

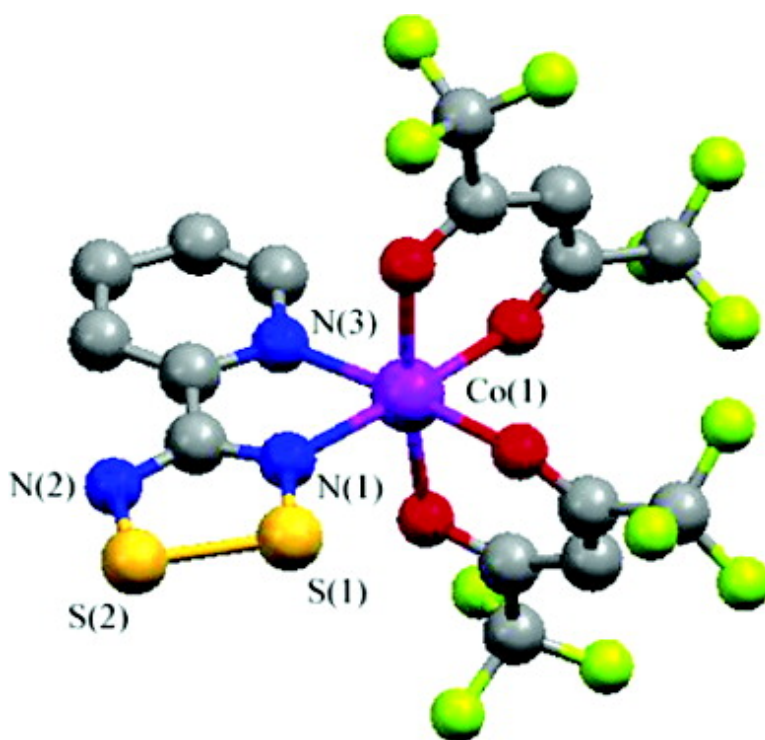
Communication

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J. Am. Chem. Soc., **2004**, 126 (32), 9942-9943 • DOI: 10.1021/ja046304t • Publication Date (Web): 23 July 2004

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Design and Synthesis of a 4-(2'-Pyridyl)-1,2,3,5-Dithiadiazolyl Cobalt Complex

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The rational design of materials with predictable or controllable magnetic properties is a prominent objective of current materials research.¹ One possible strategy employs the mediation of magnetic coupling between high-spin metal centers via spin-bearing chelating ligands. Chelation, as opposed to monodentate coordination, of the metal to the ligand is a key strategic element, as it fixes the orientation of the ligand and metal magnetic orbitals with respect to one another. At present, appropriate ligands fall into one of four classes: semiquinones² and their derivatives,³ nitronyl nitroxides,⁴ verdazyls,⁵ and, most recently, azaphenylenyls.⁶ Herein, we report a new class of radical chelating ligand, based on a sulfur–nitrogen heterocycle, and demonstrate the presence of magnetic coupling between the unpaired electron on the ligand and those on a coordinated high-spin Co(II) center.

Heterocyclic molecules containing sulfur and nitrogen have been studied extensively with respect to the synthesis and properties of stable neutral radical and radical cation species. To this end, a large number of 1,2,3,5-dithiadiazolyl (DTDA) radicals, with a wide variety of substituents at the 4-position, have been prepared, isolated and characterized.⁷ The DTDA moiety is a planar ring with a seven π -electron count. The unpaired electron resides in a π^* molecular orbital that is nodal at the C atom and antibonding with respect to the S–S and S–N bonds. Ab initio calculations predict that the distribution of spin density is roughly equivalent over the S and N atoms, and this prediction is compatible with literature measured EPR spectra.^{7a} Several investigations into the reactivity of DTDA radicals have been reported. These include studies involving bonding to metal centers through the DTDA sulfur atoms⁸ and coordination to metal centers via the pyridine nitrogen atom of a 4-(3'-pyridyl)- and a 4-(4'-pyridyl)-substituted DTDA.⁹ Surprisingly, there are no literature studies involving bonding to metal centers via the DTDA nitrogen atoms. Herein, we report the synthesis of 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl **1** (Chart 1), designed as a chelating radical ligand, and the coordination of this ligand to bis(hexafluoro-acetylacetonato)-cobalt (Co(hfac)₂) to give the complex **2**.

The synthesis of **1** was achieved following standard preparatory procedures for similar known DTDA radicals.¹⁰ Dark purple blocklike crystals of **1** were obtained in moderate to high yield via sublimation in a gradient-temperature tube furnace.

The physical properties of **1** are similar to those of known DTDA radicals. The room-temperature solution EPR in CH₂Cl₂ is the 1:2:3:2:1 pattern anticipated for coupling of one unpaired electron to two equivalent nitrogens ($a_N = 5.02$ g, $g = 2.010(6)$). Cyclic voltammetry (CV) of **1** in dry CH₃CN (0.1 M *n*-Bu₄NPF₆) shows a reversible oxidation wave at $E_{1/2}(\text{ox}) = 0.62$ V (vs SCE) and a reversible reduction wave at $E_{1/2}(\text{red}) = -0.81$ V (vs SCE). In

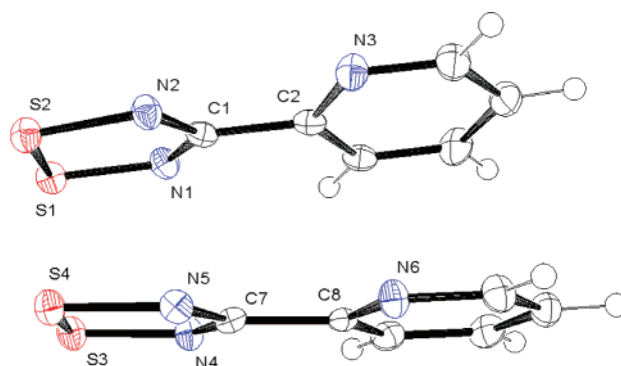
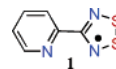


Figure 1. ORTEP depiction of a dimer of neutral radical **1**. Data collected at $T = 100$ K. Selected bond distances (Å): S1–S2, 2.093; S1–N1, 1.634; S2–N2, 1.634. Selected bond angles (deg): C1–N1–S1, 113.85; C1–N2–S2, 113.15. Selected dihedral angles (deg): N2–C1–C2–N3, 11.5; N5–C7–C8–N6, 3.8. Selected intermolecular distances (Å): S1–S3, 3.018; S2–S4, 3.005.

Chart 1



the crystalline state, the radicals form π -stacked dimers (Figure 1), with intermolecular S–S contacts of 3.005 and 3.018 Å (at 100 K). The solid is therefore expected to be diamagnetic.

Complex **2** was prepared by stirring equimolar amounts of **1** and Co(hfac)₂·2THF in dry THF, under an inert atmosphere, at ambient temperature for 20 min. The Co(hfac)₂·2H₂O, prepared using a literature procedure,¹¹ was converted to Co(hfac)₂·2THF by recrystallization from THF in order to avoid the introduction of water and potential decomposition of the radical **1**. Complex **2** was recovered from the reaction mixture as a dark brown powder. Small crystals of **2** were obtained by sublimation. Crystals suitable for single-crystal X-ray diffraction and SQUID magnetometry were grown by slow evaporation of CH₂Cl₂ from a saturated solution under an inert atmosphere.

The single-crystal X-ray structure of **2** (Figure 2) confirms the bidentate chelation of the intact DTDA **1** to the cobalt metal center via the pyridine nitrogen atom and one of the DTDA nitrogen atoms. The complex does not form dimers in the solid state. The closest intermolecular S–S contacts are 4.431 and 4.834 Å. Bond distances and bond angles within the DTDA ring do not change significantly upon chelation.

Magnetic susceptibility measurements (Figure 3) were collected between 2 and 300 K, at a field strength of 4000 G. These distinctly indicate a maximum χT of 3.66 emu K mol⁻¹ at 70 K. This increase in χT with decreasing temperature from rt strongly suggests ferromagnetic coupling between the unpaired electron on the ligand and the Co(II) center, giving an $S = 2$ electronic ground state.

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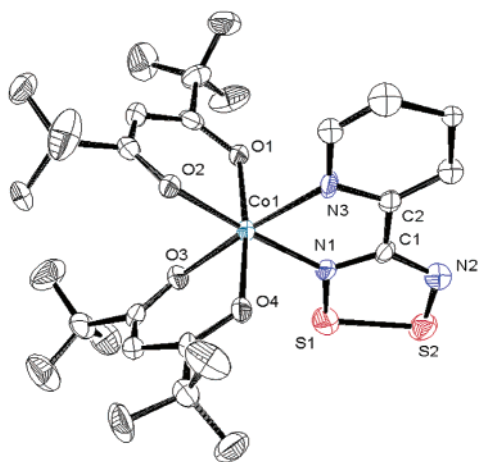


Figure 2. ORTEP depiction of complex **2** with protons excluded for clarity. Data collected at $T = 100$ K. Selected bond distances (Å): S1–S2, 2.091; N1–S1, 1.648; N2–S2, 1.619; Co1–N1, 2.122; Co1–N3, 2.103; average Co–O, 2.050. Selected bond angles (deg): C1–S1–N1, 115.11; C1–N2–S2, 114.47. Selected dihedral angles (deg): N1–C1–C2–N3, 7.4.

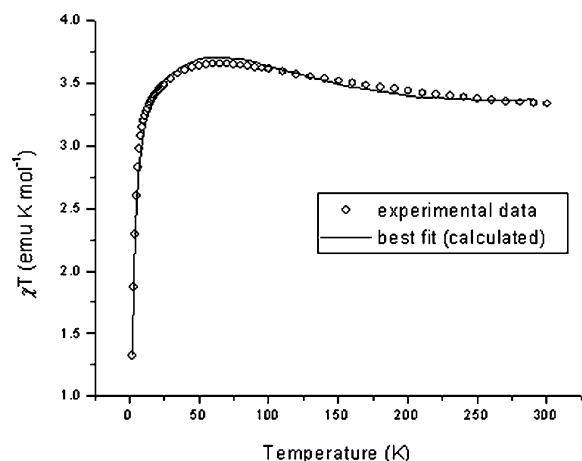


Figure 3. χT versus T plot for complex **2**, collected at 4000 G. Magnetic susceptibility was measured using two consecutive cycles, each from 2 to 300 K and back. As no variation was observed, a representative cycle (2–300 K) is shown. The data were modeled as described in the text. The best fit is shown.

Magnetic properties of high-spin Co(II) in a low-symmetry pseudo-octahedral ligand environment have been modeled by others using both isotropic¹² and anisotropic¹³ spin Hamiltonians. In this preliminary account, we present results obtained by modeling the magnetic data as a linear two-spin system using an isotropic spin Hamiltonian ($H = -J(S_{\text{Co}}S_{\text{DTDA}}) + g\beta SH - zJ' + \chi_{\text{tip}}$). The best fit yields the following parameters: $J_{\text{Co-DTDA}} = 82.2 \text{ cm}^{-1}$, $g = 3.28$, $zJ' = -0.15 \text{ cm}^{-1}$, and $\chi_{\text{tip}} = 0.0028 \text{ cm}^{-1}$, where zJ' accounts for the intermolecular coupling in the solid state and χ_{tip} accounts for the temperature-independent paramagnetism.

The results presented herein demonstrate that SN heterocycles can be used as building blocks for the design of new spin-bearing ligands. This has the potential to significantly increase the number of available synthetic strategies in the field of magnetic materials design.

Acknowledgment. We thank the Oakley group at University of Waterloo for extensive use of their sublimation furnaces and access to their EPR spectrometer. We thank David A. Shultz at N.C.S.U. for access to his SQUID magnetometer and Mike H. Whangbo at N.C.S.U. for use of his magnetic modeling program. Funding for this work was provided by NSERC of Canada through an RGPIN grant and an UFASA grant to K.E.P.

Supporting Information Available: Experimental details and CIF data for **1** and **2**, calculated Mulliken atomic spin densities for **1**, and a saturation plot for **2** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA046304T