Inorganic Chemistry Communications 21 (2012) 104–108

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Syntheses, characterization and properties of rhenium(I) tricarbonyl complexes based on tetrathiafulvalene substituted naphthyridine ligands

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ARTICLE INFO

Article history:
Received 7 March 2012
Accepted 18 April 2012
Available online 25 April 2012

Keywords:
Tetrathiafulvalenes
Naphthyridine ligands
Crystal structures
Redox chemistry
Spectroscopic properties

ABSTRACT

New amide functional tetrathiafulvalene ligands containing naphthyridine moiety ($\mathbf{L_1}$–$\mathbf{L_3}$) were synthesized. Further coordination reactions of these ligands with $Re(CO)_5Cl$ afford three interesting rhenium tricarbonyl complexes, $ClRe(CO)_3(L)$. Crystal structures of $ClRe(CO)_3(\mathbf{L_1})$ (**1**) and $ClRe(CO)_3(\mathbf{L_2})$ (**2**) have been determined. Electrochemical and spectroscopic properties of all compounds are investigated.

Introduction

Owing to the typical π donor ability and attractive redox properties of tetrathiafulvalene (TTF), the synthesis and coordination chemistry of versatile ligands containing TTF core have attracted great interest during last decades [1–5]. A variety of heteroatom-based ligands, which are famous for their coordination ability to transition metal ions, including pyridine [6–8] and bipyridine [9–12], acetylacetonate [13–15], dithiolate [16,17], phosphine [18–21], carboxyl [22–24], are linked to the TTF core by covalent linkages. However, compared to them, naphthyridine TTF derivatives have been less studied although naphthyridine is an interesting ligand, which is chelated with various metal ions and widely used as a class of fluorescent chromophores [25,26]. On the other hand, amide functional groups are well known for capturing anions through hydrogen bonding between anions and the acidic hydrogen atoms on nitrogen atoms [27]. Therefore, the association of TTF unit and naphthyridine ligand through amide bridge is intriguing in coordination chemistry. Moreover, $[ReL(CO)_3]X$ complexes (L = bidentate *N,N*-chelating ligand; X = monodentate anionic ligand) have been expanded greatly due to their interesting electronic and photochemical properties [28,29]. So, further coordination amide functional tetrathiafulvalene-based naphthyridine ligands with $Re(CO)_5Cl$ may afford new rhenium tricarbonyl complexes with interesting photophysical and photochemical properties.

In this paper, three amide functional tetrathiafulvalene-based naphthyridine ligands, (ethyldithiotetrathiafulvalene-amido-2-(5,7-dimethyl-1,8-naphthyridine) ($\mathbf{L_1}$), ethylenedithiotetrathiafulvalene-amido-2-(5,7-dimethyl-1,8-naphthyridine) ($\mathbf{L_2}$) and bezontetrathiafulvalene-amido-2-(5,7-dimethyl-1,8-naphthyridine) ($\mathbf{L_3}$), are successfully prepared (Scheme 1). After they reaction with Re $(CO)_5Cl$, the rhenium tricarbonyl complexes, $ClRe(CO)_3(\mathbf{L_1})$ (**1**), $ClRe(CO)_3(\mathbf{L_2})$ (**2**) and $ClRe(CO)_3(\mathbf{L_3})$ (**3**), are obtained, respectively. The preparation, crystal structure, spectroscopic and electrochemical properties of these new compounds are studied.

Results and discussion

Synthesis and characterization

7-Amino-2, 4-dimethyl-1, 8-naphthyridine moiety (**5**) and R_2-TTF-COOH (**4**) were prepared according to literature methods [25,30]. By coupling reaction of compounds **4** and **5** through reported procedure with slight modification [31], as shown in Scheme 2, ligands $\mathbf{L_1}$–$\mathbf{L_3}$ are obtained. Reactions of $Re(CO)_5Cl$ with 1 equivalent of $\mathbf{L_1}$–$\mathbf{L_3}$ afford rhenium(I) tricarbonyl complexes **1**–**3** with high yields, respectively. In IR spectra, all compounds display typical amide stretching bands at 3389–3486 cm^{-1}. For metal complexes **1**–**3**, three typical bands (around 2025, 1920 and 1890 cm^{-1}) are observed, which correspond to the three coordinated C═O groups.

Crystal structure description

ORTEP plots of complexes **1** and **2** are shown in Figs. 1 and 2 [32]. The coordination geometries around the rhenium atoms in **1** and **2** are distorted octahedron. The ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ are coordinated to Re (I) by two nitrogen atoms forming a strained four-membered

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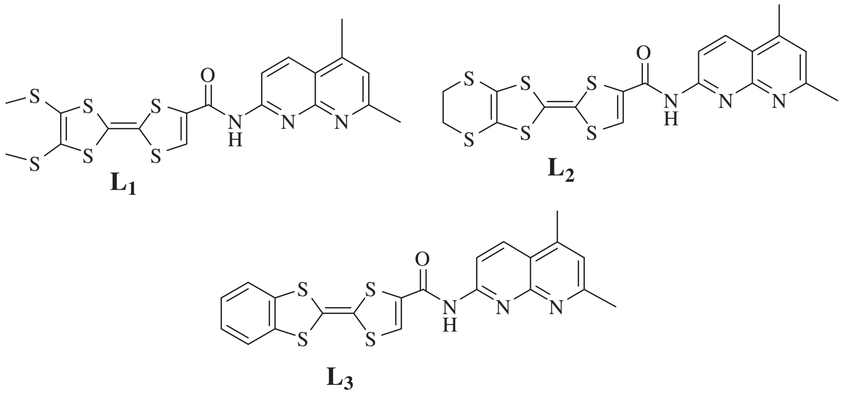
doi:10.1016/j.inoche.2012.04.024



Scheme 1. Structures of ligands L_1–L_3.

metallacycle. The rhenium atoms are also coordinated by three carbonyl ligands in a *fac* arrangement, as well as one halogen atom. The average Re–N bond length is 2.338 and 2.182 Å for **1** and **2**, respectively, which are consistent with other similar complexes [33–35]. The bite angles of N–Re–N (average 59.1° for **1** and 59.71° for **2**) are significantly deviating from the ideal value of 90°, imposed by satiric requirement of chelating geometry of the naphthyridine ring.

For **1**, TTF moiety and amido group are nearly planar, forming a dihedral angle of 2.36(1)° and 5.03(1)° between the naphthyridine rings (containing N2 or N5 atoms) and five-membered rings (containing S1 and S2, or S7 and S8 atoms), respectively. TTF moiety and amido group are also nearly planar for complex **2** with a dihedral angle of 6.78(1)° between the naphthyridine rings (containing N1 atom) and five-membered rings (containing S3 and S4 atoms).

In the solid, no non-bonded interactions are found in complex **1**. For complex **2**, the molecules are stacked in a head-tail fashion, leading to the formation of dimmer with shorter S···S contacts of 3.639 Å. Additionally, the intermolecular hydrogen bonds between the H atom of the amide group and Cl atom from the neighboring molecule (N3–H3···Cl1, N3 to H3 distance 0.860, H3 to Cl1 distance 2.664 Å, N3 to Cl1 distance 3.441, N3–H3···Cl1 angle 150.81°) lead to the formation of a one-dimensional chain motif (Fig. S1).

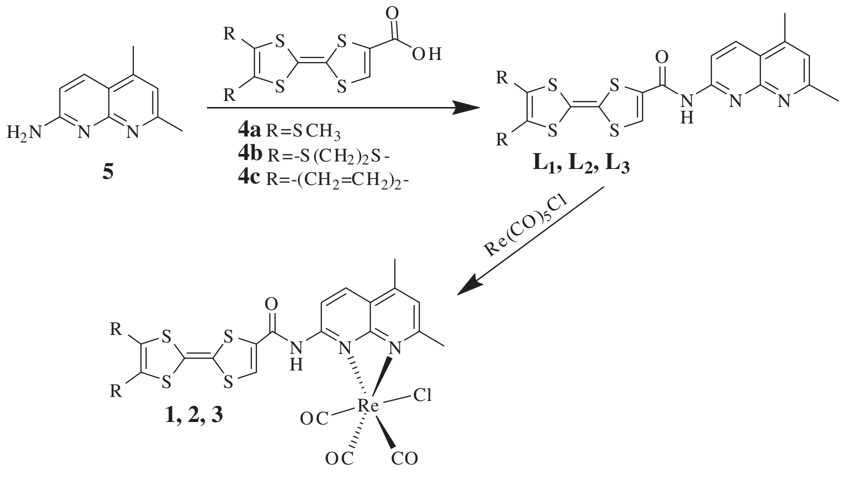
Absorption spectroscopy

Absorption spectra of all compounds were measured in dichloromethane at room temperature (Figs. 3 and S2 in Supporting information). The absorption data are summarized in Table S1 (in Supporting information). The spectra of L_1–L_3 show three absorption bands around 260–400 nm which are assigned to admixture of intra-ligand ($\pi \rightarrow \pi^*$) transitions of TTF moiety and naphthyridine moiety. The weak broad absorption band at lower energy (400–500 nm) corresponds to intra-ligand charge-transfer (ILCT, dπ (L) → π*(L)). Similarly, **1**–**3** display absorption bands around 260–400 nm, which also could be assigned to spin-allowed intra-ligand ($\pi \rightarrow \pi^*$) transitions. Since the energy of the LUMO orbital localized on the mother unit is lowered upon coordination with the rhenium(I) ion [36], these absorption bands are red-shifted in comparison with absorption bands of L_1–L_3. Moreover, around 450–600 nm, the weak broad absorptions of compounds **1**–**3** are also red-shifted compared to L_1–L_3, due to the overlap of the metal-to-ligand charge-transfer (MLCT, dπ (Re) → π*(L)) and the intra-ligand charge-transfer (ILCT, dπ (L) → π*(L)).

Emission spectra of all compounds are measured in dichloromethane at room temperature (Figs. 4 and S3 in Supporting information). The quantum efficiencies are calculated by using air-equilibrated $[Ru(bpy)_3]Cl_2$ in acetonitrile solution as standard ($\Phi_{std} = 0.018$) [37,38]. Upon excitation at 368–371 nm, ligands L_1–L_3 and complexes **1**–**3** exhibit the intense structured blue emission bands at 399–428 nm, resulting from the ligand-centered (LC) π^*–π relaxations. The emission quantum yields for complexes **1**–**3** (0.12–0.19) are much higher than the relating ligands L_1–L_3 (0.06–0.07) (Table S1 in Supporting information). However, the characteristic ^{3}MLCT emission of typical Re (I) complexes for **1**–**3** is not found.

Electrochemical properties

Electrochemical properties were investigated by cyclic voltammograms (Figs. 5 and S4). The electrochemical data are collected in



Scheme 2. Synthetic routes to complexes **1**–**3**.