

Large magnetic anisotropy of chromium(III) ions in a bis(ethylenedithio)tetrathiafulvalenium salt of chromium bis(dicarbollide), $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$

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Received: 16 April 2018 / Accepted: 11 June 2018 © Springer International Publishing AG, part of Springer Nature 2018

Abstract

The synthesis of a radical-cation salt based on a derivative of tetrathiafulvalene, $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ (ET=bis(ethylenedithio)tetrathiafulvalenium), was accomplished by electrochemical anodic oxidation of ET in the presence of $(Me_4N)[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ in the galvanostatic regime. An electric conductivity σ (293 K)=7 × 10⁻³ Ohm⁻¹ cm⁻¹ with semiconductor activation energy $E_a \cong 0.1$ eV in the range of 127–300 K was observed. The crystal structure of $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ was determined by X-ray diffraction at 173 K, revealing the presence of structural tetramers in radicalcation stacks. The magnetic properties of the complex were investigated in the temperature range 1.8–300 K using magnetometry and EPR, showing that the magnetic structure of $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ consists of two independent magnetic subsystems. Cation radicals form a rectangular magnetic lattice in the *ab*-plane with significant antiferromagnetic exchange interactions. The chromium bis(dicarbollide) anions are characterized by unusually strong positive zero-field splitting of the Cr(III) ions, which was confirmed by ab initio calculations.

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Introduction

Radical-cation salts (RCS)-incorporating tetrathiafulvalene (TTF) derivatives with anionic ligands based on *nido*-[7,8- $C_2B_9H_{11}$]²⁻ first attracted interest in the 1990s [1]. RCS compounds of the type [TTF]⁺[3,3'-M(1,2- $C_2B_9H_{11})_2$]⁻, where M = Cr, Fe, Ni, contain metal ions in the oxidation state +3, which correspond to the electronic configurations d^3 , d^5 and d^7 [2, 3]. This can lead to the appearance of states with mixed oxidation number and furthermore to the emergence of distinctive magnetic structures due to exchange interactions between two magnetic subsystems.

By varying the composition of the metallacarborane anion $[3,3'-M(1,2-C_2B_9H_{11-n}X_n)_2]^-$ (X = Cl, Br, I, OH; n=1, 2), the electrophysical properties of RCS can be modulated over a wide range [2, 3]. The distinctive combination of electrophysical and magnetic properties of RCS based on metallacarborane anions makes them promising multifunctional materials for micro- and nanoelectronics and spintronics applications [2, 3].

The RCS $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ (1), where ET is bis(ethylenedithio)tetrathiafulvalenium, was first described in 1995 [4]. Its crystal structure is formed by alternate layers

of (ET)⁺ radical cations and chromium bis(dicarbollide) anions. A study of the magnetic properties of RCS **1** showed that its effective magnetic moment is close to the pure spin value 3.87 μ_B for spin S = 3/2, which is expected for d^3 electron configuration and indicates almost complete absence of the (ET)⁺ radical-cation contributions. Taking into account the stoichiometry of RCS **1**, this could be due to spin-Peierls transition when structural tetramers (ET)₄ are formed. However, the reported structure [4] does not correspond to this case, and the question about the real state of this RCS remained open.

With these observations in mind, an electrochemical synthesis of RCS 1 was carried out, denoted further as 2. The crystal structure of 2 was determined by X-ray at 173 K, and the magnetic properties and EPR spectra were studied in the temperature range from 1.8 to 300 K. According to our investigation, this RCS consists of two independent magnetic subsystems: In the radical-cation stacks, a strong antiferromagnetic (AFM) exchange interaction is present, while the Cr(III) centers in the chromium bis(dicarbollide) anions possess much stronger (positive) zero-field splitting (ZFS) than usually observed in octahedral coordination.

Experimental methods

Synthesis

 $(Me_4N)[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ was prepared as described in the literature [5]. The RCS 2 was synthesized by the electrochemical anodic oxidation of ET in the presence of $(Me_4N)[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ in the galvanostatic regime. Single crystals of 2 were obtained from the system $(Me_4N)[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ (8 × 10⁻³ mol/dm³) + ET $(2 × 10^{-3} mol/dm^3)$ in the mixed solvent 1,1,2-trichloroethane-acetonitrile (24:1). The synthesis was carried out in a two-electrode cell with a porous glass partition and smooth platinum electrodes. The cell was powered by direct current of 5 × 10⁻⁷ A using an electronically stabilized current source. The applied current was increased discretely by $1 × 10^{-7}$ A every day until it reached a value of $1 × 10^{-6}$ A in the end of the synthesis. Over 4–5 weeks, shiny black needle-shaped crystals were formed on the anode.

Elemental analysis of the synthesized RCS was obtained on a VarioMICRO Superuser analyzer. The Cr content was found trigonometrically, the accuracy of determination being 0.1-0.2%. Found, %: C 26.67; H 3.59; S 47.14, Cr 4.93. Calculated for C₂₄H₃₈B₁₈CrS₁₆, %: C 26.54; H 3.53; S 47.23; Cr 4.79.

X-ray crystallography

X-ray diffraction analysis of RCS 2 was performed with a Bruker Smart ApexII system, using Mo-K_a radiation, at a temperature of 173 K. The crystal structure was solved by direct methods followed by Fourier difference synthesis with SHELXS-97 software and refined by the full-matrix least squares method using the anisotropic approximation for all non-hydrogen atoms [6, 7]. The reflection intensities were corrected for absorption using the APEX2 program [8]. The hydrogen atoms were calculated from geometrical considerations. Two carbon atoms of the dicarbollide ligands were positionally disordered, corresponding to atoms C(2) and B(7) with site occupancies of 0.62(6) and 0.38(6). General crystallographic and experimental data are given in Table 1, and the bond lengths and angles are given in Table 2. CCDC-1838605 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.

Magnetic measurements

The magnetic properties of RCS **2** were investigated with a Quantum Design MPMS-XL instrument. The magnetic susceptibility (determined as the ratio of measured magnetic moment and applied magnetic field) was studied in

 Table 1
 Basic crystallographic data for compound 2

Compound	(ET) ₂ [3,3'- Cr(1,2- C-B-H)-1
Chemical formula	$C_{24}H_{38}B_{18}CrS_{16}$
Molecular mass	1086.08
Crystal system	triclinic
Space group	P^{-1}
a/Å	6.565(1)
b/Å	7.866(2)
c/Å	21.876(4)
$\alpha /^{\circ}$	83.877(3)
β/°	84.070(4)
$\gamma/^{\circ}$	76.670(4)
V/Å ³	1089.3(4)
Z	1
$D_{calc}/g \text{ cm}^{-3}$	1.65
μ/mm^{-1}	1.057
$(2\theta)_{\rm max}$,°	53.36
The total number of reflections	7414
Number of independent reflections	3834
Number of refinement parameters	269
R-factor for 2599 reflections with $[F_0 > 4\sigma(F_0)]$	0.063

Table 2	Selected bond	lengths (Å)	for compound 2
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{cccccccc} Cr(1)-C(2) & 2.199(6) & S(5)-C(8) & 1.749(6) \\ Cr(1)-B(7) & 2.208(6) & S(6)-C(8) & 1.718(6) \\ Cr(1)-B(8) & 2.244(6) & S(6)-C(10) & 1.746(6) \\ Cr(1)-B(4) & 2.246(6) & S(7)-C(9) & 1.744(6) \\ S(1)-C(5) & 1.736(6) & S(7)-C(11) & 1.805(5) \\ S(1)-C(3) & 1.815(6) & S(8)-C(10) & 1.726(6) \\ S(2)-C(6) & 1.738(6) & S(8)-C(12) & 1.794(6) \\ S(2)-C(4) & 1.821(6) & C(3)-C(4) & 1.504(8) \\ S(3)-C(5) & 1.739(6) & C(5)-C(6) & 1.350(8) \\ S(3)-C(7) & 1.745(6) & C(7)-C(8) & 1.355(8) \\ S(4)-C(7) & 1.732(6) & C(9)-C(10) & 1.352(8) \\ S(4)-C(6) & 1.744(5) & C(11)-C(12) & 1.506(8) \\ \end{array}$	Cr(1)–C(1)	2.174(6)	S(5)-C(9)	1.745(6)
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zero-field-cooling (ZFC) and field-cooling (FC) regimes in the temperature range 1.8–300 K in a magnetic field of 100 mT and field dependence of magnetization in magnetic fields up to 5 T at a temperature of 2 K on a nascent polycrystalline sample. The measurements of magnetic susceptibility did not exhibit any differences in the ZFC and FC regimes. EPR spectra were recorded with a Bruker ELEXSYS II E500 X-band spectrometer with an operating frequency of 9.4 GHz equipped with an ESR910 flow-type cryostat, in the temperature range from 2.2 to 300 K on the same polycrystalline sample mixed with Apiezon N grease.

Computational details

Ab initio calculations were done using the ORCA 4.0.1 computational package [9-17]. The zeroth-order regular approximation (ZORA) together with the scalar relativistic contracted version of basis functions ZORA-Def2-TZVP(-f) was used. The calculations of zero-field splitting (ZFS) parameters were based on state-averaged complete active space self-consistent field (SA-CASSCF) wave functions, followed by N-electron valence second-order perturbation theory (NEVPT2). The active space of the CASSCF calculations was defined at the beginning as CAS(3,5), then CAS(3,10) to account for double-shell effects, CAS(7,7)including bonding orbitals of the ligand and CAS(7,12) including bonding orbitals of the ligand and the doubleshell effect for the Cr(III) ions. The state-averaged approach was used with all 10 quartet states and 40 doublet states equally weighted. The calculations utilized the RI approximation with appropriate decontracted auxiliary basis set and the chain-of-spheres (RIJCOSX) approximation to exact exchange. Increased integration grids (Grid4) and tight SCF convergence criteria were used. The ZFS parameters were calculated through the quasi-degenerate perturbation theory, in which an approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) and the effective Hamiltonian theory were utilized.

Results and discussion

The crystal structure of compound **2** is formed by $(ET)^+$ radical cations located at a general position, together with $[3,3'-Cr(1,2-C_2B_9H_{11})_2]^-$ anions in the special centrosymmetric position (Fig. 1). RCS **2** has a layered structure, in which the cationic and anionic layers alternate along the *c* axis (Fig. 2). The $(ET)^+$ radical cations have β' -type packaging in the layers and form a stack along the *b* axis, such that the $(ET)^+$ radical cations are characterized by two types of overlap, namely full and partial (Fig. 3). The stacks are less regular than in the isostructural salt $(ET)_2[3,3'-Fe(1,2-C_2B_9H_{11})_2]$ [18].

The distances between the average planes of the ET donors in stacks drawn through the S atoms of the heterocycles are 3.70 Å within the dimers and 3.72 Å between dimers; the radical-cation planes are parallel by the symmetry conditions. Shortened intermolecular S...S interactions in the range of 3.346(2)-3.631(2) Å are found in the layer between ET donors. Unlike the isostructural salt $(ET)_{2}[3,3'-Fe(1,2-C_{2}B_{9}H_{11})_{2}]$, the compound $(ET)_{2}[3,3' Cr(1,2-C_2B_0H_{11})_2$, in addition to shortened S...S-type intermolecular interactions (side to side), also has slightly shorter (3.631(2) Å) (plane to plane) type interactions between cations in the stacks; at the same time, analogous interactions between the stacks were not found (Fig. 4). The $(ET)^+$ radical cations are characterized by significant non-planarity: The maximum deviation of the S atom out of its average plane is 0.12 Å (for atom S(7)), and the protrusions of the terminal carbon atoms C(3), C(4), C(11) and C(12) out of this sulfur plane are 1.11, 0.47, -0.50 and 0.25 Å, respectively, which is slightly more than the equivalent values in the isostructural salt $(ET)_{2}[3,3'-Fe(1,2-C_{2}B_{9}H_{11})_{2}]$.

The Cr–C and Cr–B distances in the anion are 2.174(6)–2.199(6) and 2.208(6)–2.246(6) Å, respectively. Overlapping bond lengths for Cr–C(2) and Cr–B(7) are associated with the positional disorder of atoms C(2) and B(7). The distance from the C_2B_3 plane to the Cr atom is 1.68 Å. The carborane ligands are mutually rotated by 180°, resulting in a transoid conformation of the anion. The planes of the C_2B_3 ligands are parallel by the symmetry conditions.

The electrophysical measurements show that the salt is a semiconductor, with an activation energy $E_a \cong 0.1$ eV in the range of 127–300 K. The conductivity of the crystals σ (293 K) = 7 × 10⁻³ Ohm⁻¹ cm⁻¹ at room temperature (Fig. 5). This is 3.5 times higher than the previously reported value [4]. In addition, as shown in Fig. 5, the dependence of log*R*(*T*) is linear over the entire studied temperature range, whereas the previous report [4] noted a change in activation



Fig. 1 Radical-cation ET and $[3,3'-Cr(1,2-C_2B_9H_{11})_2]^-$ anion in 2

energy from 0.073 eV in the range 76-120 K up to 0.11 eV in the range 138-298 K. A possible reason for this discrepancy could be the use of the two-contact scheme of measurements in the earlier report [4], which is not applicable for highly anisotropic solids. Hence, in our work the four-contact scheme of measurements was applied.

The magnetic susceptibility increases with decreasing temperature over the whole temperature range (data not shown). The main difference in comparison with previous studies concerns the magnetic properties of the RCS 2. As shown in Fig. 6, the magnetic moment decreases with decreasing temperature from the value of 4.4 μ_B at room temperature down to about 2.4 $\mu_{\rm B}$. The room-temperature value is close to the pure spin contribution expected for the four unpaired electrons, of 4.90 μ_B , but more than expected for an isolated Cr(III) ion with spin S = 3/2. The sharp decrease in magnetic moment in the vicinity of 15 K indicates sizable ZFS of Cr(III) ions, with the possible presence of exchange interactions between them. The temperatureindependent susceptibility of conduction electrons due to the relatively high conductivity of the cation-radical subsystem in 2 does not allow the direct identification of cation-radical spin contributions to the total magnetic moment.

In order to better elucidate the contribution from the cation radicals, EPR experiments were performed in a wide temperature range. A sharp resonance with g-factor g=2, typical for radical spins, was observed in the temperature range 45–300 K, as shown in the inset of Fig. 7.

This confirms that pairs of $(ET)^+$ radicals have a spin and contribute to the overall magnetic properties. Since the integral intensity, obtained by double integration of the EPR spectrum, is proportional to magnetic susceptibility, one can analyze its temperature dependence (Fig. 7) using available theoretical spin models. An AFM spin-chain or dimerized AFM spin-chain model (often realized in cation-radical or anion-radical salts) gave a poor fit to the obtained experimental dependence. While the susceptibility for the dimerized AFM spin-chain model decreased too steeply at the low-temperature shoulder of the susceptibility maximum in comparison with the experimental data, the susceptibility for the uniform spin-chain model takes a rather high finite value at low temperatures (retaining finite signal intensity even at the lowest temperatures, which was not observed in the experimental data). Given the short contacts between cation-radical stacks in the *ab*-plane as shown in Fig. 4, another model can account for the magnetic contribution of cation radicals in 2, specifically a two-dimensional spatially anisotropic (rectangular) model [19, 20]. The fit of the rectangular model to the experimental temperature dependence of the integral intensity gives a reasonable agreement for the AFM exchange interaction $J/k_B = -270$ K and $\alpha = 0.5$ with g-factor fixed at g=2, where α represents the ratio of a weaker inter-chain exchange interaction to the intra-chain exchange interaction. Note that a scaling factor needs to be included in the model to scale the real value of the susceptibility to the integral intensity of the EPR spectrum. The



Fig. 2 A fragment of the crystal structure of 2

simulated temperature dependence of the susceptibility for the rectangular model using the obtained parameters was then subtracted from the experimental data, and the resulting contribution from the Cr(III) ions was described by the Hamiltonian

$$H = D[\hat{S}_{z}^{2} + S(S+1)/3] + g\mu_{B}\hat{S}_{z}H - zJ'\langle\hat{S}_{z}\rangle,$$
(1)

where *D* is the ZFS parameter, *g* is average g-factor and zJ' is the intermolecular interaction introduced in the frame of the mean-field theory [21, 22]. The susceptibility (and effective magnetic moment) can be then calculated using the equation

$$\chi = \frac{\chi_D}{\left(1 - \frac{zJ'}{Ng^2 \mu_B^2} \chi_D\right)} + \chi_{\text{TIP}},\tag{2}$$

where *N* is Avogadro's constant and χ_{TIP} accounts for the temperature-independent paramagnetism. The susceptibility χ_D representing the ZFS contribution of the Cr(III) ion was calculated for the polycrystalline sample as an average

of the distribution of the magnetic field vector over the triangular orientational grid, using a custom code written for the EasySpin simulation package [23]. The fit shown in Fig. 6 yields the values $D/k_B = 5.88$ K, $g_{Cr} = 1.98$, $zJ'/k_B = -1.79$ K and $\chi_{TIP} = 1.07 \times 10^{-3}$ emu/mol. The value of χ_{TIP} is in the range observed for the Pauli paramagnetism found in other conducting radical salts with delocalized electrons [24, 25]. In addition, this analysis includes the underlying temperature-independent paramagnetism of the Cr(III) ions. The value of ZFS parameter D is bigger than the common values reported for Cr(III), even higher than the highest reported value of 3.45 K for octahedral coordination [26], and is related to lower local symmetry. The symmetry of the nearest environment of the Cr(III) ion in the first approximation can be taken as D_{5d} as shown in Fig. 1. A similar situation has been observed in some chromocenes, which have also spin S = 3/2 (in contrast to D_{5h} symmetry, where the spin state is S = 1) [27]. An extremely large anisotropy barrier of 1837 K was recently also observed in a dysprosium metallocene displaying a room-temperature hysteresis of the magnetization [28]. Replacement of two



Fig. 3 Types of radical cations overlapping in the stack

boron atoms by carbon atoms reduces the symmetry to C_i . In such a case, the ground-state term is 4A_g . A sizable ZFS can then lead to a doubly degenerate spin–orbit doublet only populated at very low temperatures and treated as an effective spin S' = $\frac{1}{2}$ system. This is supported by the field dependence of magnetization shown in Fig. 8, where the experimental data have smaller values in comparison with the Brillouin function for an ideal paramagnet with spin S = $\frac{3}{2}$, suggesting a strong reduction in magnetic moment at low temperatures. A simulation of the field dependence of magnetization accounting for strong ZFS and intermolecular interactions between Cr(III) ions using Hamiltonian Eq. (1) with the same parameters as obtained from the susceptibility fit slightly overestimates the experimental data.

Further EPR measurements below 20 K down to 2.2 K (Fig. 9) also revealed the presence of an EPR signal originating from the Cr(III) ions with S = 3/2, including a strong ZFS. EPR spectra observed in the low-field region at temperatures up to 20 K exhibit a resonance line with an effective *g*-factor g = 3.6 characteristic of Cr(III) ions with spin S = 3/2, including relatively large ZFS parameter, as has been reported previously [29, 30]. This signal disappears with increasing temperature. Such behavior is typical for

a positive sign of the ZFS parameter *D* (easy-plane type of the magnetic anisotropy). Unfortunately, in the present experimental range and using polycrystalline samples only, one cannot distinguish the EPR spectra for different values of the ZFS parameter $D/k_B > 1.5$ K; to achieve this, high-field high-frequency EPR would be necessary. Consequently, the simulation was performed using the ZFS parameter *D* and *g*-factor obtained from the analysis of magnetic properties (isotropic convolutional broadening $\Delta B = 35$ mT was used). The overall agreement is good, although clearly some anisotropic broadening is present in the experimental spectra.

To confirm the presence of strong ZFS in this RCS, simple ab initio calculations using the ORCA package [9–17] on the $[3,3'-Cr(1,2-C_2B_9H_{11})_2]^-$ anion using the atomic coordinates obtained from single-crystal X-ray data for RCS 1 [4] and **2** were done. ZFS parameters calculated using the effective Hamiltonian theory with different active space configurations are summarized in Table 3. It is apparent that CAS-SCF calculations using larger active space yield almost the same value of the parameter *D* as obtained from the analysis of experimental data, confirming the very high ZFS of the Cr(III) ion in this complex. The parameter *E*, representing the rhombic term of the ZFS, is very small as given in Table 3



Fig. 4 Packing of radical cations ET in 2



Fig. 5 The temperature dependence of the resistance of a single crystal of compound ${\bf 2}$



Fig. 6 The temperature dependence of effective magnetic moment of compound **2** before (full symbols) and after (open symbols) subtraction of the contribution from the cation radials. The solid line represents the fit of Eq. (2) to the experimental data accounting for the magnetic moment of Cr(III) ions with parameters as described in the text. The inset shows the orientation of the anisotropy axes in the chromium bis(dicarbollide) anions as calculated from NEVPT2 calculations based on CAS(7,12) active space. Hydrogen atoms are omitted for clarity



Fig. 7 The temperature dependence of the integral intensity (open symbols) of a narrow EPR signal of compound **2** with g=2 shown in the inset. The solid line represents the fit using a rectangular model as described in the text



Fig. 8 The field dependence of magnetization of compound **2** at 2 K. The dashed line represents the Brillouin function for an ideal paramagnet with spin S=3/2, and the solid line represents a simulation using Hamiltonian (1) with the parameters obtained from the susceptibility fit



Fig. 9 The temperature evolution of EPR spectra of compound 2 at temperatures below 20 K including the simulation with parameters $D/k_{B} = 5.88$ K and g = 1.98 obtained from the susceptibility fit

 Table 3
 Results of ab initio calculations of ZFS parameters using ORCA with effective Hamiltonian theory

	$D/k_B(\mathbf{K})$	E/D	g _{avg}	Structure
RCS 1, CAS(3,5)	6.68	0.007	1.982	Ref. [4]
RCS 1, CAS(7,7)	5.49	0.001	1.985	Ref. [4]
RCS 1, CAS(7,12)	5.70	0.006	1.99	Ref. [4]
RCS 1, CAS(3,10)	6.46	0.0035	1.981	Ref. [4]
RCS 2, CAS(3,5)	6.64	0.0018	1.982	This work
RCS 2, CAS(7,7)	5.50	0.0032	1.985	This work
RCS 2, CAS(7,12)	5.65	0.0034	1.99	This work
RCS 2, CAS(3,10)	6.31	0.0017	1.981	This work

Parameter E represents a rhombic term of ZFS

by the ratio *E/D* obtained from our calculations. Thus, it can be neglected in the analysis of the experimental data to avoid overparameterization.

Conclusion

In this paper, the results of X-ray diffraction analysis and an investigation of the magnetic properties and EPR spectra of $(ET)_2[3,3'-Cr(1,2-C_2B_9H_{11})_2]$ are reported. The results suggest that there are two independent magnetic subsystems: The stacks of radical cations exhibit significant AFM interactions $(J/k_B = -270 \text{ K})$, while the chromium bis(dicarbollide) anions show very strong positive ZFS of Cr(III) ions $(D/k_B = 5.88 \text{ K})$. An ambiguity in the reported contribution of $(ET)^+$ radicals to the total magnetic moment of this RCS [4] has been clarified. Our results suggest that the transition-metal carbollides and related complexes present a great opportunity to design molecular magnets with much higher anisotropies than those usually observed in complexes with octahedral transition-metal ions.

Acknowledgements This work was supported by the Slovak Research and Development Agency under Contracts Nos. APVV-14-0073 and APVV-14-0078 and by ERDF EU projects under the Contract No. ITMS26220120047. A. V. Fedorchenko thanks P.J. Šafárik University for the opportunity to carry out research.

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