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First Paramagnetic 4d Transition-Metal Complex with a Redox-Active Tetrathiafulvalene Derivative, [Ru(salen)(PPh$_3$)(TTF-CH=CH-Py)]BF$_4$ [salen^{2-} = *N,N′*-Ethan-1,2-diylbis(salicylidenamine), PPh$_3$ = Triphenylphosphine, TTF-CH=CH-Py = 4-(2-Tetrathiafulvalenylethenyl)pyridine]

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The first paramagnetic 4d transition-metal complex with a redox-active tetrathiafulvalene ligand has been synthesized. The preparation, X-ray structure, electrochemistry, and electron paramagnetic resonance measurements of [Ru(salen)(PPh$_3$)(TTF-CH=CH-Py)](BF$_4$) [**1**(BF$_4$)] are reported. The crystal structure reveals that the paramagnetic Ru^{III} ($s = {}^1/_2$) center is in a tetragonally elongated octahedral geometry and the TTF-CH=CH-Py ligand is coordinated to the axial position of the Ru^{III} ion through the nitrogen atom of the pyridine group. Thus, **1**(BF$_4$) is an attractive precursor to study future $\pi-$4d interactions in dual-property conducting and magnetic materials.

Intense investigations are devoted to multifunctional molecular materials. In particular, chemists and physicists are attracted to the design of new molecules and materials that possess synergy or interplay between electrical conductivity with magnetism.[1] The objective of this combination is to establish a coupling between conduction electrons (π electrons) coming from organic donors and localized electrons (d electrons) coming from paramagnetic centers, through the so-called $\pi-$d interaction. To fill this goal, two approaches are investigated: (a) a through-space approach but with $\pi-$d interactions that are usually very weak;[1] (b) a covalent link between both systems. The latter approach appears as a promising alternative to obtaining strong $\pi-$d interactions, and a large number of coordination complexes employing this approach have been studied.[2] However, only few of them have been successfully oxidized as radical cation complexes.[3] The possibility of observing a synergy between conducting and magnetic properties depends on the overlap between π and d orbitals. Whereas all of the previous attempts involve interactions between π and 3d electrons, we try to explore the possible stronger $\pi-$4d interactions. The 4d ions are characterized by more radially extended valence orbitals compared with their 3d congeners, a trend following the sequence 5d > 4d ≫ 3d. To magnetochemists,

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a more diffuse, singly occupied orbital suggests that an enhanced exchange interaction might be expected between interacting magnetic centers.[4]

We report in this paper the coordination of the 4-(2-tetrathiafulvalenylethenyl)pyridine (TTF-CH=CH-Py) ligand on the [Ru(salen)(PPh$_3$)]$^+$ moiety [salen^{2-} = *N*,*N′*-ethan-1,2-diylbis(salicylidenamine) and PPh$_3$ = triphenylphosphine]. The resulting complex formulated as [Ru(salen)(PPh$_3$)(TTF-CH=CH-Py)](BF$_4$) [**1**(BF$_4$)] is characterized by single-crystal X-ray diffraction, electrochemistry, and magnetic measurements [electron paramagnetic resonance (EPR) and SQUID properties]. The [Ru(salen)(PPh$_3$)(Cl)] precursor[5] and TTF-CH=CH-Py[8] were synthesized as described in the literature. To a stirred solution of [Ru(salen)(PPh$_3$)(Cl)] (66.5 mg, 0.1 mmol) in boiling chloroform (5 mL) was added solid AgBF$_4$ (19.5 mg, 0.1 mmol), and stirring and heating was continued for 1 h and 30 min. After this time, a solution of chloroform (5 mL) containing TTF-CH=CH-Py (30.7 mg, 0.1 mmol) was added, and stirring and heating was continued for an additional 2 h. Then, the formed solid AgCl was filtered off. The solvent was evaporated under reduce pressure, the resulting solid was dissolved in CH$_2$Cl$_2$ (10 mL), and toluene was added to this solution (10 mL). Slow evaporation in the dark at room temperature gave dark-purple single crystals of **1**(BF$_4$), which were suitable for X-ray diffraction. IR (KBr): ν 3056, 2923, 2856, 1600, 1527, 1485, 1434, 1290, 1054, 748, 697, 521 cm^{-1}. The X-ray crystal structure data of **1** at 293 K are given as Supporting Information.[6] Compound **1**(BF$_4$) crystallizes in the $P\bar{1}$ (No. 2) triclinic space group. An ORTEP view of the corresponding asymmetric unit is shown in Figure S1 in the Supporting Information. The Ru^{III} ion is coordinated to a salen^{2-} ligand, with its two axial positions occupied by one PPh$_3$ ligand and one TTF-CH=CH-Py ligand. The Ru^{III} ion is localized in the plane of the salen^{2-} ligand. The Ru−O [2.007(5) Å] and Ru−N$_{salen}$ [1.993(6) Å] distances are identical (Figure 1).

The coordination polyhedron of the Ru^{III} ion can be described as an elongated octahedron of tetragonal symmetry. The geometry of the coordination polyhedron around the Ru^{III} ion and the arrangement of the coordinated ligand is similar to those observed with the previous structures obtained from the [Ru(salen)(PPh$_3$)(Cl)] precursor.[5,7] The coordinated TTF-CH=CH-Py ligand is quasi-planar, with an angle of 1.5° between the pyridine ethylenic moiety and the TTF skeleton.

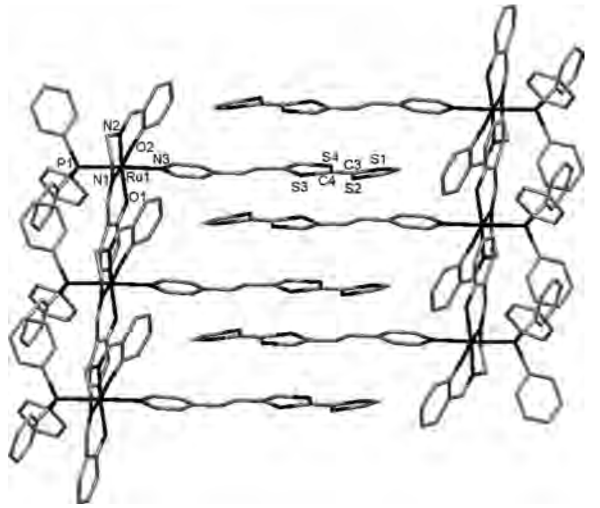

Figure 1. Packing view of the **1**(BF$_4$ compound showing the inorganic and organic networks linked by conjugated bridges. Tetrafluoroborate anions are omitted for clarity. Selected bond lengths (Å): Ru1−O1, 2.004(5); Ru1−O2, 2.009(5); Ru1−N1, 2.009(6); Ru1−N2, 1.976(6); Ru1−N3, 2.152(5); Ru1−P1, 2.371(2); C3−C4, 1.315(10).

The bond lengths and angles of the TTF-CH=CH-Py ligand are close to those reported for the noncoordinated[8] and coordinated neutral units,[2q,v] indicating that the TTF derivative is neutral. An analysis of the crystal packing (Figure 1) shows alternating layers of organic and inorganic entities linked by conjugated bridges. The shortest intermolecular Ru−Ru distance is 9.28 Å. In the organic network, the shortest intermolecular S···S contacts are equal to 4.014 Å (S4···S4), which is much larger than the sum of the van der Waals radius (3.7 Å) but is in the same range as the shortest intermolecular S···S distances (3.955 Å) reported previously for the *trans*-Cu(hfac)$_2$(TTF-CH=CH-Py)$_2$ coordination complex.[2q] This packing is reminiscent of what is usually observed for conducting radical-ion salts containing organic donors and inorganic anions. Therefore, it is favorable for electrical conductivity in the hypothesis that the packing remains almost unchanged upon oxidation. Finally, the electroneutrality of the structure is assured by one tetrafluoroborate anion per [Ru(salen)(PPh$_3$)(TTF-CH=CH-Py)]$^+$ monocationic entity.

The redox properties of **1** were determined by cyclic voltammetry (Figure 2).[9] For **1**, four reversible single-electron oxidation waves were observed. The E^1_{ox}, E^2_{ox}, E^3_{ox}, and E^4_{ox} values are −160, +400, +850, and +1050 mV vs SCE. The waves localized at the potential of −160 (E^1_{ox}) and +1050 mV (E^4_{ox}) correspond to the formation of a [Ru^{III}(salen)(PPh$_3$)(TTF-CH=CH-Py)]$^+$ monocation and a [Ru^{IV}(salen)(PPh$_3$)(TTF-CH=CH-Py)]$^{2+}$ dication, respectively, and are anodically shifted in comparison with the potentials measured for the [Ru(salen)(PPh$_3$)(Cl)] precursor (−223 and +947 mV; Figure S2 in the Supporting Information).[9]

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(6) Crystal data for **1**(BF$_4$): C$_{47}$H$_{38}$N$_3$O$_2$S$_4$P$_1$B$_1$F$_4$Ru$_1$, M = 1022.8 g·mol^{-1}, T = 293(2) K, triclinic space group $P\bar{1}$ (No. 2), a = 9.2822(7) Å, b = 14.7823(6) Å, c = 19.4265(15) Å, α = 97.028(4)°, β = 100.201(3)°, γ = 105.040(4)°, V = 2493.5(3) Å^3, Z = 2, diffraction reflection 3.92° < 2θ < 52.18°, ρ_{calcd} = 0.678 g·cm^{-3}, μ = 0.284 mm^{-1}, R1 = 0.0674, wR2 = 0.1541 for 19 008 reflections, 9847 independent reflections, 4316 $F_o > 4\sigma(F_o)$ and 568 parameters, S = 0.893.

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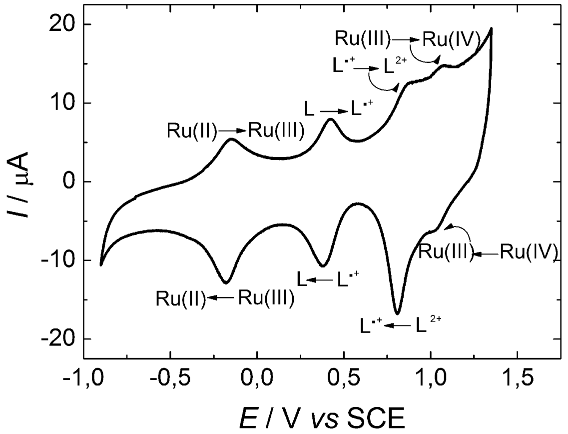

Figure 2. Cyclic voltammetry of [Ru(salen)(PPh$_3$)(TTF-CH=CH-Py)]$^+$ **1** in CH$_2$Cl$_2$ at a scan rate of 100 mV$\cdot$s^{-1}. L = TTF-CH=CH-Py.

The electron-withdrawing nature of the TTF-CH=CH-Py ligand bonded to the metal through the nitrogen atom of the pyridine ring compared to the electroactive chloride atom makes oxidation of the [Ru(salen)(PPh$_3$)] moiety more difficult in **1**, whereas E^1_{ox} and E^4_{ox} of **1** are similar to those of the [Ru(salen)(PPh$_3$)(py)]$^+$ complex (-170 and $+1060$ mV), leading to an electron-withdrawing nature similar to that for the TTF-CH=CH-Py and pyridine ligands. The waves localized at the potentials of 400 (E^2_{ox}) and 850 mV (E^3_{ox}) correspond to the formation of the radical cation and dication of TTF, respectively, and are anodically shifted in comparison with the potentials measured for the parent TTF (380 and 770 mV).[9] The electron-withdrawing nature of the pyridine ring via the conjugated bridge makes oxidation of the TTF core more difficult in **1**. Complexation to the Ru$^{\mathrm{III}}$ ion leads to changes for oxidation potentials E^2_{ox} and E^3_{ox}. Both of these potentials are shifted to more positive potentials compared to the free TTF-CH=CH-Py (392 and 819 mV; Figure S2 in the Supporting Information) and TTF parents because of the decreased electron density in the TTF core caused by complexation of the Ru$^{\mathrm{III}}$ ion. Similar shifts have been previously reported.[2i,q] The oxidation waves of the TTF derivative are measured to lower potentials than the one for the oxidation of Ru$^{\mathrm{III}}$ in Ru$^{\mathrm{IV}}$. It is a fundamental point to perform a galvanostatic oxidation.

The EPR spectrum of **1**(BF$_4$) at 67 K is shown in Figure 3. In a low-spin d^5 system, the $^2T_{2g}$ (octahedral) ground state is orbitally degenerate, and it is affected by spin$-$orbit coupling and low-symmetry ligand-field effects.[10] EPR measurements clearly demonstrate the presence of a rhombic ligand-field component (tetragonally elongated octahedral geometry), as one might expect from the nature of the ligands around the metal ion. This distortion is in agreement with the observed distances between the Ru$^{\mathrm{III}}$ and coordinated ligands in the crystal structure of **1**.

The resolution is improved, and a three-line spectrum, similar to that found for low-spin Fe$^{\mathrm{III}}$ systems, is obtained for **1**. In a first-order approximation for a metal ion $t_{2g}{}^5$ configuration (as Fe$^{\mathrm{III}}$ and Ru$^{\mathrm{III}}$) under the effect of a ligand field of axial geometry, only two of three g values are larger than 2.00. The best simulation of the EPR spectrum of **1** gives g_1=2.28, $g_2 = 2.12$, and $g_3 = 1.92$. The EPR properties of **1** are similar to those of some Ru$^{\mathrm{III}}$ compounds[11,12] and Ru(acac)$_3$ (acac$^-$ = acethylacetonate anion).[13] The three-line EPR spectrum and the g values confirm that the paramagnetism of **1**(BF$_4$) comes from Ru$^{\mathrm{III}}$ ($s = {}^1/_2$).

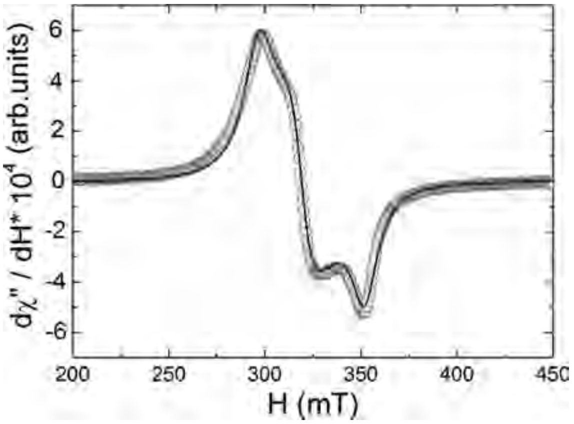

Figure 3. Experimental X-band (9.470 GHz) EPR spectrum of a powder sample of **1**(BF$_4$) at 67 K (gray circles) and its best simulation (full black line).

The $\chi_M T$ product is quasi-constant (~0.42 cm$^3\cdot$K$\cdot$mol^{-1}) over a 2$-$300 K temperature range. This value is consistent with noninteracting spins $^1/_2$ for Ru$^{\mathrm{III}}$ ions. Simultaneously, the field dependence of the magnetization at 2 K matches perfectly the Brillouin function for $s = {}^1/_2$ with $g = 2.045$ (Figure S3 in the Supporting Information).

In summary, we synthesized the first paramagnetic 4d transition-metal complex containing organic donors as ligands covalently linked through π-conjugated bridges. In **1**, TTF is neutral and therefore the magnetic properties reveal a paramagnetic behavior corresponding to $s = {}^1/_2$ of the Ru$^{\mathrm{III}}$ ion. The crystal structure and electrochemical properties are appropriate for its potential use as a molecular brick for conducting and magnetic materials. It is already known in our group that the TTF-CH=CH-Py ligand can be partially[3b] or fully oxidized[3c] when it is coordinated to a transition metal. So, chemical and electrochemical partial oxidation of **1** is under current investigation. The possibility of coordinating a paramagnetic 4d transition-metal ion to TTF derivatives opens the way of new multifunctionnal materials with significant interaction between mobile and localized electrons.

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Supporting Information Available: Crystallographic information in CIF format, ORTEP view, cyclic voltammetry for [Ru(salen)(PPh$_3$)(Cl)] and TTF-CH=CH-Py, and field dependence of the magnetization for **1**(BF$_4$). This material is available free of charge via the Internet at http://pubs.acs.org.

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