C. R. Chimie 16 (2013) 679–687

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3*d* and 4*d* coordination complexes and coordination polymers involving electroactive tetrathiafulvalene containing ligands

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ARTICLE INFO

Article history:
Received 19 October 2012
Accepted after revision 26 November 2012
Available online 16 January 2013

Keywords:
Coordination complexes
Coordination polymers
Electroactive ligands
Tetrathiafulvalene

ABSTRACT

The "through bond" approach has been recently developed to increase the interaction between the mobile π and localized *d* electrons in multifunctional molecular materials involving tetrathiafulvalene-based ligands. This article reviews the 3*d* and 4*d* coordination complexes and polymers elaborated from a library of tetrathiafulvalene derivatives containing ligands obtained recently in our group. The different synthetic ways of the complexes are highlighted as well as their chemical and physical properties.

1. Introduction

Intense investigations are devoted to multifunctional molecular materials. Chemists and physicists are attracted to designing new molecules and materials which possess synergy or interplay between two or more physical properties such as electrical conductivity, magnetic interactions, luminescence, light, chirality, etc. [1–9]. For the particular class of compounds involving electrical conductivity and magnetism, the objective is to establish a coupling between mobile electrons (π) and localized electrons (*d*). In molecular-based materials, conduction electrons mainly arise from organic moieties assembled in networks while the spins mainly arise from transition metal ions. The strategy is to assemble these moieties with supramolecular chemistry tools. Two approaches are developed: (a) a through-space approach, the interaction between mobile and localized electrons takes place through short contacts between chemical units, which usually lead weak interactions [10–17]; (b) a covalent approach, the interaction between localized and mobile electrons takes place through covalent bonds. Whereas the first strategy leads to very weak π-*d* interactions, the second approach appears as a promising alternative to obtain strong π-*d* interactions and a large number of coordination complexes employing this approach have been studied [18–51]. In the latter case, two procedures are used to prepare such materials: (i) a "one-pot" procedure which consists in a galvanostatic or chemical oxidation from the starting metal salts and neutral donor moieties; and (ii) a "step-by-step" procedure which consists in the synthesis of a paramagnetic transition-metal-based coordination complex involving neutral TTF derivatives, followed by a galvanostatic or chemical oxidation. However, only few of them have been successfully oxidized as radical cation complexes [52–57]. In order to realize the coordination of the 3*d* metal ions, a great variety of coordinating acceptors have been used such as amino, nitrilo, phenolate, phosphino, β-diketonate, pyrazine, pyrimidine, pyridine, pyridine-*N*-oxide, bipyridine groups.

Following the "through bond" approach, our group published in 2001 and 2003 one of the first Cu(II) coordination complex involving a TTF derivative as ligand [34] and its partially oxidized analogue [54], respectively. In this article, we review the 3*d* and 4*d* coordination complexes obtained recently in our group using this

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http://dx.doi.org/10.1016/j.crci.2012.11.016

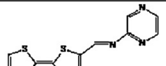
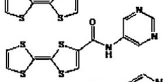
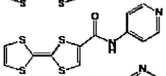
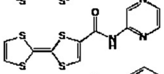
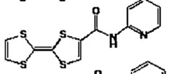
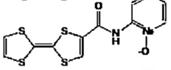
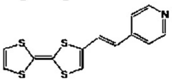
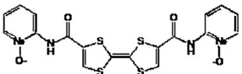
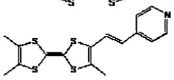
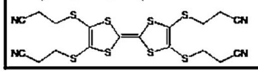
Ligands		Compounds		References
	L^1	$[M(hfac)_2)(L^1)_2]$ M(II) = Mn, Cu and Zn	(1), (2) and (3)	[40]
	L^2	$[Cu(hfac)_2)(L^2)]\cdot H_2O$	(4)	[61]
	L^3	$[Mn(hfac)_2)(L^3)_2]\cdot(THF)_2$	(5)	[61]
	L^4	$[Cu(hfac)_2)(L^4)_2]$	(6)	[61]
	L^5	$[Cu(hfac)_2)(L^5)_2]$	(7)	[61]
	L^6	$[M(hfac)_2)(L^6)_2]$ M(II) = Mn, Cu and Zn	(8), (9) and (10)	[61]
	L^7	$[Ru(salen)(PPh_3)(L^7)](BF_4)$	(11)	[41]
		$[Cu_2(LH)_2(L^7)(H_2O)](ClO_4)_2\cdot 1.5(H_2O)$	(12)	[64]
		$[Co_2M(PhCOO)_6(L^7)_2]\cdot 2(CH_3CN)$ M(II) = Mn and Co	(15) and (16)	[39]
	L^8	$[Cu_2(L^8)_2]$	(13)	[66]
	L^9	$[Co_2(PhCOO)_4(L^9)_2]$	(14)	[68]
	L^{10}	$[M(L^{10})_2M(H_2O)_4](X)_6\cdot 2(H_2O)$ M(II) = Mn, Co, Zn and Cd, $X = BF_4^-$ and ClO_4^-	(17)-(20)	[76]

Fig. 1. Functionalized ligands and related coordination complexes.

approach (Fig. 1). The different and rational synthetic ways to design mono-, di-, trinuclear and polymeric compounds are presented as well as their physical properties.

2. Mononuclear complexes

The first imine-bridged pyridyltetrathiafulvalene building block has been synthesized via the Schiff base condensation of formyltetrathiafulvalene and 2-aminopyridine [43]. Using this synthetic method, the tetrathiafulvalene-imino-2-pyrazine ligand $\mathbf{L^1}$ was synthesized [40]. Its coordination reaction with the $[M(hfac)_2]\cdot xH_2O$ precursors led to two families of molecular complexes [40]: *Cis*-$[Mn(hfac)_2(\mathbf{L^1})_2]$ (**1**) (Fig. 2a) and *Trans*-$[M(hfac)_2(\mathbf{L^1})_2]$ (Fig. 2b) (M = Cu (**2**), Zn (**3**)) in which two organic ligands $\mathbf{L^1}$ were covalently linked through the delocalized π imine systems in *cis* or *trans* conformation. Efficient electronic communication between the imino-pyrazine systems and the TTF core was demonstrated by cyclic voltametry experiments because the oxidation of complexes occurs at higher potentials than for the free ligand. The dissociation of **1** in solution was observed by kinetic electrochemical measurements while **2** and **3** do not dissociate attesting the stability of the *trans* conformation compared to the *cis*.

The amido bridge is a famous chemical linker to assemble the TTF core and the coordinating acceptor because of its ability to interact with neighbours through hydrogen bonds. This fact comes from the H-bond acceptor (carbonyl group) and H-bond donor (amido group). The most studied TTF-based ligands involving such bridge are based on the ethylenedithio-TTF (EDT-TTF) and bisthiomethyl-TTF (BTM-TTF) [23,58–60]. Our objective was to use the amido bridge due to its easy chemical procedure to link the TTF core to diverse acceptor moieties. With this in mind, we designed a library of amido-TTF ligands with 2-pyrimidine ($\mathbf{L^2}$), 4-pyridine ($\mathbf{L^3}$), 2-pyrazine ($\mathbf{L^4}$), 2-pyridine ($\mathbf{L^5}$) and 2-pyridine-N-oxide ($\mathbf{L^6}$) (Fig. 1) [61]. All these ligands were used to synthesize 3*d* transition-metal-based mononuclear coordination complexes (Fig. 2). For $\mathbf{L^2}$, a 1:1 complex of penta-coordinated Cu(II) is obtained $(Cu(hfac)_2(\mathbf{L^2}))\cdot H_2O$ (**4**) (Fig. 2c) while for the $\mathbf{L^2}$-$\mathbf{L^6}$ ligands, 1:2 complexes **5-10** are isolated (Fig. 2d-g).

The cyclic voltametry of the ligands and related complexes present two reversible monoelectronic oxidations at 0.50 and 0.90 V vs SCE attributed to the formation of radical cation and dication species. The coordination effect of the $M(hfac)_2$ units is not assessable using this technique since no significant shift of the oxidation potentials is observed. To realize such a study, all the compounds were investigated by solid-state UV-visible absorption spectroscopy. In this review, the discussion focuses on the two compounds **7** and **9**. The experimental curves are fitted by Gaussian deconvolutions and the absorption bands assigned by Time-Dependent Density Functional Theory (TD-DFT) calculations (Fig. 3) [61].

The low energy transitions are identified as monoelectronic HOMO → LUMO charge transfers (CTs) from TTF donor fragment to acceptor moiety (Fig. 3), whereas the high-energy region is composed of π-π* intraligand excitations. The CTs are red-shifted in the coordination complexes compared to the free ligands by a value of 2500 cm^{-1} for **9** (Fig. 3) while the energy-shift is weaker in