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High-Spin Ribbons and Antiferromagnetic Ordering of a Mn^{II}-Biradical-Mn^{II} Complex

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Supporting Information

ABSTRACT: A binuclear metal coordination complex of the first thiazyl-based biradical ligand **1** is reported (**1** = 4,6-bis(1,2,3,5-dithiadiazolyl)pyrimidine; hfac =1,1,1,5,5,5,-hexafluoroacetylacetonato-). The $Mn(hfac)_2$-biradical-$Mn(hfac)_2$ complex **2** is a rare example of a discrete, molecular species employing a neutral bridging biradical ligand. It is soluble in common organic solvents and can be easily sublimed as a crystalline solid. Complex **2** has a spin ground state of $S_T = 4$ resulting from antiferromagnetic coupling between the $S_{birad} = 1$ biradical bridging ligand and two $S_{Mn} = 5/2$ Mn^{II} ions. Electrostatic contacts between atoms with large spin density promote a ferromagnetic arrangement of the moments of neighboring complexes in ribbon-like arrays. Weak antiferromagnetic coupling between these high-spin ribbons stabilizes an ordered antiferromagnetic ground state below 4.5 K. This is an unusual example of magnetic ordering in a molecular metal-radical complex, wherein the electrostatic contacts that direct the crystal packing are also responsible for providing an efficient exchange coupling pathway between molecules.

Organic biradicals have an important place in the historical development of bond theories. In 1936, Hückel outlined a molecular orbital approach elucidating π-conjugated (non-Kekulé) biradicals[1] and laid the foundation for a simple topological model used to predict the ground state of biradical alternant hydrocarbons.[2] From a synthetic standpoint, noteworthy contributions include those of Tschitschibabin,[3] Schlenk,[4] and Yang,[5] however Ullman's biradical, bis(nitronyl) nitroxide,[6] changed the field by demonstrating unprecedented stability of a light-atom π-biradical species. More recent developments have been primarily application driven, including biradical designs for dynamic nuclear polarization (DNP) agents,[7] possible spin-pump devices,[8] and conductive[9] and magnetic materials.[10] While monoradicals have been employed as paramagnetic bridging ligands between metal ions (the so-called "metal-radical approach" to molecular magnets),[11] similar use of biradicals is less common.[12] As noted by Rajca,[13] designs featuring biradicals as bridging ligands typically result in coordination polymers[14] and often suffer from weak exchange coupling due to loss of coplanarity, or twisting, that destroys the extended π-conjugation.[15] Discrete, soluble metal-biradical-metal complexes are relatively rare with one notable contribution, a binuclear complex of a bis(semiquinone) biradical dianion reported by Shultz.[12] Such species can act as model systems to study magnetic interactions. They also provide a further element with which to modify application-driven biradical architectures.

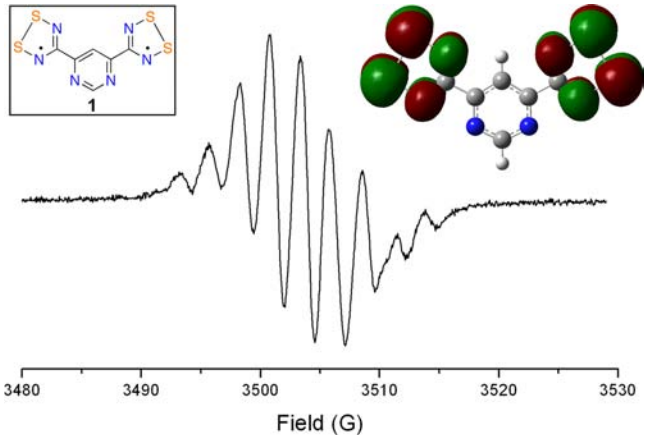

Figure 1. EPR spectrum of **1** in 50/50 mixture of MePh/CH_2Cl_2 at RT. Inset left: line drawing of **1**. Inset right: one of two π* SOMOs of biradical ligand **1**.

In devising the first thiazyl-based biradical ligand, 4,6-bis(1,2,3,5-dithiadiazolyl)pyrimidine **1** (Figure 1), we have two goals. One is to create a discrete, molecular π-biradical-bridged metal complex designed to maintain coplanarity of the extended π-system. To this end, we use chelation of two $Mn(hfac)_2$ fragments to anchor the bridging biradical ligand in complex **2** in a roughly planar geometry (hfac =1,1,1,5,5,5-hexafluoroacetylacetonato-) (Figure 2). Planarity is important because it stabilizes the triplet ground state of the *meta*-substituted pyrimidine biradical ligand. It is worth noting that the architecture used to maintain planarity in **2** is different from

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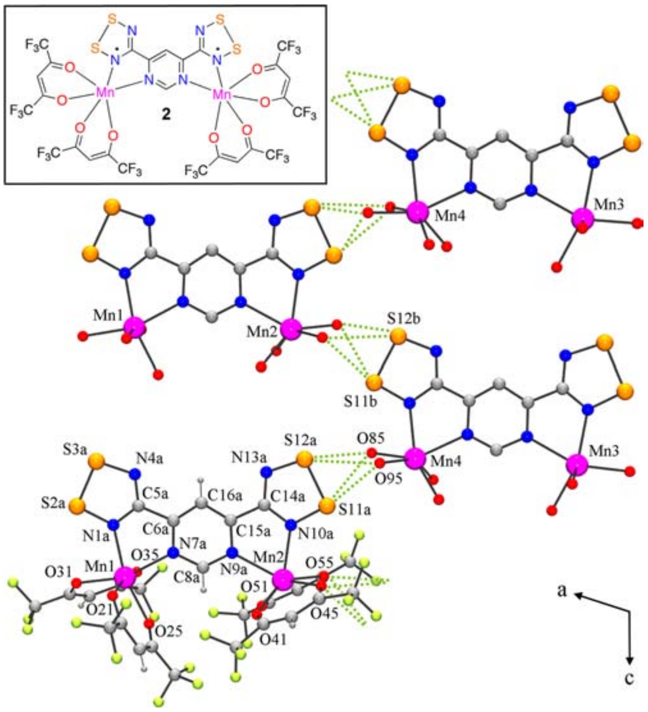

Figure 2. A ribbon-like assembly of molecules in **2** governed by the close $S^{\delta+}\cdots O^{\delta-}$ contacts; H atoms have been omitted and only O atoms of the hfac are shown on all but one molecule. Inset: line drawing of **2**.

that of the bis(semiquinone) analog,[12] wherein planarity must be maintained as a function of crystal packing rather than by molecular design. The second goal is to achieve magnetic ordering of a discrete, molecular metal-radical complex by harnessing the properties of thiazyl radicals, particularly the large spin density and partial positive charge at unencumbered peripheral sulfur atoms. We have previously shown that strong electrostatic contacts between $S^{\delta+}$ atoms of a thiazyl radical and $O^{\delta-}$ atoms of a neighboring hfac ligand direct the solid-state packing of thiazyl-metal complexes and provide an efficient pathway for exchange-coupling between molecules.[16,17] By using a biradical complex, we aim to increase the dimensionality of these contacts and create an exchange-coupled network. High-spin ribbons of complex **2** are formed in the solid state and weak antiferromagnetic (AF) interactions between these ribbons are sufficient to generate an AF ordered ground state. Thus, **2** is a rare example of a magnetically ordered, nonpolymeric, metal-radical complex.

Biradical ligand **1** is prepared starting from 4,6-dicyanopyrimidine[18] which is converted to N^4,N^4,N^4,N^6,N^6,N^6-hexakis-(trimethylsilyl)pyrimidine-4,6-dicarboxamidine. Ring closure is effected by reaction with excess S_2Cl_2 generating the dication chloride $[\mathbf{1}^{2+}][Cl^-]_2$. An efficient reduction to the biradical ligand **1** is achieved using triphenylantimony, a common reducing agent for generating 1,2,3,5-dithiadiazolyl (DTDA) radicals.[19] Sublimation of **1** results in high-purity, microcrystalline material, however neither sublimation nor recrystallization produces crystals suitable for structural analysis. In the solid state, **1** is diamagnetic, which is readily explained by the propensity of DTDA radicals to form diamagnetic π-stacked "dimers".[20] Although insoluble in most organic solvents, **1** is moderately soluble in a 1:1 mixture of toluene and methylene chloride. Solubility is important for subsequent coordination reactions employing **1** as a ligand but also facilitates characterization of this biradical species. The formation of π-stacked "dimers" of DTDA radicals is known to be reversible, such that a monomer/dimer equilibrium exists in solution,[21] making it possible to measure the EPR spectrum of a very dilute solution of **1** in $MePh/CH_2Cl_2$ at ambient temperature (Figure 1). A 9-line pattern centered at $g = 2.0104$ is evident, with a peak-to-peak distance of roughly 2.55 G. This is consistent with a biradical species wherein the exchange coupling between the two unpaired electrons is significantly larger than the hyperfine interactions with four approximately equivalent ^{14}N nuclei ($a_N \approx 5.1$ G)[22] and suggests a preference for planarity of the ring systems in solution.

Using a simple topological model, a triplet ground state is predicted for *meta*-substituted biradical alternant hydrocarbons.[2] Density functional theory calculations (uB3LYP/6-31g(d,p)) on the gas-phase geometry-optimized biradical ligand **1** predict a planar structure and also assign an $S_{\text{birad}} = 1$ ground state to biradical **1** ($\Delta E_{\text{S-T}} = 28.33$ cm^{-1}). The singly occupied molecular orbitals (SOMOs) are π^* in nature, with coefficients on the S and N atoms of the DTDA heterocycles (Figure 1) and closely resemble the SOMO of typical DTDA radicals.[23] The result is large alpha spin density on the DTDA sulfur and nitrogen atoms (Figure S1).

Coordination complex **2** is prepared by reacting biradical ligand **1** and $Mn(hfac)_2(THF)_2$ in a mixture of toluene and CH_2Cl_2. Despite its high molecular weight, complex **2** is significantly more volatile than ligand **1**, and sublimation is the most facile method of purification and crystal growth for structural analysis.

Complex **2** crystallizes in $P2_1/c$ with two molecules per asymmetric unit. The molecular structure of **2** (Figure 2) can be described as *N,N*-chelation of two $Mn(hfac)_2$ fragments by the roughly planar biradical ligand **1**. However, the most important feature is the abundance of close intermolecular contacts between sulfur and oxygen atoms. Electrostatic interactions between the $S^{\delta+}$ atoms of DTDA rings and electronegative atoms of neighboring molecules, such as $O^{\delta-}$, $N^{\delta-}$, and $Br^{\delta-}$,[24] are known to influence the packing of DTDA radicals. In the present case, multiple short $S^{\delta+}\cdots O^{\delta-}$ contacts between the two distinct molecules in the asymmetric unit are apparent. Further short $S^{\delta+}\cdots O^{\delta-}$ contacts between the symmetry-unrelated molecules in adjacent asymmetric units define ribbon-like structures propagating along the *c*-axis in the (010) plane (Figure 2).

The magnetic properties of **2** were investigated between 300 and 1.8 K with an applied field of 1000 Oe (Figure 3). At 300 K, the χT product is 9.7 cm^3 K mol^{-1}, which is close to the expected value (9.75 cm^3 K mol^{-1}) for two noninteracting *hs*-d^5 ions ($S_{\text{Mn}} = 5/2$) plus one organic biradical ($S_{\text{birad}} = 1$), assuming $g \approx 2$. As the temperature is lowered, the χT product decreases to 8.4 cm^3 K mol^{-1} at 33 K and then increases rapidly with further cooling to a maximum value of 13.9 cm^3 K mol^{-1} at 5.5 K. This magnetic behavior is consistent with AF coupling between the Mn^{II} ions and the $S_{\text{birad}} = 1$ biradical ligand, generating a spin ground state of $S_T = 4$ for a single molecule of **2**. It should be noted that AF exchange coupling is anticipated by simple orbital overlap arguments (nonorthogonal overlap between the π^* magnetic orbitals of the ligand and at least one of the 3d orbitals of each *hs*-d^5 Mn^{II}).[25] The magnetic data can be numerically fitted down to 9 K using an isotropic Heisenberg spin Hamiltonian, $\hat{H} = -2J(\hat{S}_{\text{Mn1}} + \hat{S}_{\text{Mn2}})\cdot\hat{S}_{\text{birad}}$, treating the molecule as a spin trimer composed of two $S_{\text{Mn}} =$

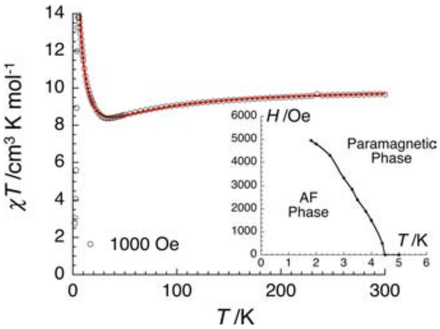

Figure 3. Temperature dependence of χT product for **2** at 1000 Oe (χ defined as M/H per complex); open circles indicate measured data points; red line represents best fit as described in text. Inset: (T, H) magnetic phase diagram determined from data shown in Figure 4.

5/2 and one $S_{\text{birad}} = 1$ and including intercomplex magnetic interactions zJ' in the frame of the mean-field approximation.[26] The best values for this model are $J/k_B = -5.9(1)$ K, $zJ'/k_B = +0.17(3)$ K, and $g = 2.03(5)$.

Importantly, the above model of the magnetic susceptibility leads to *effective* and *dominant* intercomplex interactions of a ferromagnetic nature. The closest actual intermolecular contacts in the structure of **2** are the short $S^{\delta+}\cdots O^{\delta-}$ distances (2.92 − 3.28 Å) between the thiazyl ring of one molecule and the hfac oxygen atom of a neighboring molecule. We have previously shown that contacts of this kind in Mn(hfac)$_2$ complexes of DTDA monoradicals[17] provide an efficient pathway for AF coupling between the radical and a neighboring Mn$^{\text{II}}$ ion and can be understood in the context of molecular orbital theory.[16] Since the coupling between the biradical ligand and the coordinated Mn$^{\text{II}}$ ions is also AF, the net result in **2** is a ferromagnetic arrangement of the Mn-biradical-Mn complex moments in the ribbon-like networks. As described below, an additional AF coupling between these networks is enough to stabilize a three-dimensional ordered AF ground state.

The temperature dependence of the susceptibility χ has been measured at various applied fields (Figure 4a) and shows a maximum in χ below 5 K. The temperature at which this peak occurs shifts to lower values with increasing applied field. The field dependence of the magnetization (M vs H) has been recorded at various temperatures (Figure 4b,c) and shows no clear saturation up to 7 T (reaching 8.5 μ_B at 1.83 K). Below 4.5 K, the dM/dH vs H curves exhibit a characteristic maximum (at 1.83 K roughly around 5000 Oe; Figure 4d). This feature is indicative of a field-induced transition between an AF ordered phase at low fields and a paramagnetic phase at higher fields. In order to determine the temperature dependence of this critical field, the maximum of the dM/dH vs H and χ vs T plots (Figure 4d, a) has been followed, allowing the construction of the (T, H) phase diagram shown in Figure 3 inset. This critical field extrapolates to zero at a Néel temperature (T_N) of ~4.5 K. Under an applied dc field, **2** displays metamagnetic behavior associated with a critical field extrapolated at 0 K to be $H_C(0) \approx$ 5500 Oe. From this field, the average inter-ribbon interaction is estimated to be $zJ_{\text{perp}}/k_B \approx -94$ mK through the relation $2z|J_{\text{perp}}|S_T^2 = g\mu_B H_C(0) S_T$.

Ligand **1** is the first biradical thiazyl-based ligand. Unlike most bi- or multiradical ligands, **1** has been designed to maintain coplanarity of the extended π-system when coordinated to two metal ions, thereby ensuring an $S_{\text{birad}} = 1$ spin ground state. The two *N,N*-coordination "pockets" of ligand **1** allow for chelation of two Mn(hfac)$_2$ fragments, generating a rare example of a discrete (i.e., noncoordination polymer) biradical-bridged coordination complex **2** that is soluble and volatile. The judicious design of **1** provides complex **2** with a means of engaging in multiple close electrostatic contacts between atoms with large spin density. These contacts enable a ferromagnetic arrangement of the moments of neighboring complexes in a ribbon-like array. Weak antiferromagnetic coupling between the high-spin ribbons is sufficient to stabilize an antiferromagnetically ordered ground state (T_N = 4.5 K). Magnetic ordering of discrete molecular metal-radical complexes, particularly through an established exchange mechanism, is rarely observed.

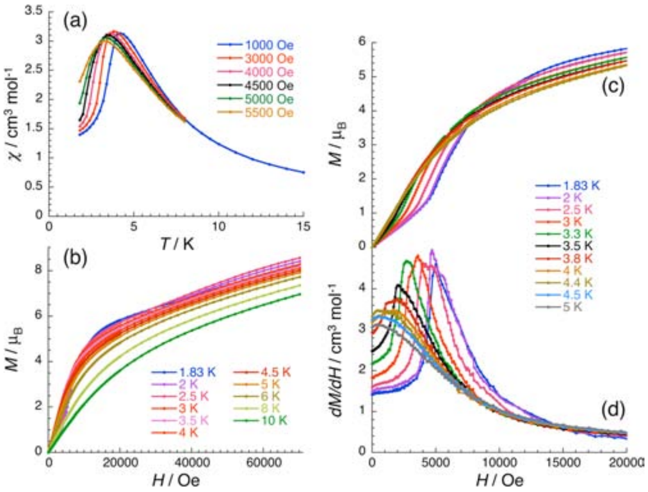

Figure 4. (a) Temperature dependence of the magnetic susceptibility below 15 K for applied dc field below 5500 Oe; (b) field dependence of the magnetization below 10 K up to 7 T; (c) enlarged view of the field dependence of the magnetization below 4.4. K up to 2 T; (d) field dependence of the field derivative of the magnetization (dM/dH) below 5 K up to 2 T, highlighting the antiferromagnetic-paramagnetic phase transition. Dots represent data points, and lines provide visual aid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic, computational, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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