

Heterospin π -Heterocyclic Radical-Anion Salt: Synthesis, Structure, and Magnetic Properties of Decamethylchromocinium [1,2,5]Thiadiazolo[3,4-c][1,2,5]thiadiazolidyl

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Received May 26, 2010

Decamethylchromocene, Cr^{II}(η^5 -C₅(CH₃)₅)₂ (**2**), readily reduced [1,2,5]thiadiazolo[3,4-c][1,2,5]thiadiazole (**1**) in a tetrahydrofuran solvent at ambient temperature with the formation of radical-anion salt [2]⁺[1]⁻ (**3**) isolated in 97% yield. The heterospin salt **3** ([2]⁺, S = 3/2; [1]⁻, S = 1/2) was characterized by single-crystal X-ray diffraction as well as magnetic susceptibility measurements in the temperature range 2–300 K. The experimental data together with theoretical analysis of the salt's magnetic structure within the CASSCF and spin-unrestricted broken-symmetry (BS) density functional theory (DFT) approaches revealed antiferromagnetic (AF) interactions in the crystalline **3**: significant between anions [1]⁻, weak between cations [2]⁺, and very weak between [1]⁻ and [2]⁺. Experimental temperature dependences of the magnetic susceptibility and the effective magnetic moment of **3** were very well reproduced in the assumption of the AF-coupled [1]⁻...[1]⁻ (J₁ = -40 ± 9 cm⁻¹) and [2]⁺...[2]⁺ (J₂ = -0.58 ± 0.03 cm⁻¹) pairs. The experimental J₁ value is in reasonable agreement with the value calculated using BS UB3LYP/6-31+G(d) (-61 cm⁻¹) and CASSCF(10,10)/6-31+G(d) (-15.3 cm⁻¹) approaches. The experimental J₂ value is also in agreement with that calculated using the BS DFT approach (-0.33 cm⁻¹).

Introduction

Chalcogen–nitrogen open-shell π -heterocyclic systems, both neutral and charged, are of interest to fundamental chemistry and its applications in the field of functional materials.^{1–4} During the past 2 decades, numerous chalcogen–nitrogen π -heterocyclic neutral radicals and radical cations

were synthesized and successfully used as building blocks in the design and synthesis of both molecular magnets and conductors,^{2–4} whereas radical anions (RAs; known since the 1960s from electron spin resonance experiments)⁵ remained a missing link because of the lack of approaches to their isolation.

Recently, it was found that some derivatives of the 1,2,5-chalcogenadiazole ring system (chalcogen: S, Se), in particular

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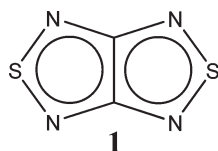
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Chart 1



[1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**1**; Chart 1), can be transformed into RAs with a number of reducing agents including early alkali metal (Li, Na, and K) and tris(dimethylamino)sulfonium thiophenolates, tetrakis(dimethylamino)ethene (TDAE), and CoCp_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). The RAs were isolated in the form of crystalline salts of corresponding cations and characterized by X-ray diffraction (XRD), and their magnetic properties were studied by experimental and theoretical methods.⁶ In all cases, except $[\text{TDAE}]^{2+}[\mathbf{1}]^{-2}$ featuring diamagnetic π dimers of the RAs, antiferromagnetic (AF) interactions in the salts' spin systems were observed.⁶ These interactions were also found in some other 1,2,5-thiadiazolidyl-type RA salts, for example, in $[\text{K}(\text{THF})]^+[\text{C}_6\text{H}_4\text{N}_2\text{S}]^-$ (THF = tetrahydrofuran).⁷ In all studied RA salts, including $[\text{CoCp}_2]^+[\mathbf{1}]^-$, the cations were diamagnetic; i.e., the salts were homospin ($S = 1/2$).^{6,7}

An interesting challenge is changing the character of magnetic interactions in the salts from AF to ferromagnetic (FM). The molecular design of FM π -heterocyclic RA salts is possible, in principle, with the McConnell I model⁸ dealing with spin polarization (for a discussion of some other prospects, see ref9). To achieve a FM ground state, this model requires paramagnetic moieties of two types, with a positive spin density at one interacting with a negative spin density at another.⁸ Because, according to available data, the spin density on the van der Waals (VdW) surfaces of the 1,2,5-thiadiazolidyl-type RAs is mostly positive,⁹ paramagnetic cations

with peripheral negative spin density are necessary as counterions. Such cations are known to be, for example, $[\text{MCp}^*_2]^+$ [$\text{M} = \text{Cr, Mn, Fe}$; $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$].¹⁰

It is believed that the McConnell I mechanism stands behind the FM properties of a number of the $[\text{MCp}^*_2]^+[\text{TCNE}]^-$ and $[\text{MCp}^*_2]^+[\text{TCNQ}]^-$ salts, with $T_C = 8.8$ K for $[\text{MnCp}^*_2]^+[\text{TCNE}]^-$.^{10–13} At the same time, it should be emphasized that creation of the FM ground state with the McConnell I model critically depends on the crystal packing of the target salt (mutual orientation and spatial proximity of fragments with required spin polarization), i.e., on property that can hardly be a priori predicted and/or controlled.¹⁴ For the aforementioned $[\text{TCNE}]^-$ and $[\text{TCNQ}]^-$ salts' polymorphs (where known), the typical situation is that only one has FM properties, whereas the others do not.^{11–13} Some other structural problems are illustrated by the fact that nonstoichiometric salt $[\text{V}^{11}]^{2+}[\text{TCNE}]_z^-[\text{TCNE}]_{1-z/2}^-$ ($1 < z < 2$), whose T_C exceeds room temperature, is a non-crystalline kinetic phase, whereas the crystalline phase is not a magnetically ordered material.¹⁵

In this work, we report the reduction of compound **1** with CrCp^*_2 (**2**) and the XRD structure and magnetic properties of the RA salt $[\mathbf{2}]^+[\mathbf{1}]^-$ (**3**) obtained.

Experimental and Computational Details

General Procedures. All operations were carried out under argon; in the synthesis and manipulation of salt **3**, the glovebox and Schlenk techniques were used. Compound **2** was received from Dalchem and additionally purified by crystallization from hexane. All solvents were distilled under argon with common drying agents.

Syntheses. Compound 1. A solution of 3-chloro-4-fluoro-1,2,5-thiadiazole¹⁶ (2.77 g, 0.02 mol) and $(\text{Me}_3\text{SiN}=\text{C})_2\text{S}^{17\text{T}}$ (4.12 g, 0.02 mol) in absolute MeCN (25 mL) was added dropwise, for 30 min, to a refluxed and stirred suspension of freshly calcinated CsF (6.08 g, 0.04 mol) in MeCN (75 mL). After an additional 30 min, the reaction mixture was cooled to 20 °C and filtered, and the solvent was distilled off under reduced pressure. The residue was chromatographed on a silica column with hexane, the solvent evaporated, and the residual solid sublimed in vacuo and recrystallized from hexane. Compound **1**^{6c} was obtained as long colorless needles [1.67 g (58%), mp 117–118 °C].

Compound 3. The reaction was carried out in an H-shaped Schlenk vessel. A solution of **1** (21.3 mg, 0.15 mmol) in THF (1 mL) was placed into one tube and a solution of **2** (47.6 mg, 0.15 mmol) in THF (1 mL) into the other tube. Then pure THF was gently layered over both solutions up to the middle level of the horizontal tube (ca. 30 mL in total). The reaction vessel was kept at ambient temperature over 3 weeks. Salt **3** formed red-brown crystals suitable for XRD [yield 67 mg (97%), mp (sealed capillary) > 300 °C]. Calcd for $\text{C}_{22}\text{H}_{30}\text{CrN}_4\text{S}_2$: C, 56.62; H, 6.48; N, 12.01. Found: C, 56.60; H, 6.15; N, 11.90.

Crystallographic Analysis. The XRD data for salt **3** were collected with a Bruker X8Apex diffractometer with Mo K α ($\lambda = 0.71073$ Å) radiation and a graphite monochromator. The

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