ChemComm

Thiacrown ether tetrathiafulvalene derivatives as redox responsive ligands

Franck Le Derf,[a] Miloud Mazari,[a] Nicolas Mercier,[a] Eric Levillain,[a] Pascal Richomme,[b] Jan Becher,[c] Javier Garín,[d] Jesus Orduna,[d] Alain Gorgues[a] and Marc Sallé*[a]

[a] *Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France. E-mail: salle@univ-angers.fr*
[b] *SC RMN, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France*
[c] *Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark*
[d] *Instituto de Ciencia de Materiales de Aragon, Unidad de Nuevos Materiales Orgánicos, Facultad de Ciencias, CSIC-Universidad de Zaragoza E-50009 Zaragoza, Spain*

Received (in Liverpool, UK) 29th March 1999, Accepted 17th June 1999

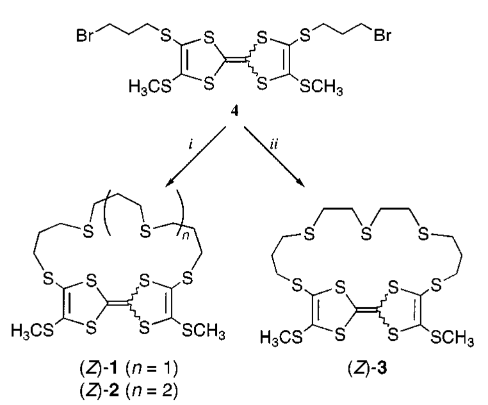
Thiacrown ether TTF derivatives have been synthesized; one of them, whose X-ray molecular structure has been determined, is shown to combine Ag^+ recognition and reversible binding properties as a function of the electrochemical potential applied.

The design of redox-responsive ligands able to recognise cationic guests constitutes an area of active research.[1] In this context, a substantial amount of work has been devoted to the covalent association of a polyether subunit to the tetrathiafulvalene (TTF) moiety.[2,3]

Surprisingly, very few examples of *soft* ligands designed to bind transition metal cations, such as azacrown [4] or thiacrown [5] TTF analogues, have been described. Furthermore, all polythioether-TTFs described so far are poorly soluble, which has precluded any proper characterisation of their metal binding ability.[5]

We now report the synthesis of new sulfur ligands involving various polythioether chains connected to the 2,7-positions of the TTF core, as well as the selective Ag^+ complexing properties of one of them. Receptors **1**–**3**† were prepared (60%, 49% and 52% respectively) under high dilution conditions in DMF, from the [1 + 1] cyclocondensation of compound **4** [4] with suitable ω-dithiole polythioethers,[6] in the presence of caesium carbonate (Scheme 1). Compounds **1**–**3** whose structures were established by 2D NMR (DQF COSY, ROESY, HMQC, HMBC), were obtained as (*Z/E*) isomeric mixtures in relative amounts of 60:40 (**1**), 65:35 (**2**), 60:40 (**3**) as determined by ^{1}H-NMR.

X-Ray structural determination of (*Z*)-**1** shows that the increased chain length relative to the previously described thiacrown TTF derivative[5b] considerably decreases the degree of bending of the TTF skeleton (Θ = 16.4°) (Fig. 1). This constitutes a structural prerequisite in order to reach reversible redox processes.



Scheme 1 *Reagents and conditions*: (i) propane-1,3-dithiol (synthesis of **1**), 4-thiaheptane-1,7-dithiol (synthesis of **2**), Cs_2CO_3, DMF; (ii) 3-thiapentane-1,5-dithiol, Cs_2CO_3, DMF.

Binding properties of compounds **1**–**3** were evaluated using different techniques (LSIMS, ^{1}H-NMR and cyclic voltammetry (CV)). LSIMS experiments show that the progressive addition of a silver triflate solution leads to the appearance of a peak corresponding to the formation of the 1:1 complex $[\mathbf{L}\text{-Ag}]^+$. Notably, addition of an excess of Ag^+ results in formation of the additional $[\mathbf{L}\text{-2Ag}]^+$ and $[\mathbf{L}\text{-3Ag}]^+$ complexes in the case of ligands **1** and **2**.

For ligands **1** and **2**, this result may be attributed to the competing Ag^+ binding process between the thiacrown part and both terminal $SC{=}CSCH_3$ fragments, as observed for the parent tetramethylsulfanyl-TTF.[7]

This observation was confirmed by ^{1}H-NMR titration studies ($CDCl_3$–CD_3CN [1:1]), the signal corresponding to the methylsulfanyl fragments of **1** and **2** being the only one significantly affected by addition of $AgCF_3SO_3$.[8] For macrocycle **3**, the signals which are shifted to lower fields upon titration correspond to the polythioether methylene protons of the (*Z*) isomer only, confirming that in this case complexation preferentially involves the thiacrown cavity. This good Ag^+ binding ability of the polythioether chain in **3** may be attributed to a better orientation of the coordinating S atoms, contrary to compounds **1** and **2** for which insertion of propylene fragments cannot ensure a correct structural environment, as shown by X-ray data (Fig. 1).‡

Interestingly, the Ag^+ titration curves obtained from ^{1}H-NMR shifts for the crown ether methylene protons of **3** exhibit a plateau for 0.6 equiv. of added cation (Fig. 2). This result is in good agreement with the 60/40 ratio of (*Z*)-**3**/(*E*)-**3** isomers, confirming that Ag^+ binding occurs through the (Z)-isomer only. Analysis of these data with the program EQNMR [9] shows that the crown thioether recognition site of (*Z*)-**3** forms a 1:1 complex with Ag^+, with an average stability constant $K°$ = $10^{3.26}$ ($CDCl_3$–CD_3CN [1:1]).

As expected from the quasi-planar character of the TTF skeleton discussed above in the case of **1**, compounds **1**–**3** exhibit two reversible one-electron redox processes, with

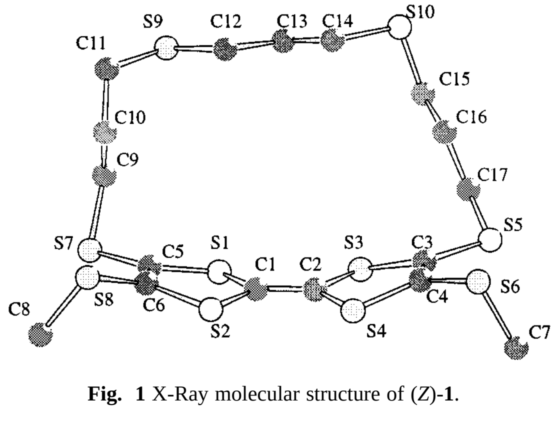


Fig. 1 X-Ray molecular structure of (*Z*)-**1**.

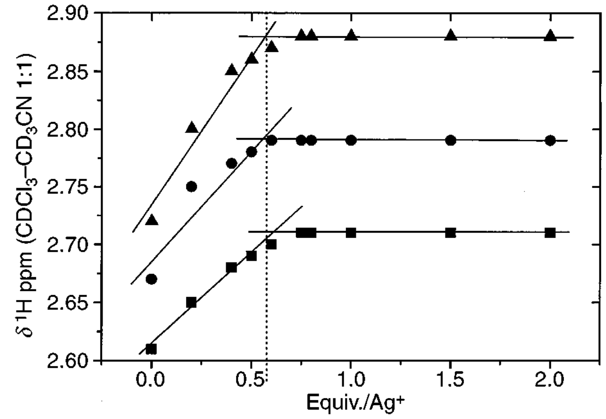


Fig. 2 Proton NMR titration curve of the perturbation of the CH_2S protons of the polythiaether bridge in **3**, upon addition of silver cation.

oxidation potentials similar to those observed for the parent tetramethylsulfanyl-TTF (*e.g.* compound **1**: $E_1^{ox} = 0.59$ V and $E_2^{ox} = 0.89$ V *vs.* Ag/AgCl). Whereas no change is observed in CV of compounds **1** and **2** upon addition of Ag^+ and in agreement with the solution NMR study, the progressive addition of controlled amounts of silver triflate to **3** results in a positive shift of E_1^{ox}. This phenomenon is attributed to the electrostatic inductive effect of the crown ether bound metal cation which causes an increase of E_1^{ox} (Fig. 3). The fact that the E_2^{ox} remains unchanged is attributable to the expulsion of the metal ion from the cavity, due to the doubly charged TTF moiety. Values of the binding constant of the Ag^+ complex as a function the redox state of the TTF core in ligand **3** were evaluated using the DIGISIM 2.1® simulation program (BAS Inc.). A strong Ag^+ affinity is found for the neutral ligand (TTF: $K^\circ = 10^{3.53}$) in good agreement with the value determined by ^1H-NMR. Oxidation of TTF into $TTF^{\cdot+}$ leads to a decrease of the complexation ability ($K^{\cdot+} = 10^{1.95}$) and to the expulsion of the metal for the dicationic TTF^{2+} state, as shown by the constant E_2^{ox} value ($K^{2+} \approx 0$).

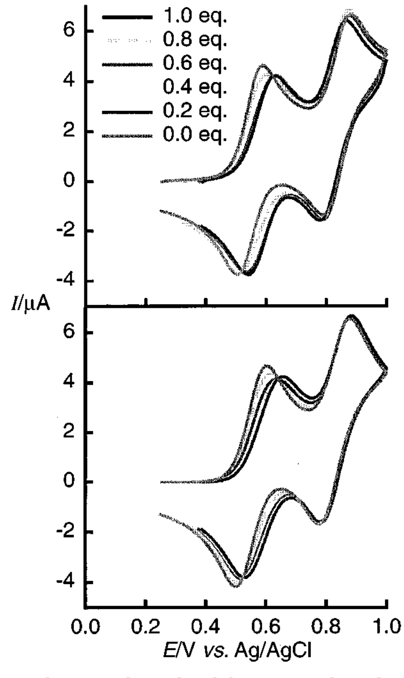


Fig. 3 Experimental (top) and simulated (bottom) cyclic voltammograms of **3** in the presence of increasing amounts of Ag^+. The simulated data were fitted to experimental results for **3** (10^{-3} mol L^{-1} in CH_2Cl_2–CH_3CN [1 : 1], Bu_4NPF_6 (0.1 mol L^{-1})) at 293 K and 100 mV s^{-1}. All simulations were carried out with the same set of parameters, only the Ag^+ equivalent concentration being changed according to the experimental voltammograms. Charge transfer parameters: $k_s = 3.5 \times 10^{-3}$ cm s^{-1}, $\alpha = 0.5$. Chemical reaction parameters: $K^\circ = 3.35 \times 10^3$ L mol^{-1}, $k_f{}^\circ = 1.3 \times 10^6$ L mol^{-1} s^{-1} and $K^{\cdot+} = 90$ L mol^{-1}, $k_f{}^{\cdot+} = 3 \times 10^7$ L mol^{-1} s^{-1}. Diffusion coefficient: $D = 3.6 \times 10^{-6}$ cm^2 s^{-1}.

It is noteworthy that no shift of E_1^{ox} has been observed upon addition of a wide variety of groups 1 or 2 or transition metal ions (Na^I, K^I, Cs^I, Mg^{II}, Ba^{II}, Cr^{III}, Ni^{II}, Zn^{II}, Cd^{II}),[10] which illustrates the good selectivity of ligand **3** for Ag^+.

In conclusion, the efficiency in modulation of the trapping properties of ligand **3** has been demonstrated thanks to an unprecedented metal cation binding ability among crown thioether TTF derivatives (neutral TTF state) associated the controllable releasing of the metal cation upon electrochemical oxidation to the dicationic TTF state.

Financial support DGES (PB 97-1186 and Action Intégrée HF 1997-0042) is gratefully acknowledged.

Notes and references

† All new compounds gave analytical and spectroscopic data consistent with their structures.

‡ *Crystal data* for (*Z*)-**1**: orange crystals, $C_{17}H_{24}S_{10}$, $M = 547.91$, triclinic, $P\bar{1}$, $Z = 2$, $a = 9.482(3)$, $b = 11.870(7)$, $c = 12.393(5)$ Å, $\alpha = 80.90(4)$, $\beta = 69.89(3)$, $\gamma = 70.75(4)^\circ$, $V = 1235(1)$ Å^3, $Z = 2$, $D_c = 1.48$ g cm^{-3}, $T = 293$ K, μ(MoKα) = 0.862 mm^{-1}, 7523 reflections measured, 3706 independent reflections ($R = 0.016$) with $I/\sigma(I) > 3$ available for calculations. The structure was solved by direct methods (SIR program of MoLEN), $R = 0.054$, $R_W = 0.069$ (use of F magnitude, 340 parameters, static disorder appears for several atoms (2 S and 2 C): each of them was located on two positions with half occupancy rate). CCDC 182/1319. See http://www.rsc.org/suppdata/cc/1999/1417/ for crystallographic data in .cif format.

1 For a recent review, see : P. L. Boulas, M. Gómez-Kaifer and L. Echegoyen *Angew. Chem. Int. Ed.*, 1998, **37,** 216.

2 (*a*) For a recent review, see : M. Brøndsted and J. Becher, *Liebigs Ann.*, 1997, 2177; (*b*) R. Dieing, V. Morisson, A. J. Moore, L. Goldenberg, M. R. Bryce, J. M. Raoul, M. C. Petty, J. Garin, M. Saviron, I. K. Lednev, R. E. Hester and J. N. Moore, *J. Chem. Soc., Perkin Trans. 2,* 1996, 1587.

3 F. Le Derf, M. Mazari, M. Sallé, N. Mercier, E. Levillain, P. Richomme, J. Becher, J. Garin, J. Orduna and A. Gorgues, submitted.

4 F. Le Derf, M. Sallé, N. Mercier, J. Becher; P. Richomme, A. Gorgues, J. Orduna and J. Garin, *Eur. J. Org. Chem.*, 1998, 1861.

5 (*a*) M. Wagner, S. Zeltner and R. M. Olk, *Liebigs Ann.*, 1996, 551; (*b*) T. Jorgensen, B. Girmay, T. K. Hansen, J. Becher, A. E. Underhill, M. B. Hursthouse, M. E. Harman and J. D. Kilburn, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2907; (*c*) S. Zeltner, R. M. Olk, M. Wagner and B. Olk, *Synthesis*, 1994, 1445.

6 H. T. Stock and R. M. Kellog, *J. Org. Chem.*, 1996, **61**, 3093.

7 M. Munakata, L. P. Wu, X. Gan, T. K. Sowa and Y. Suenaga, *Mol. Cryst. Liq. Cryst.*, 1996, **284**, 319.

8 $AgCF_3SO_3$ 99+%, purchased from Aldrich.

9 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.

10 Addition of $Cu(CF_3SO_3)_2$ or $Hg(CF_3CO_2)_2$ to **3** in CH_2Cl_2–CH_3CN led to oxidation of the ligand.

Communication 9/02497B