

Cobaltocenium [1,2,5]Thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl: Synthesis, Structure, and Magnetic Properties

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Cobaltocene, $[\text{Co}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$, readily reduced [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) to the [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**) which was isolated in the form of the thermally stable salt $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2][\textbf{1}]$ (**5**) in 93 % yield. The XRD structure of **5** displays layers of radical anions **1**, with S...N contacts of 358.2 and 366.0 pm between neighboring species. The salt was further characterized by ESR spectroscopy in the solid state as well as in solution. The temperature dependence of its magnetic susceptibility (χ) in the range of 2–300 K with a maximum at (9.7 ± 0.5) K indicates antiferromagnetic ordering of the spin system. The magnetic structure of **5** was analyzed in terms of dimeric exchange integrals calculated by a spin-unrestricted broken-

symmetry approach at the DFT/UB3LYP/6-31+G(d) level of theory and was found to be 2D. Further analysis of the $\chi(T)$ dependence was performed by using the low- and high-temperature series expansion methods for the $S = 1/2$ square lattice antiferromagnetic Heisenberg model. The exchange interactions between radical anions **1** were estimated to be $J = (-4.2 \pm 0.7) \text{ cm}^{-1}$. With the general form of the Van Vleck equation for a $[3 \times 4]$ grid of spins $1/2$, the best fit of the experimental $\chi(T)$ was achieved with $J_1 = -5.0 \text{ cm}^{-1}$ and $J_2 = -0.23 \text{ cm}^{-1}$. Thus, the exchange interactions in **5** are stronger than those observed for previously studied salts of **1**.

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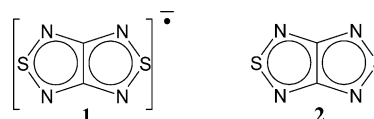
Introduction

Spin-carrying chalcogen–nitrogen π -heterocycles belong to the most promising building blocks in the design and synthesis of magnetic and conducting molecular materials.^[1–7] In particular, the neutral 4-R-1,2,3,5-dithiadiazolyl radical (R = 4-NCC₆F₅) reveals spin-canted antiferromagnetism (weak ferromagnetism) with $T_c = 36$ K at normal pressure and $T_c = 65$ K at 16 kbar.^[3d] Some resonance-stabilized neutral radicals of the dichalcogenazolyl type (chalcogen = S, Se) display properties of molecular conductors

together with those of weak (spin-canted) ferromagnets ($T_c = 17$ and 28 K, depending on the structure), or even bulk ferromagnets ($T_c = 12$ K).^[1a,1b] While neutral and positively charged chalcogen–nitrogen heterocyclic radicals (radical cations) have been the subject of extensive studies, related negatively charged systems (radical anions) have been less studied as they are much rarer.^[1–7]

Recently, we found that thermally stable salts of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**, Scheme 1) (and its Se congener) can be easily prepared by chemical reduction of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**, Scheme 1) with PhX^- (X = S, Se) anions or with tetrakis(dimethylamino)ethene (**3**).^[7] In the latter case a dicationic salt of **1** was obtained,^[7a] which indicates that **2** behaves toward **3** similar to X_2 halogens (X = Cl, Br),^[8a] that is, its electron affinity is high enough for two-electron oxidation of **3**. In the He^I photoelectron spectrum of **3**, the vertical IE_1 and IE_2 are ca. 6.0 and ca. 7.5 eV, respectively.^[8] Consequently, other neutral compounds with IE_1 lying in this range should also reduce **2** to its radical anion **1**. These compounds in particular are $[\text{M}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$ (M = V, Cr,

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Scheme 1.

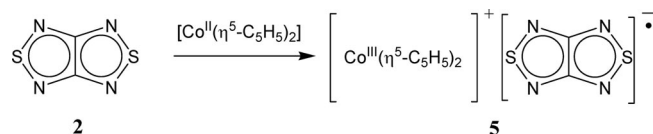
Mn, Fe, Co, Ni), especially decamethyl derivatives, as well as $[M(\eta^6\text{-C}_6\text{H}_6)_2]$ ($M = \text{Cr, Mo, W}$).^[9]

In this work we report the reduction of compound **2** with cobaltocene, $[\text{Co}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$ (**4**, $IE_1 \approx 5.6 \text{ eV}$),^[9] which led to the radical anion salt $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2][\textbf{1}]$ (**5**) in high yield. The salts prepared with other sandwich organometallics as reducing agents will be described elsewhere.

The salt **5** was characterized by XRD and by ESR spectroscopy (in the solid state and in solution). Magnetic susceptibility (χ) measurements of **5** in a temperature range 2–300 K revealed antiferromagnetic interactions with $T_c = (9.7 \pm 0.5) \text{ K}$. The magnetic structure of **5** was analyzed in terms of dimeric exchange integrals calculated by the spin-unrestricted broken-symmetry DFT method and was found to be 2D. Further analysis of the $\chi(T)$ dependence was performed using the $S = 1/2$ square lattice antiferromagnetic Heisenberg model (2D-AFHM).^[10] The low- and high-temperature series expansion methods (LTSE and HTSE, respectively) were employed to analyze $\chi(T)$.^[11,12] The exchange interactions between radical anions **1** were found to be $J = (-4.2 \pm 0.7) \text{ cm}^{-1}$. With the general form of the Van Vleck equation for a $[3 \times 4]$ grid of spins $1/2$, the best fit of the experimental $\chi(T)$ was achieved with $J_1 = -5.0 \text{ cm}^{-1}$ and $J_2 = -0.23 \text{ cm}^{-1}$. Thus, the exchange interactions in **5** are stronger than those observed for previously studied salts of **1**.

Results and Discussion

In thf as solvent and at ambient temperature, cobaltocene **4** readily reduced compound **2** with the formation of the salt **5** (Scheme 2) in nearly quantitative yield. In the salt, the cobaltocenium cation is an 18-electron closed-shell



Scheme 2.

diamagnetic system,^[13] and the heterocyclic anion is an 11- π -electron open-shell paramagnetic system.^[17]

The structure of the salt **5** was confirmed by X-ray diffraction (Figures 1 and 2). In the crystal, the cobalt atom of the cation and the center of the radical anion lie at centers of symmetry. The radical anions form $\pi \cdots \pi$ contacts with C_5H_5 (Cp) moieties of two neighboring cations. The angle between the best planes through the atoms of the anion **1** and the carbon atoms of the Cp ligand is 17.2° , and the distance between the planes' centroids is 367.1 pm. The closest contacts observed are the distances between the atoms C6 and C6' of the anion and the atom C3 of the ligand which are 331.4 and 350.2 pm, respectively (Figure 1; the sum of the van der Waals radii is 354 pm,^[14] and the interplanar distance in graphite is 335.4 pm^[13]). Because of these $\pi \cdots \pi$ contacts, the cations and anions are combined to form zigzag chains which are oriented parallel to the crystallographic ab plane. Different chains are connected by weak $\text{C-H} \cdots \text{N}$ hydrogen bonds with an $\text{H} \cdots \text{N}$ distance of 260 pm and a $\text{C-H} \cdots \text{N}$ angle of 131° . In two neighboring layers these chains are oriented in different directions, that

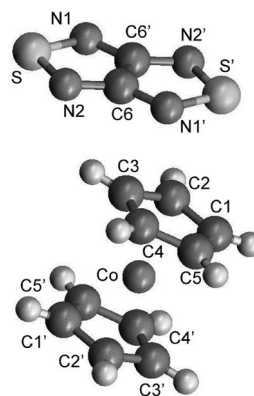


Figure 1. Structure of salt **5**; selected bond lengths [pm] and angles $^\circ$: S–N1 165.7(3), S–N2 166.0(3), N2–C6 133.9(4), N1–C6' 134.2(4), C6–C6' 144.1(6), average C–Co 203.2, average C–C in the C_5H_5 rings 141.2; N1–S–N2 101.23(13), S–N2–C6 104.6(2), S–N1–C6' 104.6(2), N2–C6–N1' 130.5(3), N2–C6–C6' 114.8(3), N1'–C6–C6' 114.7(3), C2'–Co–C2 180.0.

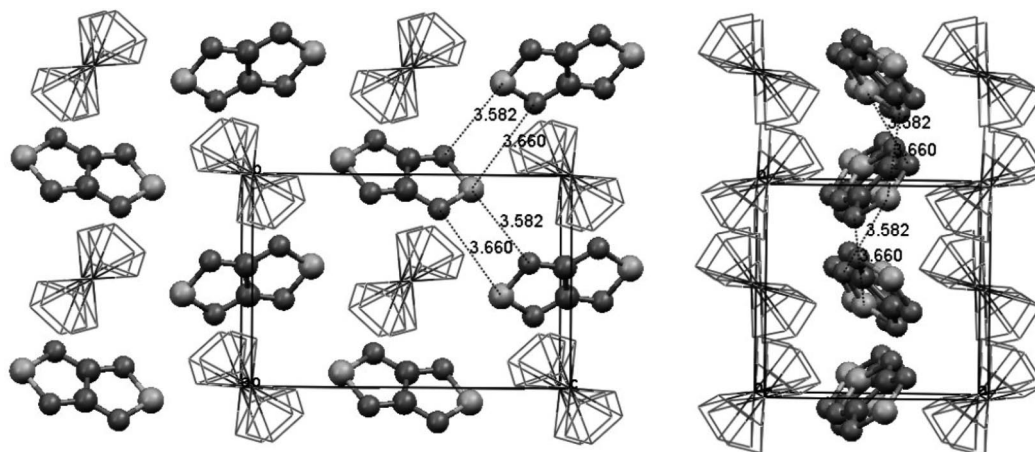


Figure 2. Layers of radical anions **1** in the crystal of salt **5** viewed along crystallographic axes a (left) and c (right).

is, the $a + b$ and $a - b$ ones, as depicted in Figure 2. The neighboring layers are connected again by weak C–H $\cdots$ N hydrogen bonds with an H $\cdots$ N distance of 264 pm and a C–H $\cdots$ N angle of 163° to give a 3D network in **5** built up from $\pi\cdots\pi$ interactions and hydrogen bonds. To conclude the crystallographic part, the most important information for the following discussion is the fact that layers of the radical anions **1** can be identified in the crystal lattice of **5** as demonstrated in Figure 2 (right). Within these layers, the radical anions form zigzag belts by S $\cdots$ N contacts of 358.2 and 366.0 pm (the sum of the van der Waals radii is 355 pm).^[14] These relatively short nonbonding distances between radical anions in the solid state are favorable for magnetic exchange interactions (see later).

The salt **5** is ESR-active in both the solid state (Figure 3) and in solution. The solution ESR spectrum (nine-line pattern, $a_N = 0.314$ mT, $g = 2.0045$) is in full agreement with that reported for similar salts.^[7c,7d]

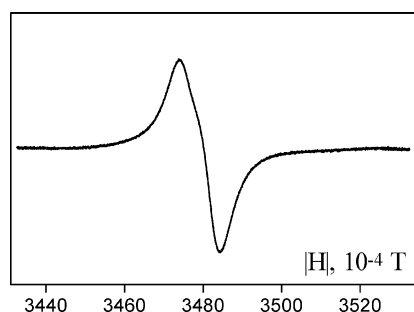


Figure 3. Solid-state ESR spectrum of salt **5**.

The effective magnetic moment (μ_{eff}) of **5** at 300 K was found to be (1.74 ± 0.01) Bohr magneton (Figure 4B), which corresponds to one unpaired electron per molecule. In the range 300–2 K, the magnetic susceptibility χ of **5** increases steadily with temperature down to (9.7 ± 0.5) K and then it drops (Figure 4A). This maximum on the $\chi(T)$

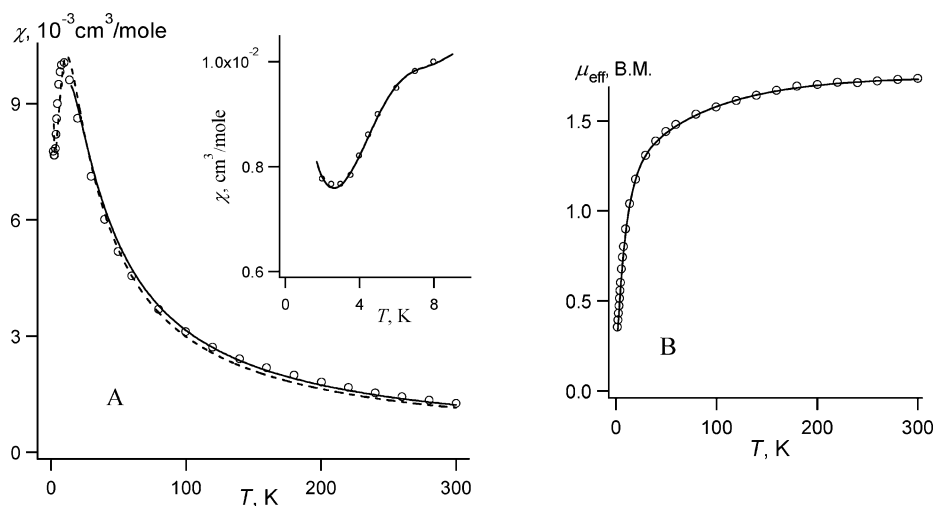


Figure 4. Dependences of $\chi(T)$ (A, open circles) and $\mu_{\text{eff}}(T)$ (B, open circles) of the salt **5** in the temperature range 2–300 K. Solid curves: low-temperature series expansion fit (A, inset), high-temperature series expansion fit (A, solid curve), and twisted-to-tube $[3 \times 4]$ grid fit (A, dashed curve).

curve indicates low-temperature antiferromagnetic ordering of the spin system of **5**.

To understand the magnetic structure of the salt **5** and to choose a model for a decent analysis of the experimental $\chi(T)$ dependence, calculations of the dimeric exchange interactions in its crystals were performed. In former contributions^[7a,7b] it was found that the magnetic structures of some similar salts of the radical anion **1** could be satisfactorily reproduced by such calculations based on the spin-unrestricted broken-symmetry approach^[15] at the DFT/UB3-LYP/6-31+G(d)^[16] level of theory. Therefore, a similar approach was used for an analysis of the magnetic behavior of **5**.

In the crystal of **5**, all radical anions **1** are structurally equivalent. As mentioned earlier, the layers of **1** can be identified in the crystal lattice. It is possible to select a radical anion and calculate the J_{AB} values with all first-nearest neighbors of the same layer, and then with the closest second-nearest neighbors of the *same* layer or of the *neighboring* layers. Figure 5 demonstrates that every radical anion **1** has eight first-nearest neighbors. These eight first-nearest neighbors give rise to only three unique pairs (r1–

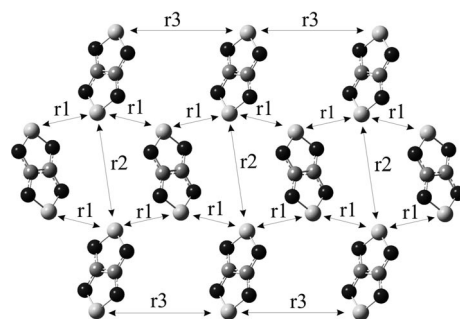


Figure 5. The layer of the radical anions **1** in the crystal packing of salt **5** analyzed in terms of the shortest S–S distances in the pairs r1–r3.

r3, Figure 5) with the calculated J_{AB} values presented in Table 1. The table also displays the shortest S...S distances found within pairs of radical anions. For only two of three pairs, the calculated J_{AB} values (J_1 and J_2) are higher than the given accuracy of calculations of 0.04 cm^{-1} . All J_{AB} values with closest second-nearest neighbors were found to be less than 0.04 cm^{-1} .

Table 1. Spin-unrestricted broken-symmetry results obtained at the DFT/UB3LYP/6-31+G(d) level of theory for the dimeric exchange interaction (J_{AB}) of the radical anion **1** with first-nearest neighbors in the crystal of salt **5**.

Pair	Shortest S...S distance in pair [Å]	$-J_{AB} [\text{cm}^{-1}]$
r1	3.870	2.8
r2	6.665	0.13
r3	7.257	≤ 0.04

It follows from Table 1 that the magnetic structure of salt **5** could be represented as a 2D layer magnetic motif (Figure 6A). This is different from previously studied salts of **1** where magnetic motifs were satisfactorily described as 1D Bonner–Fisher chains.^[7] Calculations on **5** predict that the value of J_2 (-0.13 cm^{-1}) is 21.5 times smaller than J_1 (-2.8 cm^{-1}). If one neglects J_2 , the magnetic motif simplifies (Figure 6B) to the extent it can be described by the 2D version of the antiferromagnetic Heisenberg model (AFHM) for 1/2 spins.^[10] The model is well known. In particular, the AFHM has previously been extensively investigated by different techniques including the Green function method,^[17] Monte Carlo simulations,^[18] high-temperature series expansion method (HTSE),^[12,19] etc.

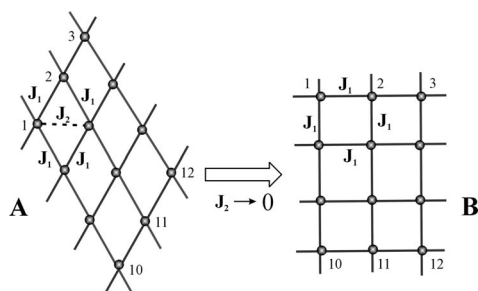


Figure 6. Magnetic motif for salt **5** defined in terms of dimeric exchange interactions J_1 and J_2 between pairs of radical anions **1** (A). The simplified magnetic motif for salt **5** obtained after neglecting the exchange integral J_2 (B), which corresponds to the 2D antiferromagnetic Heisenberg model.

To analyze the experimental $\chi(T)$ dependence of the salt **5** in the low-temperature range (2–8 K), we used the LTSE formula of Johnston^[11] which was parameterized to reproduce the results of quantum Monte Carlo simulations for spin 1/2 2D-AFHM.^[18a,18b] A small correction on the paramagnetic impurity (fraction ρ) was also included as shown by Equation (1) where $x = kT/2|J|$, g is the gyromagnetic factor, and N , k , μ_B are the Avogadro constant, Boltzmann constant, and Bohr magneton, respectively.

$$\chi(T) = \frac{Ng^2\mu_B^2}{2|J|} (0.043669 + 0.039566x - 0.5341x^3 + 4.684x^4 - 11.13x^5 + 10.55x^6 - 3.57x^7) \times (1 - \rho) + \frac{Ng^2\mu_B^2}{4kT} \times \rho \quad (1)$$

The best-fitting parameters (Figure 4A, inset, solid curve) were found to be $J = (-3.5 \pm 0.1) \text{ cm}^{-1}$ and $\rho = (0.020 \pm 0.001)$. Note that in the case of spin 1/2 2D-AFHM, the Monte Carlo simulations demonstrate^[18b–18d] that $\chi(T)$ has a flat peak at $kT/2|J| \approx 1$. This relation also provides a rough estimation of $|J| \approx 3.4 \text{ cm}^{-1}$.

To analyze $\chi(T)$ in the temperature range 14–300 K, we used an HTSE method of Rushbrooke and Wood^[12] for the inverse susceptibility. Figure 4A (solid curve) demonstrates the best fit of experimental data by the HTSE with $g = (1.93 \pm 0.04)$ and $J = (-4.8 \pm 0.3) \text{ cm}^{-1}$. Therefore, analysis of $\chi(T)$ by using LTSE and HTSE techniques provides similar results with $J = (-4.2 \pm 0.7) \text{ cm}^{-1}$. This value is in good agreement with our UB3LYP calculations (-2.8 cm^{-1}).

The $\chi(T)$ dependence for magnetic materials consisting of finite-size clusters can also be calculated by using the general form of the Van Vleck equation^[20] [Equation (2)], where E_n is the n th energy level from the algebraic Heisenberg Hamiltonian [Equation (3)], S_n is the spin of the n th energy level, and g , N , k , μ_B are the same as in Equation (1).

$$\chi(T) = \frac{Ng^2\mu_B^2}{3kT} \frac{\sum_n S_n(S_n+1)(2S_n+1)e^{-E_n/kT}}{\sum_n (2S_n+1)e^{-E_n/kT}} \quad (2)$$

$$\hat{H} = -2 \sum_{A,B}^N J_{AB} \hat{S}_A \hat{S}_B \quad (3)$$

Using Equation (2), we calculated $\chi(T)$ for a $[3 \times 4]$ grid (Figure 6A) of spins 1/2. Both J_1 and J_2 were taken into account, and their ratio J_1/J_2 was kept as 21.5 as calculated by quantum chemistry. The best fit of the experimental $\chi(T)$ was obtained with $J_1 = -5.8 \text{ cm}^{-1}$. A similar calculation was performed with a $[3 \times 4]$ grid twisted to a tube ($J_{1,10} = J_{2,11} = J_{3,12} = J_1$). The best agreement of theoretical with experimental $\chi(T)$ was achieved with $J_1 = -5.0 \text{ cm}^{-1}$ (Figure 4A, dashed curve). Note that neglecting the J_2 value has no influence on $\chi(T)$, supporting the application of AFHM in our case. The use of larger grids would result in a lower value of J_1 in better agreement with LTSE and HTSE techniques.

Thus, the J value for **5** [$-4.2 \pm 0.7 \text{ cm}^{-1}$] obtained with the LTSE and HTSE methods is somewhat higher than the corresponding values for previously studied salts of **1** with [K(18-crown-6)]⁺ and [Na(15-crown-5)]⁺ cations (-1.22 cm^{-1} ; -3.24 and -1.12 cm^{-1} ; respectively),^[7c] as well as for the salt of its Se congener with the [K(18-crown-6)]⁺ cation (-1.65 cm^{-1}).^[7b] The salt of **1** with the dication of **3** is magnetically inactive since in its crystals the radical anions form π -dimers with a singlet ground state.^[7a]

Conclusions

Under mild reaction conditions, $[\text{Co}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$ readily reduced [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**) to [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anion (**1**) which was isolated from the reaction mixture in the form of the stable salt $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2][\textbf{1}]$ (**5**). The salt reveals low-temperature antiferromagnetic ordering of its spin system. Theoretical calculations demonstrate that salt **5** has a 2D magnetic structure. The magnetic motif of **5** can be approximately described by the 2D-AFHM. This is different from the previously studied salts of radical anion **1** where the antiferromagnetic motifs could be described as 1D Bonner–Fisher spin chains. The energy of the antiferromagnetic exchange interactions in the salt **5** estimated with the LTSE and HTSE methods is $J = (-4.2 \pm 0.7) \text{ cm}^{-1}$. With the Van Vleck equation, the best agreement between theoretical and experimental $\chi(T)$ was achieved with $J_1 = -5.0 \text{ cm}^{-1}$. Thus, magnetic interactions in **5** are somewhat stronger than those in previously studied salts of **1** with $[\text{K}(18\text{-crown-6})]^+$ and $[\text{Na}(15\text{-crown-5})]^+$ cations.

The synthetic approach used for preparing **5** can be clearly generalized to other sandwich organometallics, as well as to other chalcogen–nitrogen heterocycles. For example, $[\text{Cr}^{\text{II}}(\eta^5\text{-C}_5(\text{CH}_3)_5)_2]$ ($IE_1 \approx 4.9 \text{ eV}$)^[9] smoothly reduced **2** with formation of $[\text{Cr}^{\text{III}}(\eta^5\text{-C}_5(\text{CH}_3)_5)_2][\textbf{1}]$.^[21] For salts with both paramagnetic anions and cations one can expect enhanced magnetic exchange interactions.

Experimental Section

General: All operations were carried out by using inert gas Schlenk techniques. Compound **2** was prepared as described previously.^[7d] Cobaltocene (**4**) was kindly donated by Dr. Simon Duerr. All solvents used were distilled under an inert gas with common drying agents. The solid-state and solution ESR spectra of salt **5** were measured with a Bruker ESP-300 spectrometer (MW power 265 mW, modulation frequency 100 kHz, modulation amplitude 0.005 mT). The magnetic susceptibility measurements were performed with an MPMS-XL Quantum Design SQUID magnetometer in the temperature range 2–300 K in a magnetic field of 5000 Oe. The molar magnetic susceptibility of salt **5** was calculated by using the standard diamagnetism correction.^[22] The effective magnetic moment of the salt (μ_{eff}) was calculated by Equation (4).

$$\mu_{\text{eff}} = \left(\frac{3k}{N\beta^2} \chi T \right)^{1/2} \approx (8\chi T)^{1/2} \quad (4)$$

Synthesis of Salt 5: The reaction was carried out in an H-shaped Schlenk vessel with vertical tubes of the dimensions $2 \times 17 \text{ cm}$ and a horizontal tube of the dimensions $2 \times 7 \text{ cm}$. A solution of **4** (0.19 g, 0.001 mol) in thf (10 mL) was placed into one tube, and a solution of **2** (0.15 g, 0.001 mol) in thf (10 mL) into the other tube. Then pure thf was gently layered over both solutions up to the middle level of the horizontal tube (ca. 120 mL in total). The reaction vessel was kept at ambient temperature over two weeks. The solvent was removed and the crystals that had formed were washed with thf and dried under vacuum. Salt **5** formed large black-green plate-like crystals. Yield: 0.31 g (93%); m.p. (sealed capillary): $>300^\circ\text{C}$. $\text{C}_{12}\text{H}_{10}\text{CoN}_4\text{S}_2$ (333.29): calcd. C 43.24, H 3.02, N 16.81; found C 43.32, H 2.88, N 16.56.

Crystallographic Analysis: The XRD data for salt **5** were collected with a Stoe IPDS diffractometer by using Mo- K_α ($\lambda = 71.073 \text{ pm}$) radiation with a graphite monochromator. The structure was solved by direct methods using the SHELXS-97 program^[23] and refined by the least-squares method in the full-matrix anisotropic (isotropic for hydrogen atoms) approximation implemented in the SHELXL-97 program.^[23] $\text{C}_{12}\text{H}_{10}\text{CoN}_4\text{S}_2$, $M = 333.29$, monoclinic, $a = 770.54(13)$, $b = 725.67(7)$, $c = 1090.80(19) \text{ pm}$, $\beta = 95.347(19)^\circ$, $V = 0.60728(16) \text{ nm}^3$, $T = 203(2) \text{ K}$, space group = $P2_1/c$, $Z = 2$, $\rho_{\text{calcd.}} = 1.823 \text{ Mg m}^{-3}$, $\mu(\text{Mo-}K_\alpha) = 1.744 \text{ mm}^{-1}$, reflections measured = 1183, unique reflections = 1023 [$R(\text{int}) = 0.000$], no. of parameters = 88, $R_{\text{obs}} = 0.0287$, $wR_{2\text{obs}} = 0.0730$, $\Delta\rho_{\text{min,max}} = -0.449, 0.378$, g.o.f. = 1.151. CCDC-683564 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.

Calculations: As mentioned earlier, for the theoretical analysis of the magnetic structure of the salt **5** we used a Heisenberg Hamiltonian as given by Equation (3). The exchange integrals (J_{AB}) between selected pairs of radical anions **1** were calculated for the XRD crystal structure of **5** by using the spin-unrestricted broken-symmetry approach^[15] at the DFT/UB3LYP/6-31+G(d) level of theory.^[16] The J_{AB} values were obtained from Equation (5), where E^{T} is the energy of the triplet state of the pair of radical anions, and E_{BS}^{S} is the energy of the open-shell singlet state within the broken-symmetry approach.^[15]

$$J_{\text{AB}} = E_{\text{BS}}^{\text{S}} - E^{\text{T}} \quad (5)$$

In all cases the $\langle S^2 \rangle$ value for the broken-symmetry singlet state was ca. 1.02. The accuracy of the energy calculations was chosen to be 10^{-7} H which provided calculations of J_{AB} with an accuracy of 0.04 cm^{-1} . All calculations were performed by using the Gaussian 03 suite of programs.^[24] The Van Vleck equation for $\chi(T)$ was used in the general form [Equation (2)].^[20] In this work we were able to perform an exact diagonalization of the Hamiltonian matrix for clusters not exceeding a $[3 \times 4]$ grid of the spins $1/2$.

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- [1] a) C. M. Robertson, D. J. T. Myles, A. A. Leitch, R. W. Reed, B. M. Dooley, N. L. Frank, P. A. Dube, L. K. Thompson, R. T. Oakley, *J. Am. Chem. Soc.* **2007**, *129*, 12688–12689; b) A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube, R. T. Oakley, *Chem. Commun.* **2007**, 3368–3370; c) A. A. Leitch, R. W. Reed, C. M. Robertson, J. F. Britten, X. Yu, R. A. Secco, R. T. Oakley, *J. Am. Chem. Soc.* **2007**, *129*, 7903–7914; d) J. L. Brusso, K. Cvrkalj, A. A. Leitch, R. T. Oakley, R. W. Reed, C. M. Robertson, *J. Am. Chem. Soc.* **2006**, *128*, 15080–15081; e) J. L. Brusso, S. Derakhshan, M. E. Itkis, H. Kleinke, R. C. Haddon, R. T. Oakley, R. W. Reed, J. F. Richardson, C. M. Robertson, L. K. Thompson, *Inorg. Chem.* **2006**, *45*, 10958–10966; f) 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.

- [2] a) K. Awaga, T. Tanaka, T. Shirai, Y. Umezono, W. Fujita, *C. R. Chim.* **2007**, *10*, 52–59; b) K. Awaga, T. Tanaka, T. Shirai, M. Fujimori, Y. Suzuki, H. Yoshikawa, W. Fujita, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 25–34; c) K. Okamoto, T. Tanaka, W. Fujita, K. Awaga, T. Inabe, *Angew. Chem. Int. Ed.* **2006**, *45*, 4516–4518.
- [3] a) M. Deumal, S. LeRoux, J. M. Rawson, M. A. Robb, J. J. Novoa, *Polyhedron* **2007**, *26*, 1949–1958; b) J. M. Rawson, A. Alberola, A. Whalley, *J. Mater. Chem.* **2006**, *16*, 2560–2575; c) J. M. Rawson, J. Luzon, F. Palacio, *Coord. Chem. Rev.* **2005**, *249*, 2631–2641; d) M. Mito, T. Kawai, K. Takeda, S. Takagi, Y. Matsushida, H. Deguchi, J. M. Rawson, F. Palacio, *Polyhedron* **2001**, *20*, 1509–1512; e) J. M. Rawson, F. Palacio, *Struct. Bonding (Berlin)* **2001**, *100*, 93–128; f) J. M. Rawson, G. D. MacManus, *Coord. Chem. Rev.* **1999**, *189*, 135–168.
- [4] a) T. S. Cameron, A. Decken, R. M. Kowalczyk, E. J. L. McInnes, J. Passmore, J. M. Rawson, K. V. Shuvaev, L. K. Thompson, *Chem. Commun.* **2006**, 2277–2279; b) A. Decken, S. M. Mattar, J. Passmore, K. V. Shuvaev, L. K. Thompson, *Inorg. Chem.* **2006**, *45*, 3878–3886; c) T. S. Cameron, M. T. Le-maire, J. Passmore, J. M. Rawson, K. V. Shuvaev, L. K. Thompson, *Inorg. Chem.* **2005**, *44*, 2576–2578; d) G. Antorrena, S. Brownridge, T. S. Cameron, F. Palacio, S. Parsons, J. Passmore, L. K. Thompson, F. Zarlaida, *Can. J. Chem.* **2002**, *80*, 1568–1583.
- [5] a) K. E. Preuss, *Dalton Trans.* **2007**, 2357–2369; b) M. Jennings, K. E. Preuss, J. Wu, *Chem. Commun.* **2006**, 341–343.
- [6] a) R. T. Boere, A. M. Bond, T. Chivers, S. W. Feldberg, T. L. Roemmele, *Inorg. Chem.* **2007**, *46*, 5596–5607; b) R. T. Boere, H. M. Tuononen, T. Chivers, T. L. Roemmele, *J. Organomet. Chem.* **2007**, *692*, 2683–2696; c) R. T. Boere, T. L. Roemmele, *Coord. Chem. Rev.* **2000**, *210*, 369–445.
- [7] a) N. P. Gritsan, A. V. Lonchakov, E. Lork, R. Mews, E. A. Pritchina, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2008**, 1994–1998; b) I. Yu. Bagryanskaya, Yu. V. Gatilov, N. P. Gritsan, V. N. Ikorskii, I. G. Irtegov, A. V. Lonchakov, E. Lork, R. Mews, V. I. Ovcharenko, N. A. Semenov, N. V. Vasilieva, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2007**, 4751–4761; c) V. N. Ikorskii, I. G. Irtegov, E. Lork, A. Yu. Makarov, R. Mews, V. I. Ovcharenko, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2006**, 3061–3067; d) A. Yu. Makarov, I. G. Irtegov, 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.
- [8] a) H. Bock, K. Ruppert, C. Naether, Z. Havlas, H.-F. Herrmann, C. Arad, I. Goebel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel, B. Solouki, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 550–581; b) B. Cetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, J. B. Pedley, *J. Chem. Soc. D, Chem. Commun.* **1971**, 1370–1371.
- [9] a) M. F. Ryan, D. E. Richardson, D. L. Lichtenberger, N. F. Gruhn, *Organometallics* **1994**, *13*, 1190–1199; b) J. C. Green, *Struct. Bonding (Berlin)* **1986**, *43*, 37–112; c) S. Evans, M. L. H. Green, B. Jewitt, G. H. King, A. F. Orchard, *J. Chem. Soc. Faraday Trans. 2* **1974**, *70*, 356–376; d) J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Hussain, K. Siegbahn, *J. Chem. Phys.* **1972**, *57*, 1185–1192.
- [10] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics*, Academic Press, London, **1982**.
- [11] a) D. C. Johnston, in *Handbook of Magnetic Materials* (Ed.: K. H. J. Buschow), Elsevier, Amsterdam, **1997**; b) R. Nath, A. V. Mahajan, N. Buttgen, C. Kegler, J. Hemberger, A. Loidl, *J. Phys.: Condens. Matter* **2006**, *18*, 4285–4294.
- [12] a) G. S. Rushbrooke, P. J. Wood, *Proc. Phys. Soc. London A* **1955**, *68*, 1161–1169; b) G. S. Rushbrooke, P. J. Wood, *Mol. Phys.* **1958**, *1*, 257–283.
- [13] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, **1997**, p. 1340.
- [14] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.
- [15] a) L. Noodleman, *J. Chem. Phys.* **1981**, *74*, 5737–5743; b) L. Noodleman, E. R. Davidson, *Chem. Phys.* **1986**, *109*, 131–143; c) L. Noodleman, D. A. Case, J. M. Mouesca, *Coord. Chem. Rev.* **1995**, *144*, 199–244; d) H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka, K. Yamaguchi, *Coord. Chem. Rev.* **2000**, *198*, 265–295.
- [16] a) P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793–1873; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [17] a) Z. Wei, A. Du, *Phys. Status Solidi B* **1993**, *175*, 237–245.
- [18] a) M. Takashi, *Phys. Rev. B* **1989**, *40*, 2494–2501; b) M. S. Makivic, H.-Q. Ding, *Phys. Rev. B* **1991**, *43*, 3562–3574; c) Y. Okabe, M. Kikuchi, *J. Phys. Soc. Jpn.* **1988**, *57*, 4351–4358; d) M. Kikuchi, Y. Okabe, *J. Phys. Soc. Jpn.* **1989**, *58*, 679–683; e) M. Hasenbusch, S. Meyer, *Phys. Lett. B* **1990**, *241*, 238–242.
- [19] a) M. Lüscher, P. Weisz, *Nucl. Phys. B* **1988**, *300*, 325–359; b) J. Adler, C. Holm, W. Janke, *Phys. A* **1993**, *201*, 581–592.
- [20] a) O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, **1993**, p. 112; b) M. Deumal, M. J. Bearpark, J. J. Novoa, M. A. Robb, *J. Phys. Chem. A* **2002**, *106*, 1299–1315; c) L. K. Thompson, O. Waldmann, Z. Xu, *Coord. Chem. Rev.* **2005**, *249*, 2677–2690.
- [21] S. N. Konchenko, N. P. Gritsan, A. V. Zibarev, work in progress.
- [22] V. T. Kalinnikov, Yu. V. Rakitin, *Introduction in Magnetochemistry. Method of Static Magnetic Susceptibility*, Nauka, Moscow, **1980**, p. 302 (in Russian).
- [23] G. M. Sheldrick, *SHELX-97 – Programs for Crystal Structure Analysis*, release 97-2, University of Göttingen, Germany, **1997**.
- [24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, revision B.02, Gaussian Inc., Pittsburgh PA, **2003**.

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