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A Dinuclear Ni(II) Complex with Two Types of Intramolecular Magnetic Couplings: Ni(II)–Ni(II) and Ni(II)–TTF$^{\bullet+}$

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A dinuclear Ni(II) complex involving tetrathiafulvalene (TTF) radicals as ligands has been prepared and characterized, $[Ni_2(\mu\text{-Cl})_2(L^{\bullet+})_2](I_3)_4(I_2)_3\cdot(H_2O)_2\cdot(C_4H_8O)_3$ (**1**), *L* = 4,5-bis(2-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene. There are two types of intramolecular magnetic exchange interactions, namely one ferromagnetic Ni(II)–Ni(II) and one antiferromagnetic Ni(II)–TTF$^{\bullet+}$. This study is new in the respect of revealing a magnetic exchange interaction between a TTF$^{\bullet+}$ radical and a paramagnetic transition metal ion. This is due to the fact of a direct binding of the transition metal ion to the skeleton of the TTF$^{\bullet+}$ radical.

Within the context of magnetic molecular conductors derived from tetrathiafulvalene (TTF), a great deal of interest has been devoted to the preparation of organic−inorganic hybrid materials revealing significant interaction between the conducting π-electrons and localized d-electrons.[1,2] The popular strategy for the enhancement of π−d interaction in such dual-property materials is the direct coordination of paramagnetic metal ions to organic radicals through intervening donor atoms derived from pyridine-type heterocycles[3] or phosphine,[4] amide,[5] and acetylacetone[6] substituents. However, for most of the reported coordination compounds, the TTF moieties are in the neutral state,[3,6] and up to now, only very few complexes with TTF ligands have been oxidized to afford their radical states.[7] Moreover, it is important to bear in mind that in all reported cases, there occurs a strong antiferromagnetic coupling between radical pairs.

Previously,[7c] we described the chemical oxidation of the neutral complex $[NiLCl_2]$[3a] with I_2 by a layer diffusion technique. Thereby, a black crystalline dinuclear Ni(II) compound (**1**) forms with the stoichiometry of $[Ni_2(\mu\text{-Cl})_2(L^{\bullet+})_2](I_3)_4(I_2)_3\cdot(H_2O)_2\cdot(C_4H_8O)_3$. Herein we report the solid-state structure[8] (Figure 1) and magnetic properties of the complex **1**, which shows evidence for the weak but sizable intramolecular π−d interaction.

Compound **1** crystallizes in a monoclinic space group (*C*2/*c*), and it is composed of dinuclear μ-chloro-bridged complex cations, $[Ni_2(\mu\text{-Cl})_2(L^{\bullet+})_2]^{4+}$, I_3^- anions, and I_2, in a ratio of

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(8) Crystal data for **1**: $M = 3806.52$ g·mol^{-1}, monoclinic, space group *C*2/*c*, $a = 40.858(2)$ Å, $b = 10.2830(6)$ Å, $c = 28.2342(17)$ Å, $\beta = 132.408(3)°$, $V = 8758.7(9)$ Å^3, $Z = 4$; $D_c = 2.887$ g·cm^{-3}; $T = 153(2)$ K, $\mu = 7.262$ mm^{-1}, Stoe Mark II-Image Plate Diffraction System; 54 649 reflections were collected with 7671 unique and 4513 with $I > 2.0\ \sigma(I)$ yielding $R = 0.0873$, $R_w = 0.2672$, GOF = 1.035.

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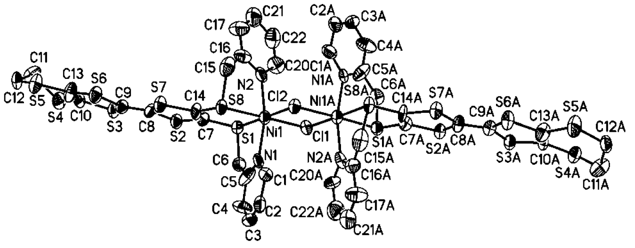

Figure 1. ORTEP (50% probability ellipsoids) structure of **1**. Hydrogen atoms, solvent molecules, and anions are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Ni1−N1 2.070(17), Ni1−N2 2.098(19), Ni1−S1 2.369(5), Ni1−S8 2.402(5), Ni1−Cl1 2.365(5), Ni1−Cl2 2.391(5), C8−C9 1.41(3), C8−S2 1.713(19), C8−S7 1.764(19), S7−C14 1.730(19), C14−C7 1.39(3), C14−S8 1.727(17), C7−S1 1.774(17), C7−S2 1.733(19), C9−S6 1.73(2), C9−S3 1.67(2), S3−C10 1.72(2), C10−C13 1.41(3), C13−S6 1.69(2), C13−S5 1.73(2), C10−S4 1.746(19), Ni1−Ni1A 3.396, N2−Ni1−S8 83.7(5), S8−Ni1−S1 90.53(17), N1−Ni1−S1 84.2(4), N1−Ni1−Cl1 92.0(4), N2−Ni1−Cl2 93.6(5), Ni1−Cl1−Ni1A 91.8(2), Ni1−Cl2−Ni1A 90.5(2).

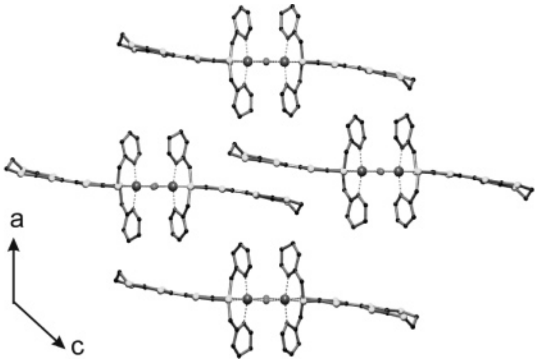

Figure 2. Crystal packing (*ac* projection) of **1**. Hydrogen atoms, solvent molecules, and anions are omitted for clarity.

1:4:3. Iodide is known for its ability to form polyiodides in the presence of iodine.[9] This structure contains asymmetric triiodide ions, as well as iodine molecules that form I_8^{2-} ions with an $[(I_3^-)_2{\cdot}(I_2)]$ configuration. The I_8^{2-} ions, which are related through a symmetry center, are linked to each other by an iodine molecule to give the I_{18}^{4-} ion (Figure S1 in the Supporting Information). Two H_2O and three THF molecules co-crystallize as solvent molecules. Figure 1 shows the molecular structure of the dinuclear complex cation, which represents twice the asymmetric unit; Cl1 and Cl2 lie on a crystallographic 2-fold rotation axis. The distorted octahedral Ni(II) coordination moiety and its bond lengths are at first sight very similar to those of the neutral mononuclear compound $[NiLCl_2]$,[3a] only two chlorides change from terminal to bridging ligands. However and coherently, the TTF moieties are mostly affected by the oxidation, with a lengthening of the central C═C bond (1.41(3) Å for **1** vs 1.334(8) Å for the neutral mononuclear complex[3a]) and a shortening of the central C−S bonds with an average difference of −0.046 Å. Thus, it can clearly be inferred that the TTF units are fully oxidized according to the correlation between the oxidation states of TTF derivatives and bond lengths of central C═C bonds.[7c,10] Compound **1** shows an insulating behavior due to the lack of highly ordered stacking in the donor sublattice which, in turn, is a consequence of the bulky coordination sphere. As depicted in Figure 2, the closest S⋯S contact is 5.80 Å, which renders the $TTF^{\bullet+}$ radicals impossible to couple with each other.

Magnetic susceptibility and magnetization measurements were made in the range 250−1.8 K using a Quantum Design SQUID magnetometer (XL-5). The polycrystalline sample was measured in a saran foil bag. The data were corrected for the experimentally determined diamagnetic contributions of the sample holder and of the sample calculated from Pascal constants; a TIP contribution of 800×10^{-6} emu·mol^{-1} was taken into account.[11] The Levenberg−Marquardt least-squares fitting algorithm, in combination with MAGPACK,[12] was used to model the experimental magnetic data. The Heisenberg−Dirac−Van Vleck Hamiltonian ($\mathbf{H} = -2J\mathbf{S}_1{\cdot}\mathbf{S}_2$) was applied.

To begin with the analysis of the magnetic data, it is important to bear in mind that there is a principal difficulty in accurately describing the electronic ground state of this actual compound. This is due to the fact that the single-ion anisotropy shows effects on the energies of the ground-state manifold with the same order of magnitude as do the exchange interactions; thus, these effects compete, and as a result, the energy splitting pattern will not be simple. Consequently, it may not be feasible to find only one unique set of physical parameters, especially while applying a model with approximated axial symmetry and neglecting for instance rhombic distortions. This should be considered while analyzing data which are based on the measurement of a polycrystalline powder sample. Furthermore, it is worth mentioning that there are two kinds of magnetic exchange interactions, namely the Ni(II)−Ni(II) and the Ni(II)−$TTF^{\bullet+}$ couplings. The interpretation of the first type of interaction can be approached from the analysis of a similar compound[13] showing also the analogous dinuclear Ni(II) core; evidently, this coupling is of ferromagnetic nature. In that case, the energy splitting diagram, expressed as a function of the ratio D/J_{Ni}, hence of the parameters for an axial magnetic anisotropy and the magnetic exchange coupling, shows that the ground-state corresponds to a $|2, \pm2\rangle$ state within a reasonable parameter range. As shown below, the experimental magnetic susceptibility and magnetization data for compound **1** also fully support this analysis.

The thermal dependence of $\chi_{mol}T$ for **1** is shown in Figure 3. The experimental $\chi_{mol}T$ value at 250 K of 3.46 emu·K·mol^{-1} is slightly higher than the calculated value of 3.30 emu·K·mol^{-1} for an uncoupled system of two Ni(II) ions and two radicals ($S_{Ni} = 1$, $g_{Ni} = 2.26$, $S_{Rad} = 1/2$, $g_{Rad} = 2.0$). With lowering the temperature, the $\chi_{mol}T$ curve exhibits a gradual increase to a maximum value of 3.79 emu·K·mol^{-1} around 26 K, followed by a steep decrease to a value of 1.86 emu·K·mol^{-1} at 1.86 K. First, the increase of the $\chi_{mol}T$

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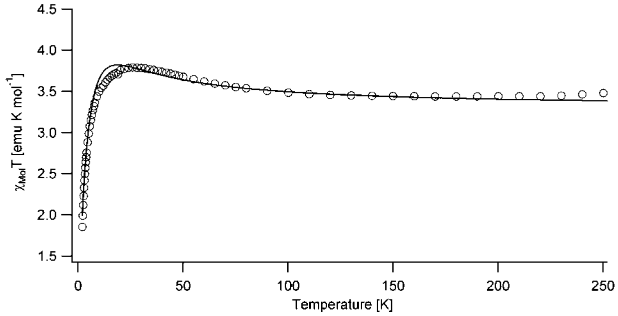

Figure 3. Temperature dependence of $\chi_{\mathrm{mol}}T$ for compound **1** measured at 1000 G. The circles correspond to the experimental data; the simulation with the parameters $J_{\mathrm{Ni}} = 5$ cm^{-1}, $J_{\mathrm{Rad}} = -1$ cm^{-1}, $g_{\mathrm{Ni}} = 2.26$, $g_{\mathrm{Rad}} = 2.0$, $D = -16$ cm^{-1} is depicted as a line.

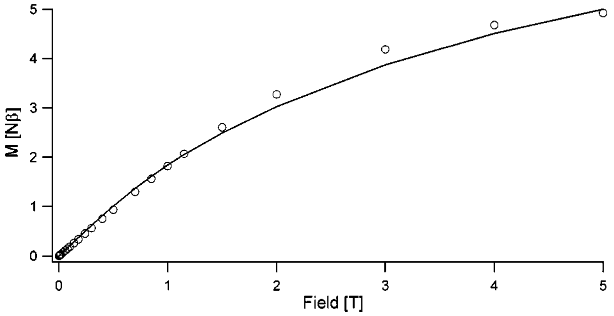

Figure 4. Field dependence of the magnetization (○) for compound **1** at 1.86 K. The solid line is a simulation with the parameters: $J_{\mathrm{Ni}} = 5$ cm^{-1}, $J_{\mathrm{Rad}} = -0.7$ cm^{-1}, $g_{\mathrm{Ni}} = 2.25$, $g_{\mathrm{Rad}} = 2.0$, $D = -10$ cm^{-1}.

curve is the signature of an overall predominant ferromagnetic exchange interaction between the two Ni(II) ions (J_{Ni}), which corroborates the results from other studies; very much the same behavior can be seen with an analogous dibromo-bridged dinuclear Ni(II) complex.[13] Second, at lower temperatures, (i) the effect of zero-field splitting (ZFS) of the pair states ($S = 2$) from the Ni(II) dimer results in an abrupt decrease of the $\chi_{\mathrm{mol}}T$ values and (ii) the additional coupling of the peripheral electronic spins ($S = 1/2$) from the two TTF$^{\bullet+}$ radicals with the Ni(II) ions (J_{Rad}) will simultaneously come into action. Very clearly, the latter exchange interactions cannot be of ferromagnetic nature since any meaningful simulation for that does not show such a decrease of $\chi_{\mathrm{mol}}T$ in the lower-temperature regime as that observed experimentally. However, while taking into account both effects, ZFS and a weak antiferromagnetic coupling (J_{Rad}), Ni(II)−TTF$^{\bullet+}$, a fairly good fit of the experimental data can be obtained, but still one has to consider that it remains an approximation with a model showing an axial symmetry; the exact symmetry is certainly lower than axial. A simulation with the following parameter set $J_{\mathrm{Ni}} = 5$ cm^{-1}, $J_{\mathrm{Rad}} = -1$ cm^{-1}, $g_{\mathrm{Ni}} = 2.26$, $g_{\mathrm{Rad}} = 2.0$, $D = -16$ cm^{-1} is presented in Figure 3.

Figure 4 exhibits the magnetization versus field plot for **1**, measured at 1.86 K. Importantly, these data can also be simulated fairly well with a parameter set which lies in a range close to that one for the analysis of the magnetic susceptibility data. The simulation shown in Figure 4 is based on the parameter set: $J_{\mathrm{Ni}} = 5$ cm^{-1}, $J_{\mathrm{Rad}} = -0.7$ cm^{-1}, $g_{\mathrm{Ni}} = 2.25$, $g_{\mathrm{Rad}} = 2.0$, $D = -10$ cm^{-1}. In summary, both results show that the dinuclear Ni(II) complex where two TTF$^{\bullet+}$ radicals are directly bound with their skeletons to the metal ions, exhibits (i) a dominant ferromagnetic exchange interaction between the two Ni(II) ions on the order of $J_{\mathrm{Ni}} = 5$ cm^{-1}, (ii) a weaker antiferromagnetic exchange interaction between the Ni(II) ions and the appended TTF$^{\bullet+}$ radicals on the order of $J_{\mathrm{Rad}} = -0.7$ to -1.0 cm^{-1}, and (iii) an axial ZFS parameter on the order of $D = -10$ to -16 cm^{-1}.

With the preparation and structural characterization of this dinuclear Ni(II) complex bearing TTF$^{\bullet+}$ radicals, we demonstrate that TTF derivatives which offer binding sites for paramagnetic transition metals are promising electroactive ligands. They allow access to dual-property molecular materials in which a metallic center lies in the close vicinity of a TTF$^{\bullet+}$ radical, leading to the enhancement of π−d interactions. Modulation of the molecular architectures and electronic properties of the resulting systems can be envisioned by changing the coordination function, the number of free coordination sites, and the geometry of π-extended TTF ligands.[14]

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Supporting Information Available: X-ray crystallographic files in CIF format for compound **1**, Figure S1 showing the formation of polyiodid anions, and Figure S2 illustrating the pronounced effect of the magnetic Ni(II)−TTF$^{\bullet+}$ interaction in the low-temperature regime. This material is available free of charge via the Internet at http://pubs.acs.org.

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