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4f Gadolinium(III) Complex Involving Tetrathiafulvalene-amido-2-pyrimidine-1-oxide as a Ligand

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A coordination gadolinium(III) mononuclear complex involving the new redox-active tetrathiafulvaleneamido-2-pyrimidine-1-oxide is synthesized. The X-ray structure of the 1:3 gadolinium complex [Gd(hfac)$_3$(TTF-CONH-2-Pym-1-oxide)$_3$](CH$_2$Cl$_2$)$\cdot$0.5C$_6$H$_{14}$ reveals that the coordination polyhedron of the paramagnetic 4f (S = $^7/_2$) Gd^{III} ion can be described as a 4,4,4-tricapped trigonal prism. The three-coordinated TTF derivatives adopt a *fac* conformation with a pseudohelicoidal arrangement. A radical-cation salt of this new ligand is reported. Such a coordination complex is an innovative building block for the $\pi-$f system and the introduction of new physical properties.

The development of $\pi-$d systems as multifunctional materials is an attractive research domain for chemists and physicists. In particular, the tetrathiafulvalene (TTF)-based $\pi-$d systems involving electrical conductivity and magnetism are intensively studied.[1] The most promising research method is the establishment of a covalent link between the TTF core (source of mobile π electrons) and the paramagnetic ions (source of d or f electrons). To realize such materials, functionalization of the TTF fragment by amido derivatives is efficient for coordination of metallic centers.[2] Some functionalized TTF ligands can be suitable for the coordination of also the lanthanides. Lanthanide ions are studied because of a wide range of potential uses due to their visible and near-IR luminescent properties.[3] They show more peculiar magnetic properties because of the magnetic anisotropy arising from the large spin$-$orbit coupling of 4f electrons. Thus, 4f complexes can present slow relaxation of their magnetization and single-molecule and chain magnet behavior.[4] In the case of the Gd^{III} ion, it is a good choice to elaborate a high-spin molecule because of its spin $^7/_2$ value and it is known that ferromagnetic interactions are observed with a numerous 3d elements[5] and organic radicals.[6] Only some radical salts of donors with rare-earth complexes are reported in the literature, showing interesting electronic conducting properties.[7] Because of the extremely weak intensity of the f$-$f transition in lanthanides, the luminescence is usually sensitized by organic antenna chromophores, which strongly absorb in the UV$-$visible region.[3] Two interesting works are reported in the literature, speaking about the coordination of a TTF derivative with lanthanides.[8] We propose to synthesize new amidotetrathiafulvalene suitable for the coordination of lanthanide ions and elaborate promising coordination complexes as building blocks for $\pi-$f systems. The ligand tetrathiafulvaleneamido-2-pyrimidine-1-oxide (**L**) is motivated by the presence of two coordination sites (see the inset of Figure 1). The N$-$O group is suitable for the coordination of oxophile 4f ions. Moreover, the remaining free nitrogen atom can coordinate 3d transition metals to build heterobimetallic complexes.

In this work, we present the synthesis of the ligand **L** and its gadolinium(III) coordination complex of formula

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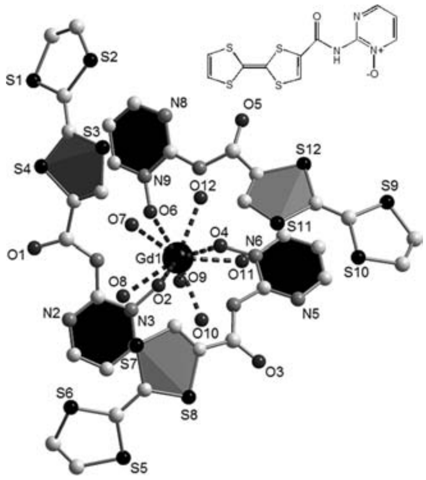

Figure 1. *fac* conformation and pseudohelicoidal arrangement of the coordinated ligands **L** in **1** with highlighting of the intramolecular $\pi-\pi$ interactions between the TTF core (gray planes) and pyrimidine-1-oxide (black planes). Inset: scheme of the ligand **L**.

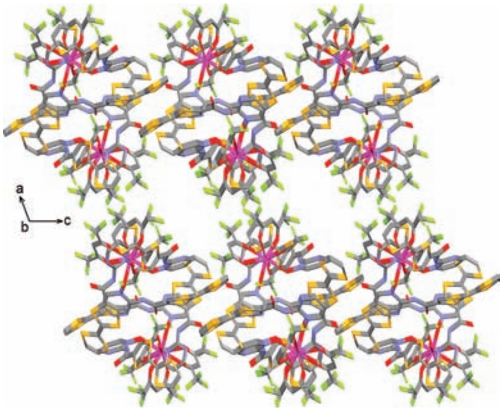

Figure 2. View of the crystal packing of **1** in the plane (101).

[Gd(hfac)$_3$(TTF-CONH-2-Pym-1-oxide)$_3$](CH$_2$Cl$_2$)$\cdot$0.5C$_6$H$_{14}$ (**1**). This complex is fully characterized.

The ligand **L** is synthesized from 4-(chlorocarbonyl) tetrathiafulvalene and 2-aminopyrimidine-1-oxide.[2] The three ^{1}H NMR resonances of **L** at 8.72, 8.21, and 7.35 ppm confirm that only one of the two nitrogen atoms of pyrimidine is oxidized. The reaction between an excess of **L** and the precursor Gd(hfac)$_3\cdot$2H$_2$O[9] in the noncoordinating dichloromethane solvent leads to **1**. First attempts of electrocrystallization of **1** have led to single crystals of ($\mathbf{L}^{\bullet+}$)(PF_6^-).

1 crystallizes in the monoclinic $P2_1/c$ space group.[10] An ORTEP view is shown in Figure S1 in the Supporting Information. The asymmetric unit is composed of a metallic Gd$^{\mathrm{III}}$ ion, three bischelate hfac$^-$ anions, and three TTF-CONH-2-Pym-1-oxide acting as monochelating ligands. Half of *n*-hexane and one dichloromethane molecules of crystallization complete the asymmetric unit. The TTF derivatives are coordinated to the Gd$^{\mathrm{III}}$ ions through the oxygen atoms of the N−O groups (O2, O4, and O6) (Figure 1). Six additional oxygen atoms (O7, O8, O9, O10, O11, and O12) from three hfac$^-$ ligands complete the coordination sphere of the Gd$^{\mathrm{III}}$ ion. The gadolinium surroundings can be described as a 4,4,4-tricapped trigonal prism, where all of the faces are triangular. The coordination polyhedron has a D_{3h} symmetry. The Gd−O distances range from 2.389(8) to 2.510(9) Å, and the coordination angles Gd−O−N from 122.3(5) to 130.2(6)°, which is lower than the usual angle value (about 150°) for $\mathrm{Ln{-}O{-}N}_{\text{nitronyl nitroxide}}$.[6] The low values of the Gd−O−N angles are probably due to the presence of three bulky ligands **L**.

The coordinated oxygen atoms from three TTF derivatives form one of the triangular faces of the coordinating polyhedron, leading to a *fac* conformation of the three ligands **L**. The arrangement of the ligands **L** can be described as a pseudopropeller. The bond lengths and bond angles of the TTF moieties [in particular, the mean C=C central bond 1.349(17) Å] are close to those reported for neutral amido-TTF, indicating that **L** ligands are neutral. Intramolecular $\pi-\pi$ interactions take place between the TTF (gray planes) and pyrimidine-1-oxide rings (black planes) thanks the mean drastic torsion angle of 43.6(1)° between these planes (Figure 1). The two organic and inorganic networks are respectively formed by the three-coordinated TTF ligands in the *fac* conformation and the Gd(hfac)$_3$ entities (Figure 2).

It is worth noticing that the three ligands **L** are on the same side of the gadolinium(III) coordination sphere and the three hfac$^-$ anions occupy the opposite site. This segregation permits optimization of the intermolecular interactions between the donors and between the perfluorated ligands (Figure 2). In the organic network, the crystalline organization of the donors takes place thanks to unusual $\mathrm{S}\cdots\mathrm{O}_{\mathrm{carbonyl}}$ and classic S$\cdots$S short contacts.[11] The inorganic network is composed of a double layer of Gd(hfac)$_3$ entities along the *c* axis (Figure 2). The Gd(hfac)$_3$ species interact through the perfluorated groups.

($\mathbf{L}^{\bullet+}$)(PF_6^-) crystallizes in the monoclinic $C2/c$ space group.[12] The asymmetric unit is composed of one radical cation of **L** and one PF_6^- anion (Figure S2 in the Supporting Information). The radical-cation TTF is planar, and the torsion angle with pyrimidine-1-oxide is equal to 13.62(13)°. The C3=C4 central bond length [1.405(4) Å] confirms the radical form of the TTF fragment. The crystal packing of ($\mathbf{L}^{\bullet+}$)(PF_6^-) is constituted of zigzag chains, in which an alternation of the strong dimers of TTF [four intermolecular short contacts S$\cdots$S ranging from 3.2596(19) to 3.3123(13) Å] and $\pi-\pi$ stacking of pyrimidine-1-oxide take place (Figure S3 in the Supporting Information).

The redox properties of **L** and **1** are determined by cyclic voltammetry (Figure S4 in the Supporting Information). For both compounds, two reversible single-electron-oxidation waves are observed at 540 and 870 mV (for **L**) and 510 and 870 mV (for **1**) vs SCE, corresponding successively to the

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[10] Crystal data for **1**: $\mathrm{C_{52}H_{33}Cl_2F_{18}GdN_9O_{12}S_{12}}$, M = 1930.74 g mol^{-1}, T = 293(2) K, monoclinic space group $P2_1/c$ (No. 14), a = 20.066(5) Å, b = 14.879(5) Å, c = 26.377(5) Å, β = 107.297(5)°, V = 7519(3) Å^3, Z = 4, diffraction reflection 4.9° < 2θ < 53.48°, ρ_{calcd} = 1.706 g cm^{-3}, μ = 1.391 mm^{-1}, R1 = 0.0981, wR2 = 0.2109 for 7673 reflections with $I > 2\sigma(I)$ and 983 parameters, S = 1.087.

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[12] Crystal data for ($\mathbf{L}^{\bullet+}$)(PF_6^-): $\mathrm{C_{11}H_7F_6P_1N_3O_2S_4}$, M = 486.41 g mol^{-1}, T = 293(2) K, monoclinic space group $C2/c$ (No. 15), a = 9.7342(4) Å, b = 17.4733(8) Å, c = 19.6120(7) Å, β = 91.493(2)°, V = 3334.6(2) Å^3, Z = 8, diffraction reflection 6.24° < 2θ < 57.40°, ρ_{calcd} = 1.938 g cm^{-3}, μ = 0.744 mm^{-1}, R1 = 0.0538, wR2 = 0.1320 for 2611 reflections with $I > 2\sigma(I)$ and 244 parameters, S = 1.040.

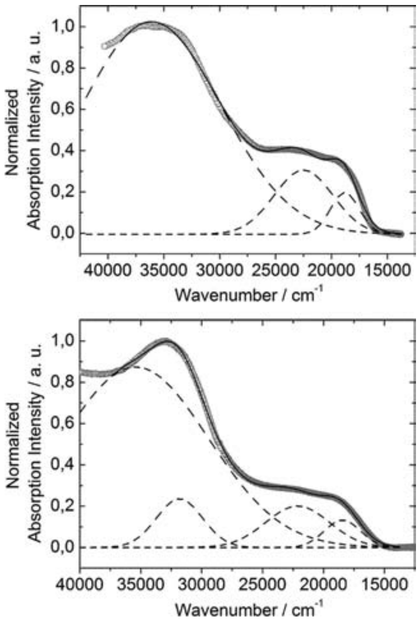

Figure 3. Experimental solid-state UV–visible absorption spectra of **L** and **1** (open gray circles), Gaussian deconvolution of the experimental curve (dash black lines), and the best-fit $R = 0.998$ (for **L**) and $R = 0.999$ (for **1**) (full black line).

formation of the radical cations and dicationic species. These values are anodically shifted in comparison with the oxidation potentials measured for the parent TTF (380 and 770 mV) due to the electron-withdrawing nature of the amido-2-pyrimidine-1-oxide substituent, which makes oxidation of the TTF core more difficult for ligand **1**. The amido bridge permits a weak electron communication, and no significant effect of coordination of the $\mathrm{Gd^{III}}$ ion is observed. Nevertheless, cyclic voltammetry attests of the redox activity of **L** and **1**.

The photophysical properties of **L** and **1** are determined by solid-state UV–visible–near-IR spectroscopy (Figures 3 and S5 in the Supporting Information). The spectrum of **L** shows three absorption bands centered at 18 800, 22 500, and 36 100 $\mathrm{cm^{-1}}$. The lowest-energy absorption bands are characteristic of monoelectronic highest occupied molecular orbital (HOMO) → lowest unoccupied molecular orbital (LUMO) and HOMO → LUMO + n charge transfers (CTs) in which the HOMO is a TTF donor-centered π orbital, the LUMO is centered on the pyrimidine-1-oxide acceptor, and the LUMO + n represents a higher-energy orbital than the LUMO, which is centered on the acceptor. The highest-energy absorption band is characteristic of an intramolecular π–π^* transition of the acceptor substituent. The spectrum of **1** shows a new absorption band in the UV (31 800 $\mathrm{cm^{-1}}$) compared to the spectrum of **L**. It corresponds to the intramolecular π–π^* transition of the $\mathrm{hfac^-}$ ligands; the intramolecular π–π^* transition of the substituent is found at 35 400 $\mathrm{cm^{-1}}$. The π–π^* CTs from the TTF core to the acceptor (18 500 and 22 100 $\mathrm{cm^{-1}}$) are red-shifted in **1** in comparison to **L**. Complexation to the $\mathrm{Gd^{III}}$ ion leads to a decrease in the electron density of the pyrimidine-1-oxide group, which causes energy stabilization of the π^* orbital of the substituent and so the energy decrease of the π–π^* CTs from the TTF core to pyrimidine-1-oxide.[13] The spectrum of $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$ shows two new absorption bands compared to the spectrum of **L** (Figure S5 in the Supporting Information). The absorption bands centered at 12 200 and 27 300 $\mathrm{cm^{-1}}$ are attributed respectively to singly occupied molecular orbital (SOMO)–n → SOMO CT from 2-pyrimidine-1-oxide to the TTF fragment and SOMO → LUMO CT of $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$. SOMO–$n$ represents an acceptor-centered lower-energy orbital than the SOMO. Both absorption bands are characteristic of oxidized TTF derivatives.[13]

Figures S6 and S7 in the Supporting Information show the magnetic behavior of **1**. The curve $\chi_M T(T)$ takes a quasi-constant value of 8.00 $\mathrm{cm^3\ K\ mol^{-1}}$ in the temperature range of 5–300 K and shows a very weak decrease below 5 K. The experimental value of 8.00 $\mathrm{cm^3\ K\ mol^{-1}}$ is in agreement with one magnetically isolated $\mathrm{Gd^{III}}$ ($S = {}^7/_2$, $g = 2.00$) (theoretical value 7.88 $\mathrm{cm^3\ K\ mol^{-1}}$).[14] The first magnetization is reproduced by the Brillouin curve (inset of Figure S6 in the Supporting Information) that is calculated for one $S = {}^7/_2$ and $g = 1.99$. The Curie–Weiss constant ($\theta = -0.67$ K; Figure S7 in the Supporting Information) confirms that the complex **1** is a paramagnetic system with very small antiferromagnetic interactions between the $\mathrm{Gd^{III}}$ centers.

In conclusion, the X-ray structure of **1** has demonstrated that the ligand **L** permits coordination of the $\mathrm{Gd^{III}}$ ion and formation of a mononuclear complex $[\mathrm{Gd(hfac)_3}(\mathbf{L})_3]$. The $\mathrm{Gd^{III}}$ ion adopts a 4,4,4-tricapped trigonal prism as its coordination geometry. Three neutral ligands **L** are coordinated through the oxygen atoms of the N–O groups in the *fac* conformation with a helicoidal arrangement. The X-ray structure of the radical cation $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$ has revealed a 1D organization with strong dimerization of the donors. The electrochemical properties demonstrate the redox activity of **L** and **1**, while the photophysical properties attest to coordination of the $\mathrm{Gd^{III}}$ ion and the oxidized form of $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$. Finally, the magnetic properties reveal a paramagnetic behavior of the isolated $S = {}^7/_2$ spins of the $\mathrm{Gd^{III}}$ centers. Efforts to obtain an oxidized complex of **1** from $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$ are currently underway in our group. The use of these kinds of ligands for coordination of the lanthanides is an interesting and promising approach to obtain new π–f systems with new physical properties as slow relaxation of the magnetization and/or luminescence. Moreover, the remaining free nitrogen atom opens the possibility of building 3d4f heterobimetallic compounds.

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Supporting Information Available: Details for physical measurements, crystallographic information in CIF format, ORTEP views, cyclic voltammetry for **L**, **1**, and $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$, crystal packing of $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$, solid-state UV–visible spectrum for $(\mathbf{L}^{\bullet+})(\mathrm{PF_6^-})$, and $\chi_M T(T)$ and $1/\chi_M(T)$ curves for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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