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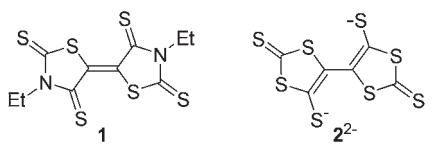
A sulfur rich electron acceptor and its $[Fe(Cp^*)_2]^+$ charge transfer salt with ferromagnetic interactions

Yann Le Gal,[a] Nathalie Bellec,[a] Frédéric Barrière,[a] Rodolphe Clérac,[b,c] Marc Fourmigué,[a] Vincent Dorcet,[a] Thierry Roisnel[a] and Dominique Lorcy[a]

The study of a side product of the aerial dithiolene oxidation allowed the rational and efficient synthesis of a sulfur rich electron acceptor, (*E*)-3,3′-diethyl-5,5′-bithiazolidinylidene-2,4,2′,4′-tetrathione, that presents easily accessible redox states and forms with decamethylferrocene a charge transfer salt exhibiting ferromagnetic coupling.

The chemistry of sulfur rich π-electron donors such as tetrathiafulvalene (TTF) and their use in forming charge transfer complexes, exhibiting either conducting or magnetic properties, are rich, especially compared with that of π-electron acceptor systems.[1,2] Only a few examples of sulfur containing electron acceptors, mainly based on thiophene–TCNQ (TCNQ: tetracyanoquinodimethane) derivatives, have been described to date, although they could open new prospects in terms of intermolecular interactions through S···S contacts.[3] During our investigations on the synthesis of bis(dithiolene) gold complexes[4] through the reaction of *N*-ethyl-1,3-thiazoline-2-thione-4,5-dithiolate with $KAuCl_4$, we observed the formation of a colorful side product **1**, (*E*)-3,3′-diethyl-5,5′-bithiazolidinylidene-2,4,2′,4′-tetrathione, in very low yield (1–5%), which did not contain any metal.



This derivative turned out to be the same side product as that obtained serendipitously and in low yield by Arca *et al.* from the reaction of ethyl-2-thioxothiazolidine-4,5-dione with Lawesson's reagent in the presence of nickel powder.[5] The molecule was only structurally characterized, together with UV-Vis and IR analyses. Its structure is very appealing since it recalls the work performed by Rauchfuss *et al.* on the reduced structure $\mathbf{2}^{2-}$, which undergoes two sequential and reversible monoelectronic oxidation processes.[6] Anticipating that a similar attractive redox behavior could be found with **1**, we have explored a more efficient synthesis of **1**.

Herein, we present the chemical route we developed for an efficient preparation of **1** together with its electrochemical properties, in order to determine its potential interest as an electron acceptor for the elaboration of molecular materials. The structure and magnetic properties of the very first charge transfer salt involving **1** as the acceptor, with decamethylferrocene, $[Fe(Cp^*)_2]$, as the donor molecule, are also reported.

Our approach towards the target molecule **1** was based on the fact that this derivative was obtained as a side product from the reaction of the dithiolate, generated *in situ* from the bis(cyanoethylthio) derivative **3** (Scheme 1) with an excess of MeONa, with $KAuCl_4$. Thus, we assumed that the formation of this byproduct was due to the oxidation of the unreacted dithiolate occurring during the work-up of the reaction. Deprotection of the dithiolate was thus performed by adding under an inert atmosphere an excess of MeONa into a THF solution of **3**. Then, after bubbling air into the THF solution for 3 days, we isolated the dimerized structure **1** in 50% yield (Scheme 1). Single crystals of **1** were obtained after slow concentration of a CH_2Cl_2 solution. The crystal structure was solved in the triclinic $P\bar{1}$ space group.‡ It is identical to that already described by Arca *et al.* with crystals obtained from $CHCl_3$–MeOH solution.[5]

The molecular structure of **1** is given in Fig. 1. **1** Exhibits a planar skeleton with (i) a short intramolecular 1,5 S1···S2 contact of 2.937(4) Å due to the *trans* arrangement of the thiazole rings and (ii) the ethyl groups pointing out of the plane.

The cyclic voltammetry (CV) of **1** shows two reversible reduction waves corresponding to two one-electron reductions (Fig. 2). These reduction processes are assigned to the reversible reduction of the neutral species to the anionic radical

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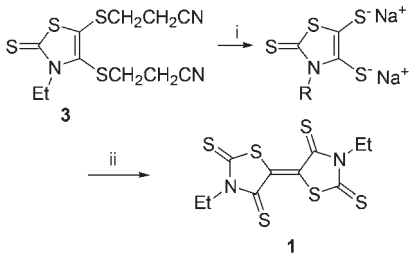


Scheme 1 Reagents and conditions: (i) MeONa, THF; (ii) O_2.

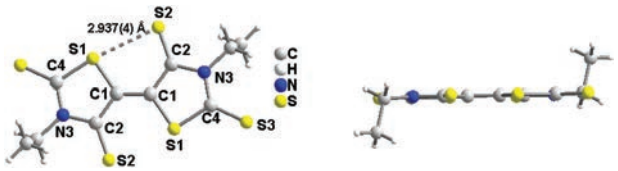


Fig. 1 Molecular structure and numbering schemes for **1**.

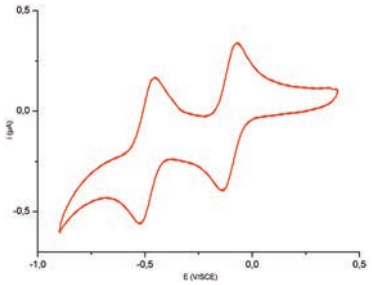
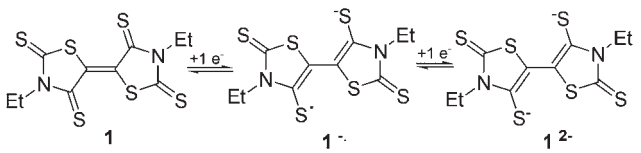


Fig. 2 Cyclic voltammogram of **1** in 0.1 M CH_2Cl_2–$[NBu_4][PF_6]$ (E in V *vs.* SCE, v = 100 mV s^{-1}).



Scheme 2 Three redox states of **1**.

and the dianion (E_1 = −0.05 V and E_2 = −0.44 V *vs.* SCE, ΔE = ($E_2 - E_1$) = 390 mV in CH_2Cl_2–[nNBu$_4$][PF_6]).

It is of interest to compare these redox potentials with those of well-known π-acceptors such as TCNE (tetracyanoethylene) (E_1 = 0.15 and E_2 = −0.57 V *vs.* SCE) and TCNQ (E_1 = 0.18 and E_2 = −0.37 V *vs.* SCE).[7] These redox potentials show that **1** exhibits a slightly lower accepting ability than TCNQ or TCNE but can give easily access to the radical anion and dianion species (Scheme 2).

As the formation of charge transfer salts depends on the relative redox potentials of the donor and the acceptor,[8] we choose a donor molecule exhibiting appropriate redox properties such as decamethylferrocene, $[Fe(Cp^*)_2]$ (E_{ox} = −0.05 V *vs.* SCE). The mixing of a dichloromethane solution of **1** with a dichloromethane solution of $[Fe(Cp^*)_2]$ afforded deep purple

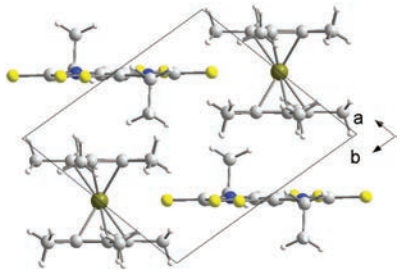


Fig. 3 Projection view in the (a,b) plane of $[Fe(Cp^*)_2][\mathbf{1}]$, showing the alternating stacks along $a - b$.

Table 1 Selected experimental and calculated (DFT) bond lengths (Å) for **1** and $\mathbf{1}^{-\bullet}$ in $[Fe(Cp^*)_2][\mathbf{1}]$

	1	Calc.	$\mathbf{1}^{-\bullet}$	Calc.
C1–C1	1.371(3)	1.376	1.408(6)	1.409
C1–C2	1.465(5)	1.466	1.418(4)	1.421
C2–S2	1.648(3)	1.660	1.679(5)	1.694
C2–N3	1.386(3)	1.385	1.405(7)	1.410
N3–C4	1.370(4)	1.376	1.359(5)	1.361
C4–S1	1.761(6)	1.772	1.746(3)	1.755
C1–S1	1.751(4)	1.765	1.752(5)	1.778
C4–S3	1.641(2)	1.646	1.665(7)	1.678

single crystals after slow evaporation of the solution. X-ray crystal structure determination reveals a 1 : 1 stoichiometry, with the formula $[Fe(Cp^*)_2][\mathbf{1}]$. It crystallizes in the triclinic $P\bar{1}$ space group, with both cations and anions located on inversion centres.‡

In the solid state, chains of alternating oxidized donor and reduced acceptor running along the ($a - b$) direction are observed (Fig. 3). This organization is reminiscent of that observed for $[Fe(Cp^*)_2][TCNE]$[9] or $[Fe(Cp^*)_2][TCNQ]$.[9,10] The intrachain Fe(III)–Fe(III) separation is 11.035 Å while the interchain Fe(III)–Fe(III) distances are shorter, namely 10.691, 10.498, 9.693 and 9.338 Å. The radical cation adopts a staggered conformation of the Cp* rings and the average Fe–C and C–C distances are essentially equivalent to those observed in the $[Fe(Cp^*)_2][C_3(CN)_5]$ compound and slightly longer (by 0.01 Å) than those in the $[Fe(Cp^*)_2][TCNE]$ salt.[9] The radical anion is planar and lies parallel to the Cp* rings with an interplanar separation of 3.77 Å. Note also that because of the donor/acceptor alternation in the perpendicular ($a + b$) direction, the radical anions are fully isolated from each other. It is interesting here to compare the geometrical characteristics of the reduced acceptor with those of the neutral one. Upon reduction, modifications of the bond lengths occur essentially on the central S2═C2–C1═C1–C2═S2 fragment (Table 1 and Fig. 1 for atom numbering). For instance, the central C1═C1 bond is lengthened as well as the closest exocyclic C2═S2 bond while the cyclic C1–C2 bond is shortened in accordance with the presence of a delocalized radical anion.

DFT calculations [Gaussian03, B3LYP/6-311G**] were carried out on the neutral and the monoanionic species, **1** and $\mathbf{1}^{-\bullet}$. Full geometry optimizations led to the molecular structure

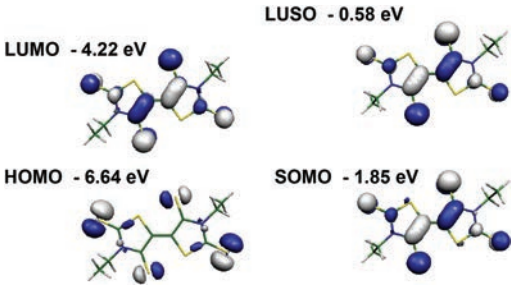


Fig. 4 HOMO and LUMO of **1** (left) and SOMO and LUSO of $\mathbf{1}^{-\bullet}$ (right) shown with a cut-off of 0.04 [e bohr^{-3}]$^{1/2}$.

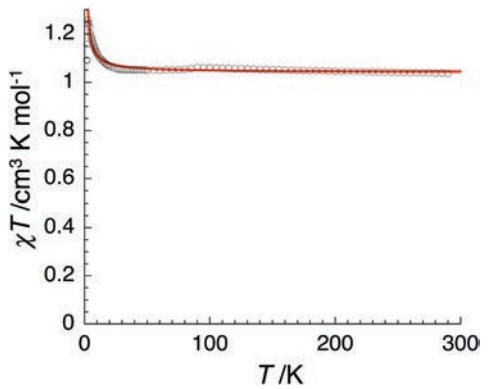


Fig. 5 Temperature dependence of the χT product for [Fe(Cp*)$_2$][**1**] at 1000 Oe (with χ defined as molar magnetic susceptibility equal to M/H per [Fe(Cp*)$_2$][**1**] unit). Black circles indicate measured data; the red line represents the best fit obtained with the chain model described in the text.

depicted in Fig. 4. The optimized geometries of **1** and $\mathbf{1}^{-\bullet}$ are in very good agreement regarding bond angle and bond length evolutions with those obtained by X-ray diffraction (Table 1). The HOMO of **1** is essentially localized on the four exocyclic sulfur atoms while the LUMO is predominantly localized on the central S2═C2–C1═C1–C2═S2 fragment with some contribution found on the C4═S3 fragment.

The magnetic susceptibility of [Fe(Cp*)$_2$][**1**] was measured between 1.8 and 290 K. As shown in Fig. 5, the χT product amounts to 1.04 cm^3 K mol^{-1} at RT. The expected value for the sum of two such S = 1/2 species reads $\chi T = 0.375 \times (g_{donor}{}^2/4 + g_{acceptor}{}^2/4)$. Considering a $g_{acceptor}$ value close to 2 for a fully organic radical anion, we deduced a g_{donor} value of 2.68, close to that reported indeed for the decamethyl ferricinium cation.[9a,10] The data can be fitted by the Baker model[11] for a chain of ferromagnetic coupled S = 1/2 Heisenberg spins, giving J/k_B = +0.30(5) K, g_{rad} = 2 (fixed) and g_{Fe} = 2.71(5). The magnetic susceptibility can also be fitted to a Curie–Weiss law that allows comparing this ferromagnetic interaction with previous systems. The obtained Weiss constant is +0.6 K (C = 1.04 cm^3 K mol^{-1}) for [Fe(Cp*)$_2$][**1**] that is much lower than the θ values found in [Fe(Cp*)$_2$][TCNE] or [Fe(Cp*)$_2$][TCNQ], respectively +30 and +3 K. While the latter two compounds order ferromagnetically at 4.8 and 2.55 K respectively,[10,12] the weak ferromagnetic interactions observed in [Fe(Cp*)$_2$][**1**] do not allow the stabilization of an ordered ferromagnetic state above 1.8 K.

In conclusion, we have synthesized in an efficient manner an original and sulfur rich electron acceptor molecule with interesting redox properties, as illustrated here with the first charge transfer salt with decamethylferrocene. Weak ferromagnetic interactions demonstrate the potential offered by this salt as many chemical modifications can be considered, on the metallocene side (Fe *vs*. Mn *vs*. Cr, and on the Cp ring) and on the acceptor side. Indeed, the strategy used to synthesize this electron acceptor opens broad perspectives in the quest for novel molecular materials, as the substituent on the nitrogen atom can be very easily modified,[13] as well as the nature of the chalcogen atoms,[14] offering a wide variety of novel acceptor molecules with controlled structural and redox properties.

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Notes and references

‡X-ray data for the structure reported by Arca[5] were collected at 93(2) K; we report here our own results based on the data collected at 150(2) K. Crystal data for **1**, ($2(C_{10}H_{10}N_2S_6)$), M = 701.12, triclinic, space group $P\bar{1}$, a = 7.4387(5), b = 8.1655(7), c = 12.5242(9) Å, α = 108.826(4), β = 101.941(4), γ = 91.319(4)°, V = 701.13(9) Å^3, Z = 1, T = 150(2) K, Mo-Kα(λ = 0.71073 Å), D_{calc} = 1.661 g cm^{-3}, μ = 0.956 mm^{-1}, 8754 reflections measured, of which 3185 independent (R_{int} = 0.037) R_F = 0.0396 [2971 data, $I > 2\sigma(I)$], w$R(F^2)$ = 0.0911, GOF = 1.033. Crystal data for [Fe(Cp*)$_2$][**1**], M = 676.84, triclinic, space group $P\bar{1}$, a = 9.3382(12), b = 9.6932(12), c = 10.4978(14) Å, α = 76.994(6), β = 64.923(6), γ = 70.853(6)°, V = 808.93(18) Å^3, Z = 1, T = 150(2) K, Mo-Kα(λ = 0.71073 Å), D_{calc} = 1.389 g cm^{-3}, μ = 0.877 mm^{-1}, 12 794 reflections measured, of which 3662 independent (R_{int} = 0.0437) R_F = 0.0396 [2971 data, $I > 2\sigma(I)$], w$R(F^2)$ = 0.0911, GOF = 1.055.

1 N. Martin, *Chem. Commun.*, 2013, **49**, 7025–7027.
2 P. Batail (Ed.), *Special issue on Molecular Conductors*, *Chem. Rev.*, 2004, **104**, 4887–5781.
3 (*a*) S. Gronowitz and B. Uppström, *Acta Chem. Scand.*, 1974, **B28**, 981–985; (*b*) K. Yui, T. Aso, T. Otsubo and F. Ogura, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1539–1546; (*c*) D. Lorcy, K. D. Robinson, Y. Okuda, J. L. Atwood and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1993, 345–346; (*d*) T. Takahashi, K. Matsuoka, K. Takimiya, T. Osubo and Y. Aso, *J. Am. Chem. Soc.*, 2005, **127**, 8928–8929; (*e*) T. M. Pappenfus, M. W. Burand, D. E. Janzen and K. R. Mann, *Org. Lett.*, 2003, **5**, 1535–1538.
4 N. Tenn, N. Bellec, O. Jeannin, L. Piekara-Sady, P. Auban-Senzier, J. Íñiguez, E. Canadell and D. Lorcy, *J. Am. Chem. Soc.*, 2009, **131**, 16961–16967.
5 M. C. Aragoni, M. Arca, F. A. Devillanova, F. Isaia, V. Lippolis, A. Mancini, L. Pala, A. M. Z. Slawin and J. D. Woollins, *Inorg. Chem.*, 2005, **44**, 9610–9612.

6 (*a*) C. P. Galloway, D. D. Doxsee, D. Fenske and T. B. Rauchfuss, *Inorg. Chem.*, 1994, **33**, 4537–4544; (*b*) J. H. Chou, T. B. Rauchfuss and L. Szczepura, *J. Am. Chem. Soc.*, 1998, **120**, 1805–1811.

7 M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan and S. Gronowitz, *J. Phys. Chem.*, 1980, **84**, 427–431.

8 (*a*) J. B. Torrance, J. E. Vazquez, J. J. Mayerle and V. Y. Lee, *Phys. Rev. Lett.*, 1981, **46**, 253–257; (*b*) G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141–2145.

9 (*a*) J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769–781; (*b*) J. S. Miller, D. T. Glatzhofer, D. M. O'Hare, W. M. Reiff, A. Chakraborty and A. J. Epstein, *Inorg. Chem.*, 1989, **28**, 2930–2939.

10 G. T. Yee and J. S. Miller, in *Magnetism: molecules to materials V*, ed. J. S. Miller and M. Drillon, Wiley, Weinheim, ch. 7, 2005.

11 G. A. Baker Jr., G. S. Rushbrooke and H. E. Gilbert, *Phys. Rev.*, 1964, **135**, A1272–A1277.

12 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385–415.

13 T. Bsaibess, M. Guerro, Y. Le Gal, D. Sarraf, N. Bellec, M. Fourmigué, F. Barrière, V. Dorcet, T. Guizouarn, T. Roisnel and D. Lorcy, *Inorg. Chem.*, 2013, **52**, 2162–2173.

14 G. Yzambart, N. Bellec, G. Nasser, O. Jeannin, T. Roisnel, M. Fourmigué, P. Auban-Senzier, J. Íñiguez, E. Canadell and D. Lorcy, *J. Am. Chem. Soc.*, 2012, **134**, 17138–17148.