Inorg. Chem. **2006**, *45*, 3152–3154

Inorganic Chemistry
Communication

One-Dimensional μ-Chloromanganese(II)–Tetrathiafulvalene (TTF) Coordination Compound

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Received January 11, 2006

A new tetrathiafulvalene derivative **1** bearing a single pyridine group and its coordination complex **2**, with stoichiometry $[\mathrm{Mn}(\mu\text{-Cl})\mathrm{Cl}(\mathbf{1})_2(\mathrm{CH_3OH})]_n$, have been synthesized and fully characterized. The complex **2** shows an extended chain structure, which is potentially favorable for electrical conductivity. Notably, this is the first monohalogen-bridged Mn(II) polymer exhibiting a moderate antiferromagnetic coupling between the Mn(II) centers.

One of the current objectives in the field of conducting molecular materials derived from tetrathiafulvalene (TTF)[1,2] is to try to correlate within the same solid two distinct physical properties such as magnetic and conducting properties, seeking to establish in this case a coupling between the conduction electrons and the magnetic spin moments. Numerous research groups are involved in this area. In addition to co-assembling organic donors and paramagnetic metal anions,[3] another strategy for constructing dual-property materials is the direct coordination of paramagnetic metal ions to organic radicals through an intervening coordination function such as pyridine-type heterocycles,[4−6] dithiolate,[7] acetylacetonate,[8] or phosphine substituents,[9,10] well-known for their chelating ability toward various transition-metal ions. Although a large number of inorganic/organic hybrid materials contain metal ions as anionic complexes, only a few complexes of the direct coordination of the paramagnetic metal ions to TTF derivatives were successfully oxidized, showing an insulating behavior due to the dimerization[6] and lack of highly ordered stacking[10] in the donor sublattice. Obviously, it is still a major challenge for synthetic chemists to construct and control the self-assembly of molecular building blocks in an ordered manner, resulting in a supramolecular system with desired structure, stability, and physical properties.

Within the context of molecular magnetism, a great deal of interest has been devoted to the preparation of discrete polynuclear moleules and coordination polymers of paramagnetic metal complexes. Although a number of one- to three-dimensional (1D to 3D) Mn(II) compounds were reported, relatively few studies of the structure and magnetic properties of halogen-bridged Mn(II) polymers have been carried out.[11]

We report here the syntheses and structures of a new organic donor 4-(4′-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene (**1**) and its coordination complex $[\mathrm{Mn}(\mu\text{-Cl})\mathrm{Cl}(\mathbf{1})_2(\mathrm{CH_3OH})]_n$ (**2**), being the first example of the mono(μ-chloro)manganese(II) polymer with a 1D chain structure. The magnetic property of **2** is also discussed.

Unless stated otherwise, all chemicals were purchased from commercial sources and used as received. The ^{1}H and ^{13}C NMR spectra were measured in $\mathrm{CDCl_3}$ at 300 and 75 MHz,

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10.1021/ic060056f CCC: $33.50 © 2006 American Chemical Society
Published on Web 03/18/2006

respectively. IR spectra were obtained on a Perkin-Elmer SYSTEM 2000 Fourier transform IR spectrometer. Mass spectra were measured on an AutoSpec Q MS spectrometer. Elemental analyses were performed on a Carlo-Erba 1106 instrument.

The synthesis of **1** was carried out as follows. To a solution of 4-(2′-cyanoethylthio)-4′,5′-ethylenedithiotetrathiafulvalene[12] (0.19 g, 0.5 mmol) in tetrahydrofuran (20 mL) under N_2 was added a solution of $CsOH{\cdot}H_2O$ (0.126 g, 0.75 mmol) in methanol (10 mL). The mixture was stirred for 0.5 h at room temperature, forming a dark-red solution. A mixture of 4-picolyl chloride hydrochloride (82 mg, 0.5 mmol) and K_2CO_3 (34.5 mg, 0.25 mmol) in methanol (15 mL) was stirred for 10 min and then added to the former solution. The reaction mixture was stirred at room temperature for another 3 h. After removal of the solvents, column chromatography of the crude product on silica gel with $EtOAc/CH_2Cl_2$ (1:7, v/v) afforded compound **1** as a red solid. Yield: 94 mg, 45%. Mp: 100−102 °C. ^{1}H NMR: δ 3.29 (s, 4H), 3.84 (s, 2H), 6.74 (s, 1H), 7.16−7.18 (dd, $J = 6$ and 1.5 Hz, 2H), 8.54−8.56 (dd, $J = 6$ and 1.5 Hz, 2H). ^{13}C NMR: δ 30.2, 39.1, 107.3, 114.0, 117.0, 123.8, 125.0, 125.3, 146.0, 150.1. MS (EI): m/z 417 (M^+). IR (KBr, cm^{-1}): 2920, 1603, 1560, 1457, 1412, 1409, 766. Anal. Calcd for $C_{14}H_{11}NS_7$: C, 40.26; H, 2.65; N, 3.35. Found: C, 40.20; H, 2.63; N, 2.99.

The synthesis of **2** was carried out as follows. A solution of **1** (80 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) was added to one side of an H tube. A saturated solution of $MnCl_2{\cdot}4H_2O$ in methanol (10 mL) was carefully added to the other side of the H tube, and the two sides were connected by additional methanol and left in the dark at room temperature. After 2 weeks, red single crystals were obtained on the bottom of the tube. Yield: 14.3 mg, 15%. IR (KBr, cm^{-1}): 3423, 1614, 1420, 1018, 772. Anal. Calcd for $C_{29}H_{26}N_2S_{14}OMnCl_2$: C, 35.07; H, 2.64; N, 2.82. Found: C, 34.84; H, 2.25; N, 2.59.

Recrystallization of **1** from CH_2Cl_2/hexane afforded X-ray-quality single crystals.[13] An ORTEP plot of the molecular structure with the atomic numbering scheme is shown in Figure 1. The molecule has no crystallographically imposed symmetry, and there are no solvent molecules within the crystal structure. The TTF core is nearly planar, with a small dihedral angle of 4.4° between the two five-membered rings. All bond lengths are within the expected range for neutral TTF.[4a,b,d]

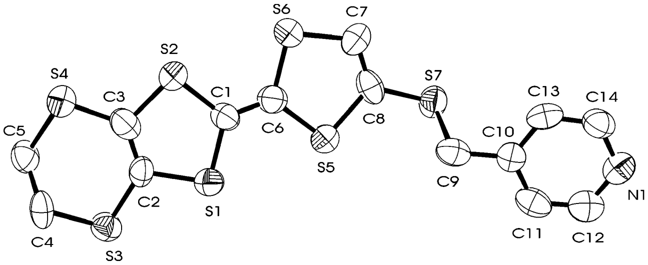

Figure 1. ORTEP (50% probability ellipsoids) structure of **1**. H atoms are omitted for clarity.

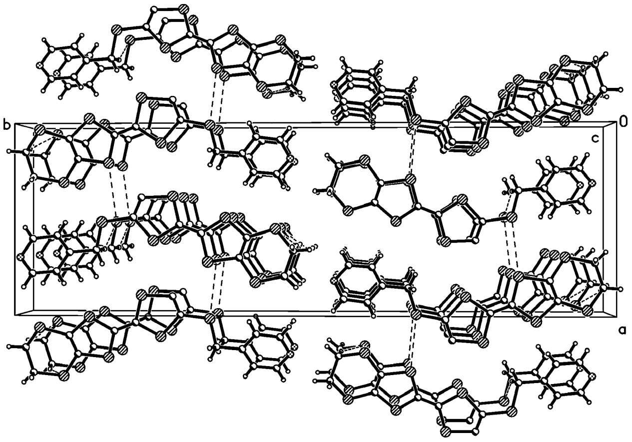

Figure 2. Crystal packing of **1**, showing H bondings and S···S close contacts.

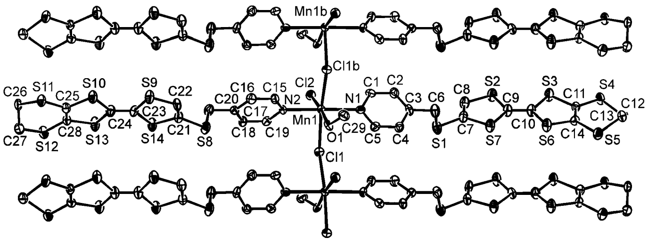

Figure 3. ORTEP (50% probability ellipsoids) structure of **2**, showing the 1D chainlike structure in the *ac* plane. H atoms are omitted for clarity.

In the crystal lattice (see Figure 2), the molecules are stacked along the *c* axis; however, the short S···S contacts (3.540 Å) exist between neighboring molecules lying in the *ab* plane, so that a bandlike structure evolves along the *a* axis. Moreover, along the *c* direction, unconventional H bonds, C−H···S, in the range of 3.672−3.725 Å are observed.

Compound **2** crystallizes in a noncentrosymmetric orthorhombic space group ($P2_12_12_1$) in the form of a 1D coordination compound with the stoichiometry $[Mn(\mu\text{-}Cl)Cl(\mathbf{1})_2(CH_3OH)]_n$.[14] As depicted in Figure 3, the Mn(II) ion adopts a distorted octahedral coordination geometry. Two ligands of **1** are bonded in trans positions to Mn(II) through two N atoms of the pyridine rings [Mn1−N1 2.262(5) Å; Mn1−N2 2.257(4) Å]. One terminal Cl^- anion and one O atom of CH_3OH occupy also opposite positions [Mn1−Cl2 2.5007(14) Å; Mn1−O1 2.269(3) Å]. Two bridging μ-Cl^- anions

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(13) Crystal data for **1**: $M = 416.65$, orthorhombic, space group $P2_12_12$, $a = 11.2835(15)$ Å, $b = 35.311(6)$ Å, $c = 4.2007(8)$ Å, $V = 1673.7(5)$ Å^3, $Z = 4$; $D_c = 1.654$ g·cm^{-3}; $T = 173(2)$ K, $\mu = 0.935$ mm^{-1}, Stoe imaging plate diffractometer system; 7972 reflections were collected with 2189 unique and 964 with $I > 2.0\sigma(I)$, yielding $R = 0.0581$, $R_w = 0.1099$, and GOF = 0.750. The structures were solved by direct methods using the program *SHELXS-97* and refined by full-matrix least squares on F^2 with *SHELXL-97*.

(14) Crystal data for **2**: $M = 993.20$, orthorhombic, space group $P2_12_12_1$, $a = 9.1967(6)$ Å, $b = 10.3605(7)$ Å, $c = 39.933(4)$ Å, $V = 3804.9(5)$ Å^3, $Z = 4$; $D_c = 1.734$ g·cm^{-3}; $T = 173(2)$ K, $\mu = 1.287$ mm^{-1}, Stoe Mark II imaging plate diffractometer system; 23 163 reflections were collected with 6652 unique and 4026 with $I > 2.0\sigma(I)$, yielding $R = 0.0380$, $R_w = 0.0665$, and GOF = 0.753. The structures were solved by direct methods using the program *SHELXS-97* and refined by full-matrix least squares on F^2 with *SHELXL-97*. **2** crystallizes as a racemic twin. The TWIN instruction has been used in *SHELXL-93*, and the BASF value was refined to 0.21(3), showing the presence of both enantiomers in the crystal in a ratio of 1:4.

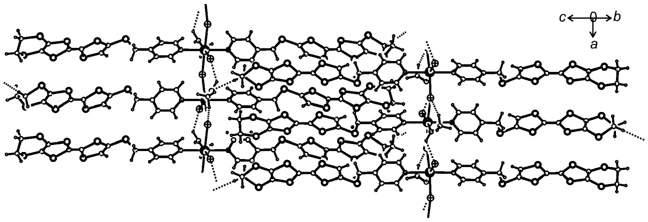

Figure 4. Crystal packing of **2**, showing the formation of a 2D network via H bondings (dashed lines).

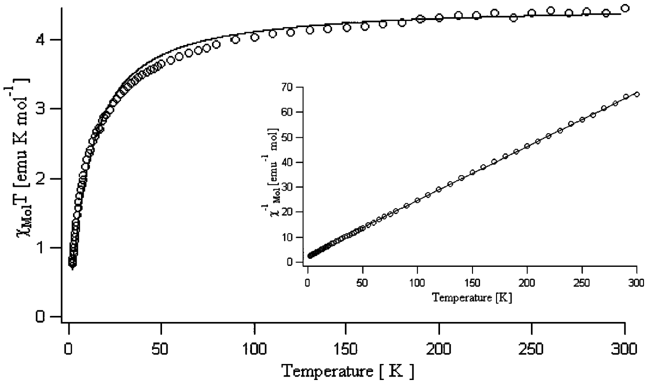

Figure 5. Plot of the $\chi_M T$ product vs T of compound **2** (applied field of 1 kG). The simulation (solid curve) is based on the parameters $g = 2.03$ and $J = -1.1$ cm^{-1}. The inset shows the inverse susceptibility vs T data with a Curie−Weiss fit ($\Theta = -14.6$ K).

[Mn1−Cl1 2.5012(16) Å; Mn1−Cl1b 2.5060(16) Å] link in trans positions the Mn(II) ions into an extended linear chain along the *a* axis with a Mn···Mn distance of 3.891 Å and a Mn1−Cl−Mn1b angle of 134.23° (Figure 3). Obviously, the H bonds O−H···Cl (3.001 Å; 130°) and C−H···Cl (3.369 Å; 126°) play the crucial role on the resulting peculiar zigzag mono(μ-chloro)manganese(II) chain structure (Figure 4).

The two pyridine rings bound to a Mn(II) ion are nearly perpendicular to each other with a dihedral angle of 85.7°. Neighboring pyridine rings on one side of the chain form a dihedral angle of 20°, while the corresponding TTF units are almost parallel to each other with a dihedral angle of 4°. There are no close S···S contacts observed. Interestingly, as shown in Figure 4, 1D Mn(II) polymers are alternatingly arranged along the *b* axis and linked by close S···S contacts (3.269−3.612 Å) and H bonds C−H···O (3.567 Å), forming a 2D network.

Within the complex, the bond lengths and angles of ligand **1** are close to those of uncoordinated **1**. According to the correlation between the oxidation states of TTF derivatives and the bond lengths of central C═C bonds, it can be inferred that the ligands in **2** are neutral,[15] suggesting that **2** is insulating. Interestingly, the resulting peculiar packing mode is reminiscent of what is usually observed for conducting radical salts. To the best of our knowledge, this is the first example of a transition-metal complex with TTF derivative ligands exhibiting an extended 1D chain structure.

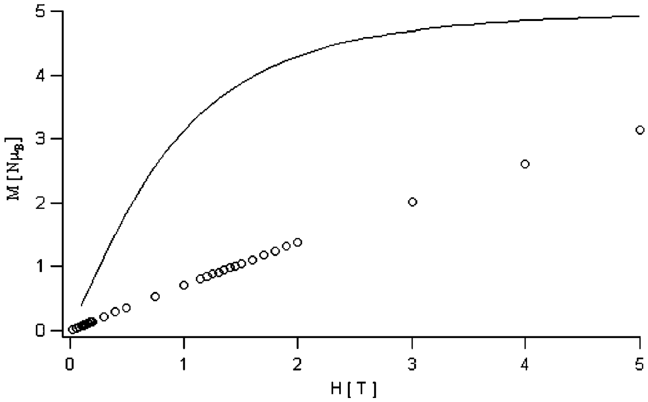

Figure 6. Field dependence of the magnetization of compound **2** measured at $T = 1.9$ K. The solid curve corresponds to a Brillouin function for a $S = {}^5/_2$ ion (see the text).

The magnetic susceptibility, χ_M, and magnetization data of compound **2** were collected on a MPMS Quantum Design SQUID magnetometer (XL-5) in the temperature range of 300−1.9 K and at applied magnetic fields up to 5 T. Figure 5 shows the $\chi_M T$ vs T and $\chi_M{}^{-1}$ vs T plots. Above 100 K, the data can be fitted to the Curie−Weiss expression with a Weiss constant $\Theta = -14.6$ K. The experimentally determined room-temperature value $\chi_M T$ of 4.46 emu K mol^{-1} is in good agreement with the calculated value of 4.38 emu K mol^{-1} for a noninteracting Mn(II) ion ($S = {}^5/_2$; $g = 2$). The rapid decrease of $\chi_M T$ below 50 K is indicative of antiferromagnetic coupling between the Mn(II) centers. A simulation of the data based on a chain model proposed by Fisher[16] gives the values $g = 2.03$ and $J = -1.1$ cm^{-1}. This coupling constant corresponds well to the magnitude and sign of the determined Weiss constant. As expected, the magnetization vs magnetic field data, at $T = 1.9$ K (see Figure 6), for an exchange-coupled chain compound deviate distinctly from a Brillouin-type behavior for isolated $S = {}^5/_2$ ions.

In summary, a new organic donor **1** and its Mn(II) complex **2** have been prepared and crystallographically characterized. The 1D complex **2** exhibits antiferromagnetic coupling between the Mn(II) centers. Further investigations on this novel attractive system will be devoted to the study of other metal ions to determine their effect on the arrangement of the TTF cores in the crystal structures. Additionally, studies on the chemical and electrochemical partial oxidation of **2** are in progress. With these promising building blocks, our next goal to obtain conducting and magnetic π−d systems might be achieved in the near feature.

Acknowledgment. Support for this research by the Swiss National Science Foundation (Grant 200020-107589 and COST Action D31) and the ESF Scientific Program−SONS (NANOSYN) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060056F

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