radical anion salts derived from 1,2,5-chalcogenadiazole bearing six π-electrons. A distinctive feature of this class of compounds is that the anion includes a negatively charged 1,2,5-chalcogenadiazole fragment with seven π-electrons and a spin S of 1/2. No restrictions are imposed on the cation.



6π (S = 0)



7π (S = 1/2)

E = S, Se, Te

Molecular design of precursors of radical anions

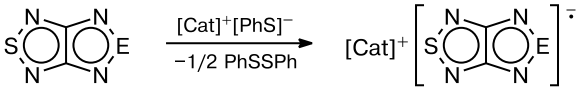
An important feature of 1,2,5-chalcogenadiazoles is associated with their positive electron affinity values. As a consequence, radical anions are more thermodynamically stable than neutral molecules; this creates prerequisites for their isolation as salts despite the *a priori* kinetic activity of the radical species. The first adiabatic electron affinity values of 1,2,5-chalcogenadiazoles noticeably vary depending on the chemical composition and molecular structure. The structures of the 1,2,5-chalcogenadiazoles **1**—**16** and the electron affinity values (in eV, numbers in parentheses) calculated for them by the (U)B3LYP/6-31+G(d) method using Def2-SVP with ECP as the basis set for Te are presented below. Note that calculations by the same method predict for the electron affinity of tetracyanoethylene, one of the strongest organic acceptors, a value of 3.48 eV.

In isostructural series, the electron affinity values increase with the atomic number of chalcogen, from S to Se and then to Te. They also depend on the nature of substituents in the 1,2,5-chalcogenadiazole ring and on the character of annelation of this ring to other carbo- and (or) heterocycles. Thus, there are great prospects for the molecular design of precursors of the target radical anions, which takes into account the properties of different reducing agents. The most promising are molecules containing at most three rings. This is required for the spin density on the atoms of the target radical anions to be not too low (a necessary condition for efficient exchange interaction between paramagnetic centers in the crystals of their salts).[35]

The synthesis and crystal structure of radical anion salts

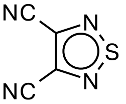
1,2,5-Chalcogenadiazoles were transformed to radical anion salts using various reducing agents.[35—42] Heterocycles **4** and **5** were reduced with thiophenolate anion[37,38] (Scheme 1). This approach made it possible to obtain homospin radical anion salts with diamagnetic cations (Li^+, Na^+, K^+) encapsulated into corresponding crown ethers as well as the salt with $(Me_2N)_3S^+$ (see Scheme 1). The structures of all salts were confirmed by X-ray analysis (examples are presented in Fig. 1) and the paramagnetic

Scheme 1



4, **5**

4: E = S, [Cat]$^+$ = [Li(12-crown-4)$_2$]$^+$, [Na(15-crown-5)]$^+$, [K(18-crown-6)]$^+$, [K(18-crown-6)(MeCN)]$^+$, [(Me$_2$N)$_3$S]$^+$
5: E = Se, [Cat]$^+$ = [K(18-crown-6)]$^+$



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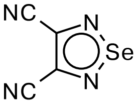

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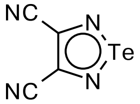

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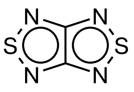

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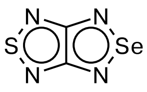

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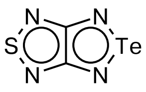

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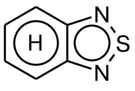

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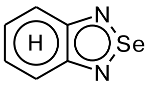

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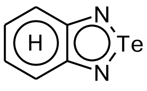

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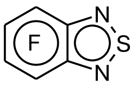

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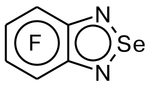
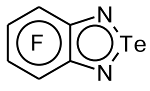


11 (1.67)



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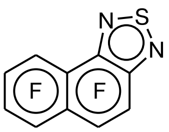

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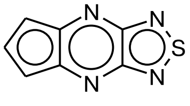

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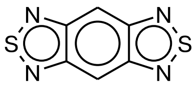
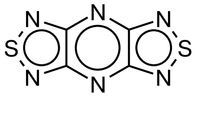


15 (2.26)



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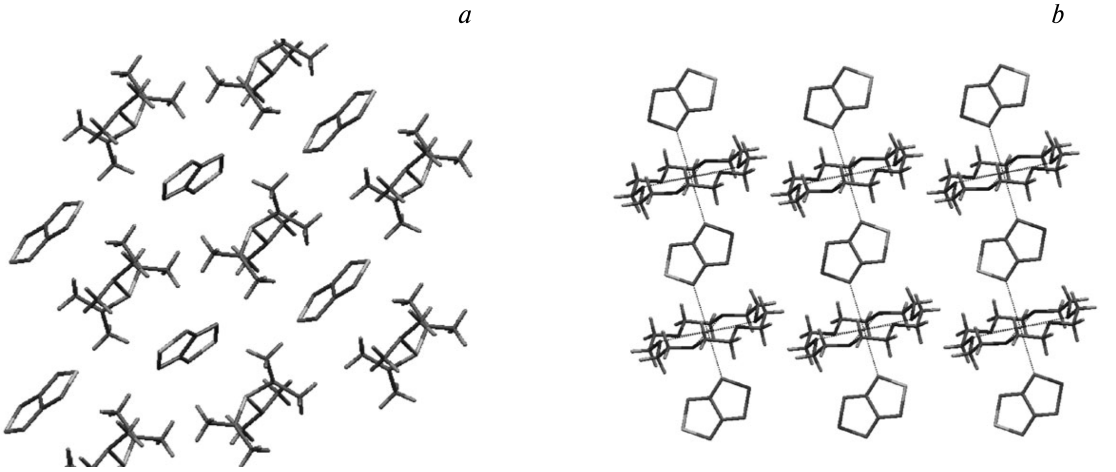


Fig. 1. Crystal structures of radical anion salts $[(Me_2N)_3S][\mathbf{4}]$ (*a*) and $[K(18\text{-crown-}6)][\mathbf{5}]$ (*b*) obtained by reduction of heterocycles **4** and **5** with thiophenolate anion.

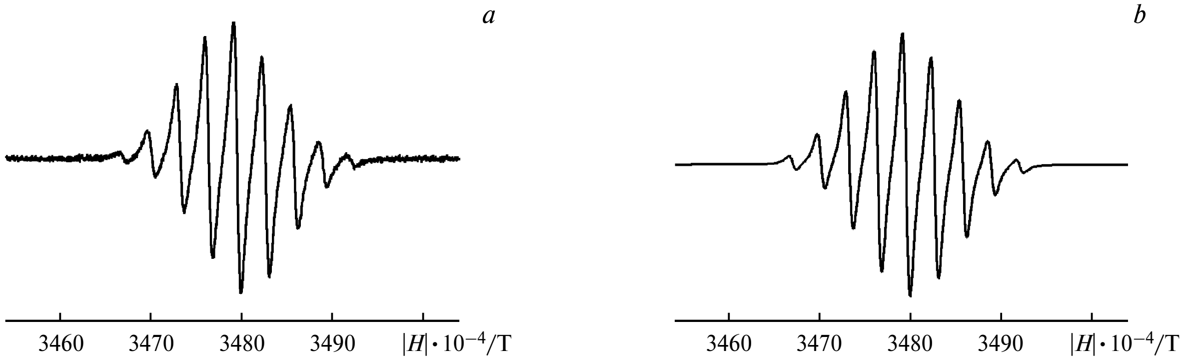
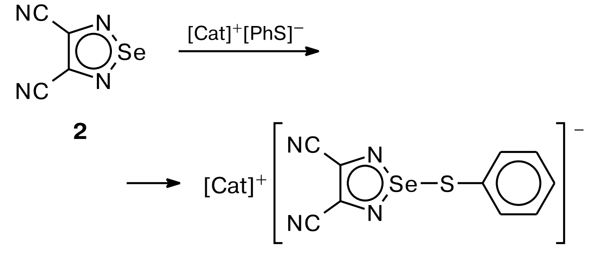


Fig. 2. Experimental (*a*) and simulated (*b*) ESR spectra of the radical anions of heterocycle **4** in MeCN at room temperature; a_N/mT = 0.314/0.238 (experiment/UB3LYP/6-311+G(d) calculations), g = 2.0045.

character of the salts was verified by ESR studies in solids and in solution (Fig. 2). A comparison of the experimental geometric parameters shows that on going from heterocycle **4** to its radical anion the S—N and C—C distances somewhat lengthen while the C—N distances and the N—S—N angle remain unchanged. According to DFT calculations, these effects can be explained by the structure of the half-filled π-MO of the radical anion (see below). The experimental HFI constants determined from the ESR spectra in solution are in good agreement with the results of UB3LYP calculations.[36—38]

However, this method has a limited potential. Namely, thiophenolate ion does not react with compounds **1** and **7**. Also, the reaction with heterocycle **2** gave a product of its hypercoordination at the Se center (Scheme 2); the structure of the product was confirmed by X-ray analysis (Fig. 3).[43] This type of reactivity was never observed earlier for 1,2,5-chalcogenadiazoles. The results obtained from quantum chemical calculations of the thermodynamic and kinetic characteristics of the reactions of some 1,2,5-chalcogenadiazoles with thiophenolate ion (see Schemes 1 and 2) in all cases agree with experimental data.[43] From the results of calculations it follows that the unusual addition observed is most probably the first example of a new type of reactions.

Scheme 2



$[Cat]^+ = [K(18\text{-crown-}6)]^+$

Reduction of heterocycle **4** with $(Me_2N)_2C{=}C(NMe_2)_2$ (TDAE) led to the radical anion salt of the corresponding dication (Scheme 3). According to X-ray analysis data

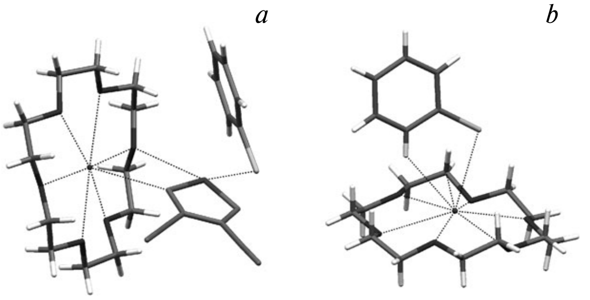
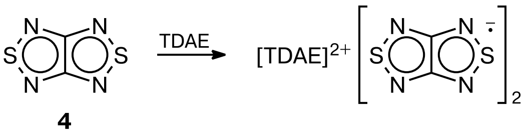


Fig. 3. Crystal structures of the product of the reaction of thiophenolate ion with heterocycle **2** (*a*) and [K(18-crown-6)]$^+$-[PhS]$^-$ (*b*).

(Fig. 4), in the crystal of this salt, radical anions form centrosymmetric π-dimers with an interplanar spacing of 3.25 Å, which is much smaller than the sum of the van der Waals radii of two sulfur atoms (3.60 Å). This homospin radical anion salt is ESR silent in the solid phase. However, the ESR spectrum of the radical anion of heterocycle **4** can be observed in solution because dissolution is accompanied by dissociation of π-dimers.**[39]**

Scheme 3



TDAE = $(Me_2N)_2C{=}C(NMe_2)_2$

Reduction of heterocycle **4** with the metallocenes $CoCp_2$ and $CrCp^*_2$ (Cp^* = η^5-C_5Me_5) resulted in the homospin radical anion salt (S = 1/2) and the first heterospin (S_1 = 1/2 and S_2 = 3/2) radical anion salt, respectively (Scheme 4). The structures of these salts were confirmed by X-ray analysis (Fig. 5). The radical anion salt $[CoCp_2][$**4**$]$ exhibits an ESR spectrum both in solution and in the solid state, whereas attempts to detect the ESR spectrum of the salt $[CrCp^*_2][$**4**$]$ failed in both cases.**[40,41]** This can be due to the properties of the cation $[CrCp^*_2]^+$, which is characterized by a large zero-field splitting and fast relaxation.**[44]** In solution, the salt $[CrCp^*_2][$**4**$]$ probably exists as an ion pair, which is characteristic of the radical anions in question.**[30,31,33]** This is most probably the reason for very fast relaxation of the radical anion, which precludes the detection of its ESR spectrum in solution. The effective magnetic moment of the salt at 300 K (4.27 μ_B) is close to the theoretically expected value (4.24 μ_B) for the system of randomly oriented uncorrelated spins S = 3/2 and S = 1/2 with g = 2.

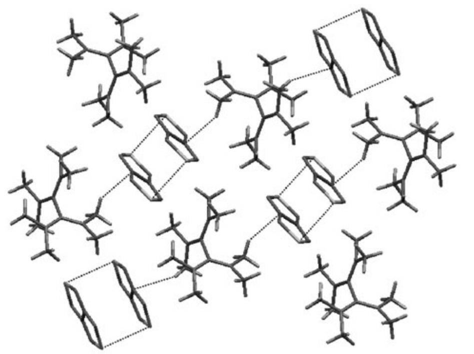


Fig. 4. Crystal structure of radical anion salt $[TDAE][$**4**$]_2$.

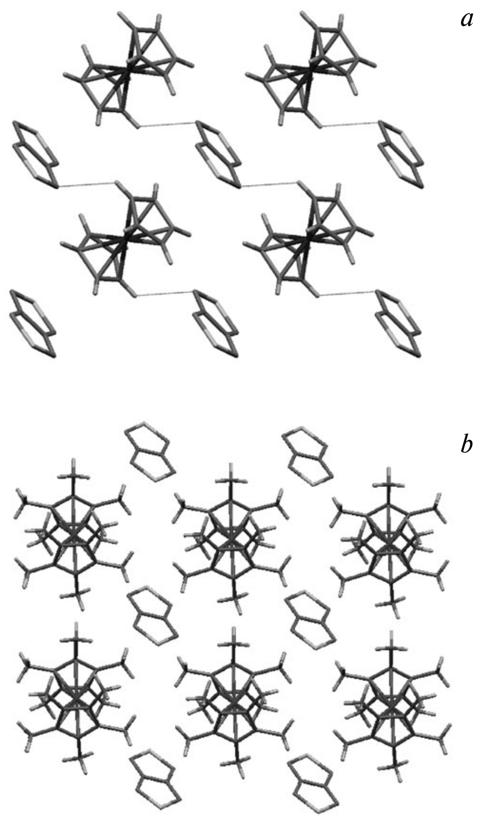
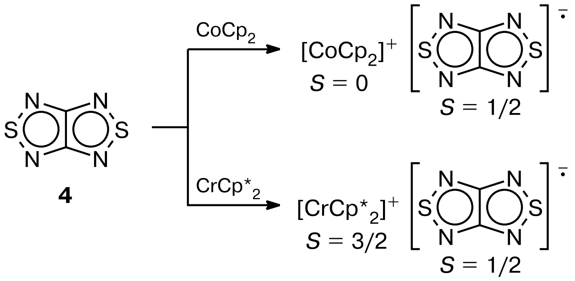


Fig. 5. Crystal structures of radical anion salts $[CoCp_2][$**4**$]$ (*a*) and $[CrCp^*_2][$**4**$]$ (*b*).

Scheme 4



Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5

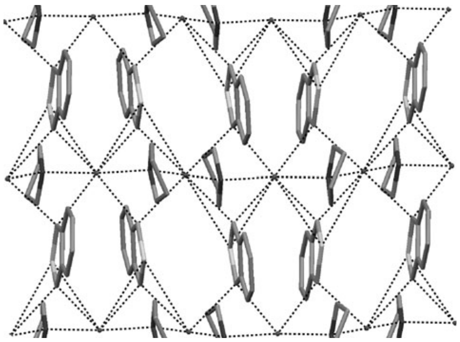
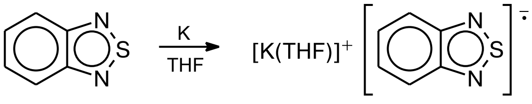


Fig. 6. Crystal structure of radical anion salt [K(THF)][**7**].

Heterocycle **7** was reduced with elemental potassium in THF (Scheme 5)[42] because thiophenolate ion appeared to be inappropriate in this case. The structure of the isolated radical anion salt [K(THF)][**7**] was confirmed by X-ray analysis (Fig. 6).

Scheme 5



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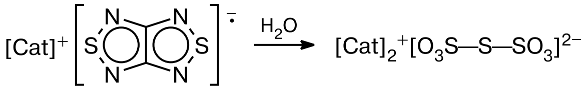
Promising precursors of the target radical anions include polyfluorinated derivatives (see structures **10**—**13**). Replacement of H atoms by fluorine atoms causes the electron affinity to increase. Unlike unstable polyfluoroarene (*e.g.*, octafluoronaphthalene) radical anions that rapidly lose the fluoride ion,[45] the electrochemically generated radical anions of compounds **10**, **11**, **13**, and their analogs appeared to be long-lived species (as follows from ESR data).[46] This creates prerequisites for isolation of the polyfluorinated radical anions as salts.

The radical anion salts synthesized are sensitive to atmospheric moisture and oxygen. However, their decomposition in air is not a fast process. Heterogeneous hydrolysis of crystalline radical anion salt [Na(15-crown-5)][**4**] with saturated water vapor at room temperature showed that it proceeds quite slowly and results in an unexpected product, a trithionate dianion salt (Scheme 6) whose structure was confirmed by X-ray analysis.[47]

Scheme 6



$[Cat]^+ = [Na(15\text{-crown-}5)]^+$

The electronic structure of radical anions and the magnetic properties of radical anion salts

The electronic structures of the radical anions produced were studied by the density functional and post-Hartree—Fock methods.[36,38—43,46,47] The results of all calculations confirmed the π-character of the radical anions. The half-filled π-MO of the radical anion of heterocycle **4** is antibonding with respect to the S—N bonds and nonbonding with respect to the C—N bonds (Fig. 7). This provides an explanation for the structural effects mentioned above, which accompany transformation of neutral molecule to the radical anion (elongation of the S—N and C—C bonds in the radical anion; the elongations of the C—C bonds offset those of the S—N bonds at the same angle N—S—N).

Multiconfiguration calculations by the CASSCF method predict an unusual electronic structure of π-dimers of radical anions for the salt [TDAE][**4**]$_2$ (see Fig. 4). It was found that the major contribution (~80%) to the wave function of the singlet ground state of the dimer comes from the electronic configuration with two electrons occupying the bonding MO composed of weakly interacting singly occupied MOs of the radical anions.[39] However, the contribution of the biradical component to this state is rather large (~20%).[39]

The theoretically predicted spin density distribution in the radical anions studied shows that the spin density on their van der Waals surfaces is mainly positive and there exist only small regions of negative spin density values (mainly in the vicinity of the C—C bond in the heterocycle (Fig. 8)).[41,46] Thus, contacts between the same-sign spin density regions are most probable for adjacent paramagnetic species in the crystals of homospin salts. This should lead to antiferromagnetic exchange interactions between radical anions.[48,49] If two paramagnetic species mainly contact each other in the regions with spin density of different sign, ferromagnetic interactions are possible.[48,49] In this context, the heterospin salt [CrCp*$_2$][**4**] characterized by extended regions with negative spin density on the van der Waals surface of the cation is of interest (see Fig. 8).[41]

The magnetic susceptibilities (χ) of the radical anion salts synthesized were studied in the temperature range

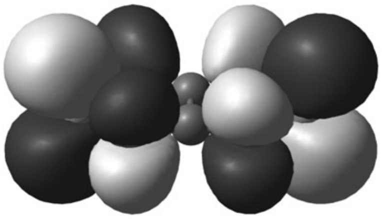


Fig. 7. Structure of the half-filled π-MO of the radical anion of heterocycle **4**.

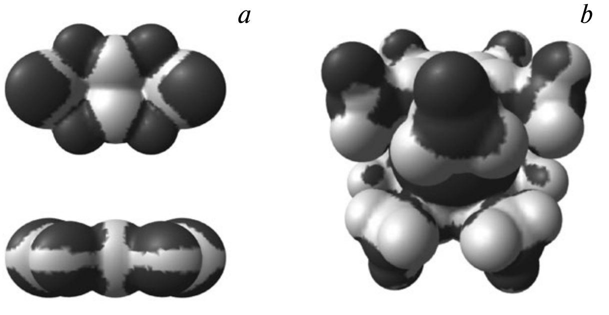


Fig. 8. Spin density (ρ) distributions over the van der Waals surface of the radical anion of heterocycle **4** (*a*) and cation $[CrCp^*{}_2]^+$ (*b*) obtained from UB3LYP/6-31+G(d) calculations: black regions correspond to $\rho > 0$ and gray regions correspond to $\rho < 0$.

from 2 to 300 K. The χ value of the homospin salt $[TDAE][\mathbf{4}]_2$ forming centrosymmetric π-dimers is temperature independent in the range 2—300 K, being equal to zero with allowance for the diamagnetic contributions.[39] The magnetic susceptibilities of other radical anion salts studied significantly increased on lowering the temperature; this is characteristic of paramagnetic compounds (Fig. 9). At very low temperatures (~10 K), the magnetic susceptibilities of some salts ([K(THF)][**7**] and $[CoCp_2][\mathbf{4}]$) reached maximum values at the Néel temperature and decreased on further lowering the temperature. A more clear qualitative idea of magnetic interactions between paramagnetic species in the sample can be obtained by analyzing the temperature dependence of the effective molar magnetic moment calculated from the equation[48]

$$\mu_{\mathrm{eff}} = \left(\frac{3k}{N\beta^2}\chi T\right)^{1/2} \approx (8\chi T)^{1/2}, \qquad (1)$$

where N is the Avogadro constant, β is the Bohr magneton, and k is the Boltzmann constant.

These dependences for some chalcogen-nitrogen radical anion salts are shown in Fig. 10. The μ_{eff} values of all salts studied monotonically increase with temperature, reach plateau regions at $T > 200$—250 K, and approach the theoretically expected value for the system of randomly oriented uncorrelated spins with $g \approx 2$, namely, $\mu_{\mathrm{eff}} = 1.73\ \mu_B$ for the homospin salts and $\mu_{\mathrm{eff}} = 4.24\ \mu_B$ for the heterospin salt $[CrCp^*{}_2][\mathbf{4}]$ (see Fig. 10). A considerable decrease in the effective magnetic moment at cryogenic temperatures observed for all salts under study suggests predominance of antiferromagnetic interactions between paramagnetic species. Modeling of the $\chi(T)$ dependences is required to determine the magnitude of such interactions.

On the molecular level, the magnetic properties of the radical anion salts studied are described by the phenomenological Heisenberg—Dirac—van Vleck isotropic spin Hamiltonian[48]

$$\hat{H} = -2\sum_{i,j}^{N} J_{ij}\hat{\vec{S}}_i\hat{\vec{S}}_j, \qquad (2)$$

where J_{ij} is the symmetric matrix of exchange coupling constants between the *i*th and *j*th species with the spins $\vec{S}_i$ and $\vec{S}_j$ respectively. Negative and positive J_{ij} values correspond to antiferromagnetic and ferromagnetic pairing, respectively. Knowledge of all exchange parameters J_{ij} allows one to determine the magnetic motif of the molecular magnet. For simple magnetic motifs, *e.g.*, a set of uniform ($J_{i,i+1} = J_{i-1,i} = J$) or alternating ($J_{i,i+1} = J, J_{i-1,i} = \alpha J$) infinite chains of radical centers, the phenomenological temperature dependences of the magnetic susceptibility are available;[50,51] they parametrically depend on J or α and J. For complex magnetic motifs characterized by a number of nonzero J_{ij} values, the experimental $\chi(T)$ dependence can be approximated by a theoretical temperature dependence calculated for a substance comprised of rather large clusters of particles. For such a cluster, one should diagonalize the matrix of the exchange Hamiltonian (see Eq. (2)) and determine the energy levels (E_n) of different states with the total spin S_n. The temperature dependence of the magnetic susceptibility of the substance composed of such clusters is described by the van Vleck formula

$$\chi = \frac{g^2\mu_B^2}{3kT}\left[\frac{\sum_n S_n(S_n+1)(2S_n+1)\exp\left(-\frac{E_n-E_0}{kT}\right)}{\sum_n (2S_n+1)\exp\left(-\frac{E_n-E_0}{kT}\right)}\right], \qquad (3)$$

where S_n and E_n are the spin and energy of the *n*th energy level of the cluster, respectively; g is the g-factor; μ_B is the Bohr magneton; k is the Boltzmann constant; and T is temperature. Thus, having known the parameters of the spin Hamiltonian, the $\chi(T)$ dependence can be calculated at least approximately.

Parameters of the spin Hamiltonian including the exchange parameters J_{ij} can be obtained from *ab initio* quantum chemical calculations.[38—42,49,54,55] The state of the art in computational methods, first of all, the density functional theory, allows the magnitude of exchange interaction to be calculated with reasonable accuracy even for paramagnetic species containing up to 100 atoms.

To determine the magnetic motifs of the radical anion salts studied, pair exchange interactions between radical anions (for homospin salts) and between radical anions, radical anions and chromocenium cations, and between chromocenium cations (for the heterospin salt) were calculated[38—42] for real crystal packings. Owing to the lattice symmetry and to the fact that exchange interactions exponentially decay with distance, the number of nonzero J_{ij} values is finite. To determine all of them, one should find all structurally unique pairs of paramagnetic species separated by at most 10 Å and carry out quantum chemical calculations of the energies of different spin states for each pair.

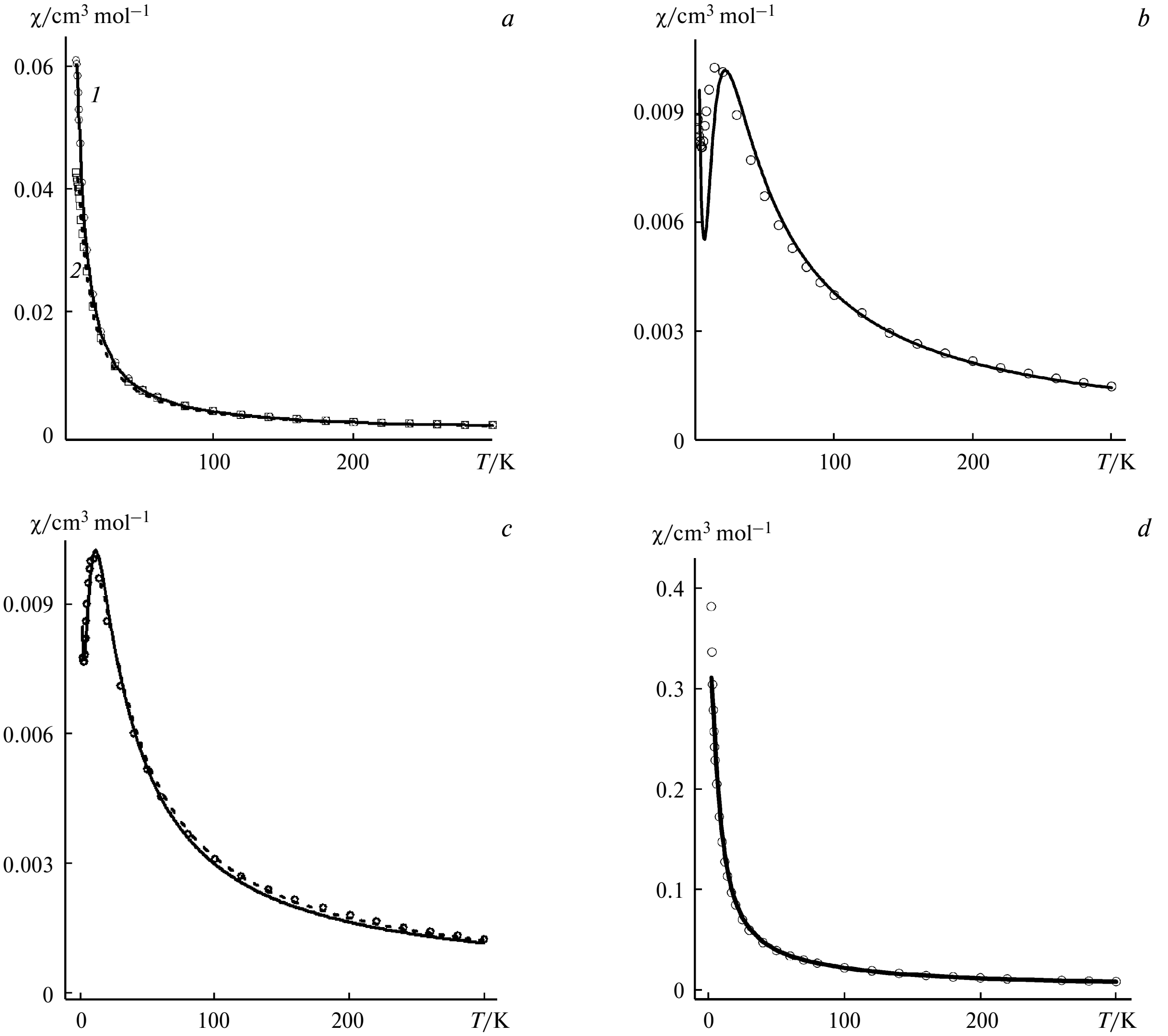


Fig. 9. Experimental temperature dependences of the molar magnetic susceptibility ($\chi(T)$) (circles) and their theoretical approximations (solid lines) for different radical anion salts: *a* — [K(18-crown-6)][**4**] (*1*) and [K(18-crown-6)][**5**] (*2*), $\chi(T)$ calculations using the Bonner—Fisher model[50,51] for uniform chains with $J = -1.22$ (*1*) and -1.65 cm^{-1} (*2*); *b* — [K(THF)][**7**], $\chi(T)$ calculations according to van Vleck[48] for a sample comprised of radical anion clusters of size [3×4] with closed boundary conditions; *c* — [CoCp$_2$][**4**], $\chi(T)$ calculations according to van Vleck[48] for a sample comprised of radical anion clusters of size [3×4] with closed boundary conditions (solid line) and using the Rushbrooke and Wood relation[52,53] for the 2D Heisenberg model (dashed line, $T > |J|/k$); *d* — [CrCp*$_2$][**4**], $\chi(T)$ calculations according to van Vleck[48] for a sample comprising antiferromagnetically coupled pairs of radical anions ($J_1 = -40$ cm^{-1}) and [CrCp*$_2$]$^+$...[CrCp*$_2$]$^+$ cations ($J_2 = -0.58$ cm^{-1}).

Most calculations of the parameters *J* were performed using the spin-unrestricted methods UB3LYP or UPBE0 withih the density functional theory. The parameter *J* was calculated from the equation

$$J_{ij} = -\frac{(E_{\mathrm{HS}} - E_{\mathrm{LS}}^{\mathrm{BS}})}{\left\langle S^2\right\rangle_{\mathrm{HS}} - \left\langle S^2\right\rangle_{\mathrm{LS}}^{\mathrm{BS}}}, \qquad (4)$$

where E_{HS} is the energy of the high-spin state of the pair ($S = S_1 + S_2$) and $E_{\mathrm{LS}}^{\mathrm{BS}}$ is the energy of the low-spin state calculated within the broken symmetry approach.[56] For the heterospin salt [CrCp*$_2$][**4**], the parameters *J* were also calculated by the multiconfiguration method CASSCF. According to calculations, the magnetic motifs of the radical anion salts studied vary from pseudo-one-dimensional ([K(18-crown-6)][**4**]) to three-dimensional ([K(THF)][**7**]) with exchange interactions of both signs (Table 1). However, the net effect in all cases is antiferromagnetic.[38,40–42]

Neglecting the small *J* values (–0.09 and –0.026; see Table 1), the magnetic motif of the homospin salt [K(18-crown-6)][**4**] can be represented as a set of infinite uniform chains.[38] Indeed, the experimental $\chi(T)$ dependence (see Fig. 9, *a*) is excellently described ($r = 0.9997$) by the

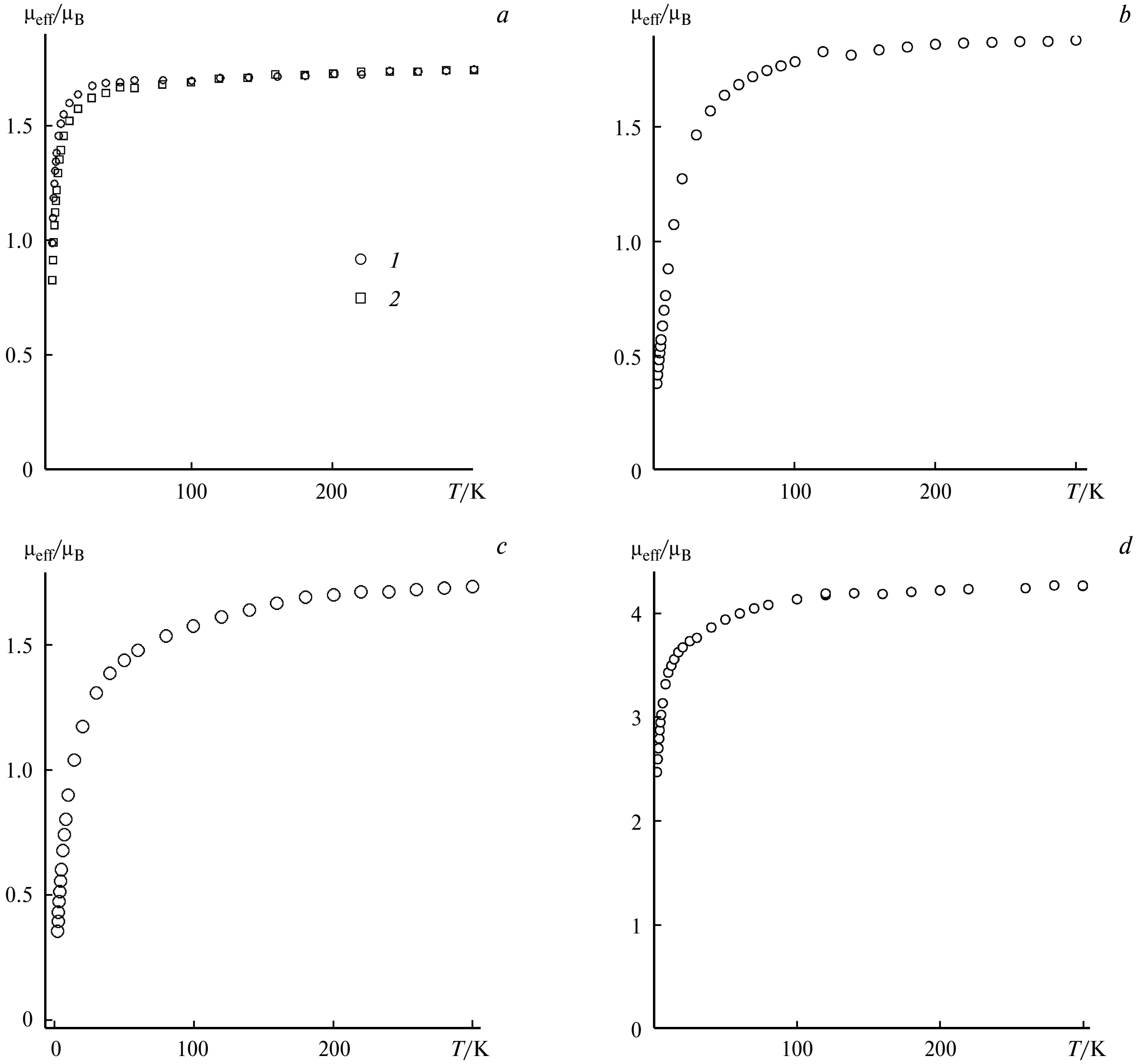


Fig. 10. Temperature dependences of the effective molar magnetic moments ($\mu_{\text{eff}}(T)$) of different radical anion salts: [K(18-crown-6)][**4**] (*1*) and [K(18-crown-6)][**5**] (*2*) (*a*), [K(THF)][**7**] (*b*), $[CoCp_2]$[**4**] (*c*), and $[CrCp*_2]$[**4**] (*d*).

known Bonner—Fisher phenomenological model.[50,51] The magnetic motif of the homospin salt [K(18-crown-6)][**5**] also represents a set of one-dimensional chains. However, the structure of this salt is disordered and the chain may include three different relative orientations of radical anions in the exchange-coupled pair, *viz.*, the shortest interparticle distance may correspond to the Se...Se, S...Se, or S...S distances. Exchange interaction is the weakest at the S...S contact (-1.69 cm^{-1}), being the strongest at the Se...Se contact (-8.08 cm^{-1}).[38] Nevertheless, the experimental $\chi(T)$ dependence can also be described using the Bonner—Fisher model, although with somewhat lower accuracy (see Fig. 9, *a*; $r = 0.997$).

The approximate magnetic motif of the homospin salt $[CoCp_2]$[**4**] obtained neglecting a very small J value (see Table 1) corresponds to a well-studied two-dimensional isotropic Heisenberg model. In this case, phenomenological $\chi(T)$ dependences for the low-temperature ($T < |J|/k$) and high-temperature ($T >> |J|/k$) regions are also available.[52,53] The experimental $\chi(T)$ dependence is excellently described (see Fig. 9, *c*) within the framework of the Heisenberg model (isotropic 2D layer of paramagnetic species).

The spin density distribution over the van der Waals surface of ions of the heterospin salt $[CrCp*_2]$[**4**] (see Fig. 8) suggests the possibility of ferromagnetic interactions. However, an analysis of the temperature dependence of the effective magnetic moment suggests that antiferromagnetic interactions dominate in the magnetic system of the salt. A theoretical analysis using a number of computa-

Table 1. The Néel temperatures (T_N) and parameters of the exchange Hamiltonian (J) describing the magnetic properties of the radical anion salts studied

Radical anion salt	T_N/K	Approximate magnetic motif[a]	J/cm^{-1}	
			Calculations	Experiment
[Na(15-crown-5)][**4**]	8	Alternating chain	—	−3.42, −1.12
[K(18-crown-6)][**4**]	<2	Uniform chain	−2.13 (−1.62[b]), −0.09, −0.026	−1.22±0.10
[K(18-crown-6)][**5**]	<2	Disordered chain	−8.08, −0.37; −4.02, −0.37, −1.69; −0.26[c]	−1.65[d]
[K(THF)][**7**]	15	Two-dimensional	−8.97, +4.81, −1.87	−13.5, +7.2, −2.8
[CoCp$_2$][**4**]	10	Isotropic 2D model	−2.8 (−4.39[b]), −0.13	−4.2±0.7
[CrCp*$_2$][**4**]	<2	Isolated pairs	−61.0, −0.28	−40±9, −0.58±0.03

Note. The Néel temperature corresponds to a maximum in the $\chi(T)$ dependence. Experimental J values were obtained by approximating the temperature dependences of the magnetic susceptibility using the calculated magnetic motifs; theoretical J values were calculated for the nearest pairs of paramagnetic species using the spin-unrestricted, broken symmetry approach in the UB3LYP/6-31+G(d) approximation.

[a] Neglecting small J values.

[b] Calculated with the TZVP basis set.

[c] $\langle J \rangle$: −4.60, −0.33.

[d] Assuming a uniform chain.

tional methods including CASSCF showed that the magnetic structure comprises two magnetic sublattices, a cationic and an anionic one. Antiferromagnetic interactions dominate in both of them. Ferromagnetic interactions between the cationic and anionic sublattices are negligibly weak.

Our further efforts will be focused on the synthesis and studying the properties of heterospin radical anion salts with cations containing d- and f-metals.

* * *

Summing up, a complex of synthetic, structural, spectroscopic, magnetochemical, and quantum chemical studies led to the discovery of a novel class of paramagnetic chemical compounds, *viz*., chalcogen-nitrogen π-heterocyclic radical anion salts. All reactions leading to the radical anion salts were unknown earlier. The approach outlined above was futrther developed by researchers from other groups.[57]

It is important that one can vary the composition and structure of the chalcogen-nitrogen π-heterocycle, the number and type of annelation of these heterocycles to one another and to other π-rings (carbo- and heterocycles) in the radical anion, as well as the chemical nature, charge, and the spin state of the cation. Taken altogether, these features make this class of compounds potentially large.

Compounds belonging to the new class can be useful in the design and synthesis of molecular magnets and molecular conductors because the half-filled π-MO of the radical anion in the crystal can undergo transformation to a half-filled electronic energy band. Undoubtedly, this requires further investigations.

Moreover, modeling the temperature dependences of the magnetic susceptibility using the results of quantum chemical calculations demonstrated that the calculations made it possible to correctly determine the magnetic motifs of the radical anion salts, to predict the exchange parameters of the spin Hamiltonian with an accuracy to a factor of about 2, and to explain the magnetic properties of the radical anion salts. Therefore, the state of the art in quantum chemical calculations of the spin Hamiltonian parameters allows the magnetic properties of molecular magnets to be predicted with reasonable accuracy.

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