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Co(II)–Co(II) Paddlewheel Complex with a Redox-Active Ligand Derived from TTF

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A new trimethyltetrathiafulvalene (Me₃TTF) derivative Me₃TTF–CH=CH–py bearing a pyridyl was synthesized and coordinated to a cobalt(II) benzoate dimer, having paddlewheel core structure, leading to a complex formulated as Co₂(PhCOO)₄(Me₃TTF–CH=CH–py)₂. Single-crystal X-ray diffraction studies of the complex performed at 293 and 100 K evidenced the existence of a weak metal–metal interaction. Magnetic studies revealed an antiferromagnetic behavior, which is explained as the result of the direct exchange between metal centers.

One of the current objectives in the field of molecular materials is to combine distinct physical properties at material scale, such as, for example, electrical conductivity and magnetism. Tetrathiafulvalene (TTF) and metal bis(dithiolene) derivatives are certainly the most popular units used to build conducting and superconducting networks.[1]

One possibility to create molecular-based conducting magnets is to design paramagnetic coordination complexes with redox-active ligands. These kinds of molecules are interesting for two main reasons: (i) the paramagnetic center and the conducting electrons are linked by a chemical bridge, which may yield sizable interactions between the two counterparts, and (ii) the metal is a very good electron transmiter between organic radicals. Several mononuclear paramagnetic transition metals coordinated to redox-active ligands through coordination functions such as pyridine-type heterocycles[2,3] have been successfully synthesized. However, only a few complexes were successfully oxidized, showing an insulating behavior due to the dimerization and lack of highly ordered stacking[3] in the donor sublattice.

It has been found recently that metallic conductivity or magnetic properties can be observed at the molecular level. A single-component metal[4] and a single-molecule magnet (SMM)[5] were discovered recently, and they led to renewed interest in the field of molecule-based materials. On the other hand, it is well-known, since the pioneering works by a Florence group on the so-called Mn₁₂ molecules, that magnetic information can be stored at the molecular scale (SMM) on polynuclear species.[5] It is then conceivable to combine these properties through supramolecular assembly. We started a systematic investigation of polynuclear paramagnetic complexes with redox-active ligands in order to examine the possibility of accessing bifunctional molecules that can act at the same time as a SMM and a single-component metal. Good candidates are binuclear complexes with the well-known paddlewheel core.[6] At first, Cotton and Kim reported a polymer formed by a strong acceptor (tetracyanoethylene) and a dirhodium tetrakis(trifluoroac-

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etate) paddlewheel.[7] More recently, these binuclear complexes have been used, for instance, in sensors.[8]

In the following, we present the synthesis and characterization of the new Me_3TTF derivative $Me_3TTF-CH=CH-$ py (**L**) bearing a pyridyl as well as its first cobalt(II) benzoate paddlewheel dimer complex $Co_2(PhCOO)_4(\mathbf{L})_2$.

All experiments were carried out under an argon atmosphere. Solvents were dried and distilled by standard procedures. **L** was obtained by using the Wittig reaction[9,10] between the $4',5,5'$-trimethyl-$\Delta2,2'$-bi-1,3-dithiole-4-carbaldehyde (**1**)[11] and triphenyl(4-pyridyl)methylphosphonium chloride hydrochloride (**2**).[12] The synthesis of $Co_2(PhCOO)_4$-(**L**)$_2$ was carried out as follows. A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (88 mg, 0.30 mmol) and benzaldehyde (3 mL, 0.03 mmol) was heated to boiling for 5–10 min. The resulting blue solution was cooled down to 80 °C, and a hot solution of **L** (70 mg, 0.195 mmol) in 5 mL of toluene was added. The reaction mixture was cooled down to room temperature, transferred in a tube, and layered with 5 mL of acetonitrile. After several days, deposited red crystals were collected by filtration, washed with acetonitrile, and dried in vacuum. IR (KBr, cm^{-1}): 2912, 1627, 1604, 1571, 1499, 1402, 1220, 1198, 1177, 1067, 1026, 933, 841, 805, 780, 718, 680, 566, 466, 437. Anal. Calcd for $C_{30}H_{25}CoNO_4S_4$: C, 55.32; H, 3.84; S, 19.67; N, 2.15. Found: C, 55.48; H, 3.78; S, 19.38; N, 2.52.

The X-ray crystal structure data of **L**·0.5H$_2$O at 293 K[13] and those of $Co_2(PhCOO)_4(\mathbf{L})_2$ at 293 and 100 K[14] are given as Supporting Information. We describe here the structure of the complex at 293 K, and we give data at 100 K in brackets.
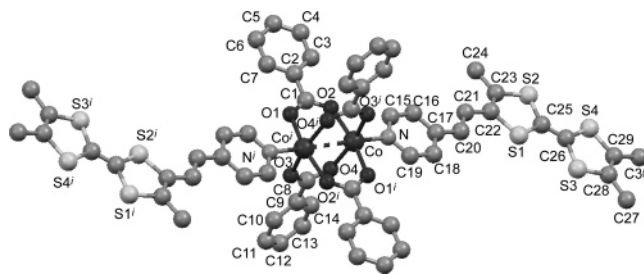

Figure 1. Drawing of the complex with labeling and symmetry i: $-x$, $-y$, $-z$. The H atoms have been omitted for clarity.

The Co(II) complex is a centrosymmetrical dimer (Figure 1). The metal lies in a distorted square-pyramidal environment formed by four O atoms of four benzoate ligands, while the apical position is occupied by the N atom of the pyridyl. Two Co–O distances are short and homogeneous (d_{Co-O1^i} = 2.019(4) [2.019(3)] Å and d_{Co-O2} = 2.019(3) [2.024(3)] Å); the two others are slightly longer (d_{Co-O3} = 2.049(4) [2.072-(4)] Å and d_{Co-O4^i} = 2.075(4) [2.053(4)] Å). The Co–N bond length is equal to 2.055(4) [2.064(4)] Å. The Co(II) core is pulled out from the base of the pyramid by the TTF moiety of 0.275(2) [0.229(2)] Å. The coordination mode of the benzoates is $\mu_2(\eta_1,\eta_1)$, so the core $Co_2(PhCOO)_4$ has the well-known paddlewheel structure with a Co–Co distance at 293 K equal to 2.772(2) Å, which is in the range of metal–metal distances measured in other $Co_2(RCOO)_4$ complexes.[15] It is worth noticing that the Co–Co distance decreases remarkably upon cooling down to 100 K [2.694(2) Å] while the Co–O and Co–N distances increase slightly. Formal Co–Co single bonds ($d_{Co-Co} \approx 2.3$ Å) have been reported in dicobalt tetrakis(formamidinate) complexes.[6] The neutral π-conjugated ligand **L** is almost planar with an angle of 3.2-(3)° [6.6(3)°] between the pyridyl and TTF moieties. The crystal packing consists of alternating organic and inorganic layers with intermolecular S···S distances greater than the sum of their van der Waals radii. Because of the neutrality of **L**, the compound is an insulator.

The cyclic voltammetry of **L** and $Co_2(PhCOO)_4(\mathbf{L})_2$ has been investigated in chlorobenzene. The first oxidation potential value of the complex (E_{OX1} = 0.51 V vs ECS) is higher than that of **L** (E_{OX1} = 0.40 V vs ECS), indicating that the complex is more difficult to oxidize than the noncoordinated ligand.

The $\chi_M T$ product of a powdered sample of $Co_2(PhCOO)_4$-(**L**)$_2$ has been measured in the temperature range 2–300 K

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(12) A dropwise addition of *n*-BuLi (1.6 M in hexane, 2.7 mL) in 2 h to a stirred anhydrous tetrahydrofuran (THF)/CH$_3$CN (3:2) solution (25 mL) of **2** (1.7 g, 4 mmol) at −78 °C led to the deprotonation of **2**. After stirring at −78 °C for 2 h, an anhydrous THF solution (50 mL) of **1** (1.03 g, 3.75 mmol) was added dropwise to the resulting mixture at −78 °C. After an additional 2 h of stirring, the mixture was allowed to reach room temperature overnight. After removal of the solvents and extraction with CH$_2$Cl$_2$, column chromatography of the crude product on silica gel, eluting initially with CH$_2$Cl$_2$ and then with Et$_2$O, afforded pure **L**. Suitable crystals for X-ray diffraction were obtained as red crystals by recrystallization in a mixture of CH$_2$Cl$_2$/hexane (1:1). Yield: 20%. Mp: 180 °C. ^{1}H NMR (CDCl$_3$): δ 1.96 (s, 6H, CH$_3$), 2.21 (s, 3H, CH$_3$), 6,26 (d, *J* = 15.65 Hz, 1H), 7.08 (d, *J* = 15.66 Hz, 1H, CH lying on pyridine), 7.26 (m, 2H, pyridine), 8.54 (m, 2H, pyridine). ^{13}C NMR (CDCl$_3$): δ 13.75, 14.27, 104.84, 111.76, 120.62; 122.04, 127.31, 128.16, 128.48, 128.57, 132.06, 132.141, 133.88, 144.27, 150.13. MS: *m/z* 349.070 (M$^+$). IR (KBr, cm^{-1}): 3553, 3481, 3411, 3233, 1637, 1609, 1597, 1572, 1410, 928, 781, 627, 493. Anal. Calcd for C$_{16}$H$_{15}$S$_4$N: C, 54.98; H, 4.33; N, 4.01. Found: C, 55.24; H, 4.53; N, 3.71.

(13) Crystal data for **L**·0.5H$_2$O: C$_{16}$H$_{16}$NO$_{0.5}$S$_4$, M = 358.54, T = 293 K, monoclinic, space group $C2$, a = 13.9701(4) Å, b = 5.9781(2) Å, c = 20.6898(6) Å, β = 99.708(2)°, V = 1703.16(9) Å^3, Z = 4, ρ_{calcd} = 1.398 g cm^{-3}, μ = 0.554 mm^{-1}, R1 = 0.0374, wR2 = 0.1122 [$I >$ 2$\sigma(I)$] for 4158 data and 195 parameters, S = 1.045, and Flack parameter x = −0.01(7).

(14) Crystal data for Co$_2$(PhCOO)$_4$(**L**)$_2$ at 293 [100] K: C$_{60}$H$_{50}$Co$_2$N$_2$O$_8$S$_8$, M = 1301.36, T = 293 [100] K, triclinic, space group $P\bar{1}$, a = 9.7041-(6) [9.667(3)] Å, b = 10.6740(8) [10.577(3)] Å, c = 16.7854(15) [16.558(4)] Å, α = 82.724(4)° [82.997(13)°], β = 75.166(3)° [75.740-(14)°], γ = 63.095(3)° [62.635(12)°], V = 1498.7(2) [1457.1(7)] Å^3, Z = 1, ρ_{calcd} = 1.442 [1.483] g cm^{-3}, μ = 0.887 [0.913] mm^{-1}, R1 = 0.0628 [0.0590], wR2 = 0.1578 [0.1567] [$I >$ 2$\sigma(I)$ for 3117 [3587] data and 361 parameters, S = 0.996 [1.041].

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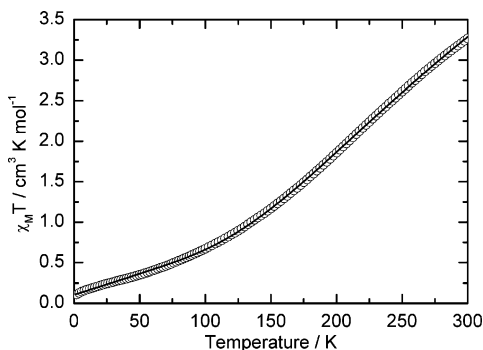
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Figure 2. $\chi_M T = f(T)$ of a powdered sample of $Co_2(PhCOO)_4(\mathbf{L})_2$ (○) and its best agreement with the Bleaney−Bowers model (—).

(Figure 2). On cooling, $\chi_M T$ decreases continuously down to zero. The ground state is therefore nonmagnetic. The paramagnetism above 70 K clearly indicates that states with single electrons are located close enough in energy from the ground state to be thermally populated. The magnetic properties of $d^9−d^9$ complexes with identical core structures have been extensively studied because they feature through-bridge superexchange pathways.[16] The situation is slightly different in Co(II) dimers $d^7−d^7$ although Boyd et al.,[17] in their pioneering work, demonstrated the importance of the through-bridge superexchange pathway. However, the magnetism of this type of dimer can be interpreted in terms of weak metal−metal interaction between the two Co(II) ions.

Figure 3 contains a schematic molecular orbital energy level diagram of the dimer d orbitals with the 14 electrons. For simplicity, we considered an ideal D_{4h} symmetry for the dimer. The d orbitals of each Co(II) with a z component significantly overlap, while those with only x and y components are not significantly disturbed. The ground state of the dimer with the electronic configuration $\delta^2 \delta^{*2} \pi^4 \pi^{*4} \sigma^2$ is formally diamagnetic with the formation of a weak σ bond $(d_{z^2}−d_{z^2})$. The paramagnetism can arise from the thermal population of the excited state with the electronic configuration $\delta^2 \delta^{*2} \pi^4 \pi^{*4} \sigma^1 \sigma^{*1}$, which possesses triplet spin multiplicity and which weakens the metal−metal interaction. Our theoretical analysis of the magnetic data includes only the ground and lowest excited states. Other excited states are not explicitly required to fit the experimental data. The Bleaney−Bowers equation taking into account the singlet−triplet gap $(−J)$, the Zeeman factor of the triplet state (g), slightly modified to take also into account the temperature-independent paramagnetism (TIP), and a small amount of paramagnetic impurities gives an excellent agreement (Figure 2) with the experimental points with $J = −420$ cm^{-1}, $g = 4.78$, TIP = 0.0052 cm^3 mol^{-1}, and paramagnetic impurities contributing by 0.1 cm^3 K mol^{-1} to $\chi_M T$.[18] It is not surprising to find important TIP contributions and such a strong Zeeman factor. Indeed, the combined influences of local distortion of the coor-
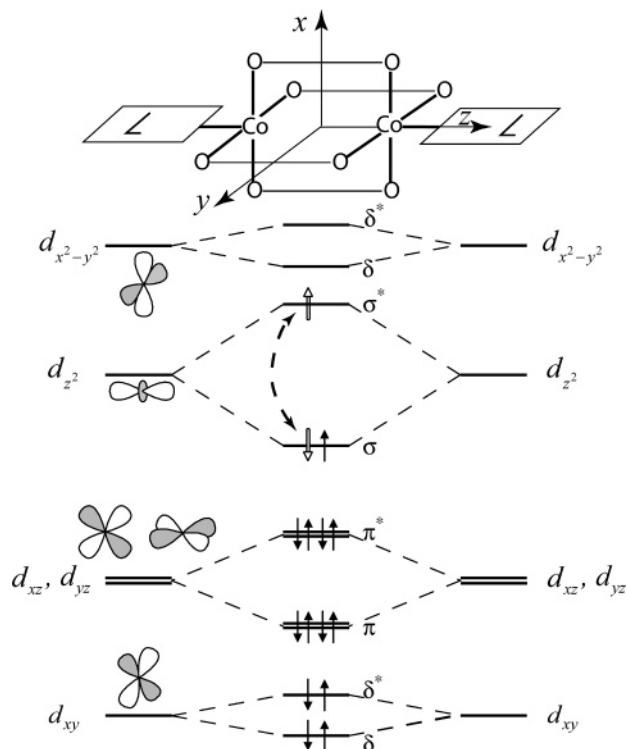

Figure 3. Qualitative molecular orbital energy level diagram of the dimer d orbitals with the 14 electrons showing the bonding ground-state electronic configuration (singlet) and the nonbonding first excited state (triplet).

dination sphere around Co(II) and spin−orbit coupling are known to produce this set of local parameters.[18]

This interpretation of the magnetic data is supported by the low-temperature molecular structure. The thermal population of the first excited state weakens the metal−metal interaction because one electron is promoted from the bonding σ orbital to the antibonding σ^* orbital. As a matter of fact, the increase of the distance between the two metals clearly shows that the strength of the interaction decreases with an increase in the temperature.

The first Co(II) dimer complex with a paddlewheel structure and having strong electron donors as an apical ligand has been successfully synthesized. The magnetic properties and the temperature dependence of the molecular structure have evidenced the existence of a weak metal−metal interaction. The electrochemical studies have shown that this molecule can be oxidized to its radical cation; it is therefore a potential building block for multifunctional conducting and magnetic molecular-based materials.

Supporting Information Available: Synthesis and characterization of the ligand **L** and X-ray crystallographic files of **L**·0.5H$_2$O at 293 K and of the complex at 293 and 100 K as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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