



A Pt(II) complex with both a phenanthroline and a tetrathiafulvalene-extended dithiolate ligand: Synthesis, crystal structure, electrochemical and spectroscopic properties

Chunyang Jia^{a,1}, Jie Ding^b, Shi-Xia Liu^{a,*}, Gaël Labat^c, Antonia Neels^c, Andreas Hauser^b, Silvio Decurtins^a

^a *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland*

^b *Département de Chimie Physique, Université de Genève, 30 Quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland*

^c *XRD Application LAB, CSEM Centre Suisse d'Electronique et de Microtechnique SA, Jaquet-Droz 1, Case postale, CH-2002 Neuchâtel, Switzerland*

ARTICLE INFO

Article history:

Received 4 January 2013

Accepted 20 February 2013

Available online 7 March 2013

Keywords:

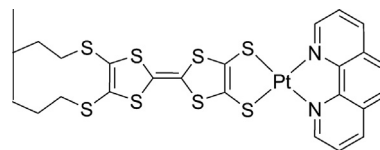
Tetrathiafulvalene

Intramolecular charge-transfer

Spectroelectrochemistry

ABSTRACT

The reaction of 4,5-bis(2'-cyanoethylsulfanyl)-4',5'-dipropylthiotetrathiafulvalene with [Pt(phen)Cl₂] (phen = 1,10-phenanthroline) with CsOH as base in CH₃OH–THF affords the target complex **1** in 44% yield. This complex crystallizes in the monoclinic space group *P2₁/c*, *M* = 790.01, *a* = 12.1732(12), *b* = 15.851(2), *c* = 14.5371(16) Å, β = 107.693(12)°, *V* = 2672.4(5) Å³ and *Z* = 4. It undergoes two reversible single-electron oxidation and two irreversible reduction processes. An intense electronic absorption band at 15200 cm⁻¹ (658 nm) in CH₂Cl₂ is assigned to the intramolecular mixed metal/ligand-to-ligand charge transfer (LLCT) from a tetrathiafulvalene-extended dithiolate-based HOMO to a phenanthroline-based LUMO. This band shifts hypsochromically with increasing solvent polarity. Systematic changes in the optical spectra upon oxidation allow precise tuning of the oxidation states of **1** and reversible control over its optical properties. Irradiation of **1** at 15625 cm⁻¹ (640 nm) in glassy solution below 150 K results in emission from the ³LLCT excited state.



1

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past decades, intense investigations have been devoted to the development of molecule-based functional materials with high electrical conductivity, superconductivity, and magnetism [1–6]. Among them, partially oxidized planar metal complexes have attracted particular attention due to one-dimensional metal–metal interactions forming an effective conducting pathway [1,2]. Specifically, planar platinum(II) complexes form a columnar

packing through Pt···Pt contacts and become electrical conductors when partially oxidized [7,8]. Within this context, platinum diimine dithiolate complexes with the coordination skeleton [Pt(NN)(SS)] are of prime interest by virtue of their redox and optical properties, which render them promising candidates for the generation of photo-induced charge separation and the realization of SOMO–HOMO level conversion, as well as for metal ion sensors and molecular photochemical devices for light-driven energy-storage reactions [9–13]. Also it has been demonstrated that for [Pt(NN)(SS)] complexes, sulfur-rich dithiolate ligands can be stably oxidized, leading to effective S···S non-bonded contacts in the solid states of one-electron oxidized metal complexes, resulting in compounds with high electrical conductivity [14,15]. However, only a few [Pt(NN)(SS)] examples containing the tetrathiafulvalene-extended dithiolate ligands have been reported [13–16].

* Corresponding author. Tel.: +41 31 6314296; fax: +41 31 6313993.

E-mail address: liu@iac.unibe.ch (S.-X. Liu).

¹ Present address: State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, PR China.

In this paper, we describe the synthesis, crystal structure, electrochemical and spectroscopic properties of a platinum complex with both a phenanthroline and a tetrathiafulvalene-extended dithiolate ligand.

2. Experimental

2.1. Materials and equipment

Unless stated otherwise, all chemicals were purchased from commercial sources and used as received. Infrared spectra were obtained on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer. ^1H NMR (300 MHz) spectra were recorded on a Bruker AC-300 NMR spectrometer using TMS as an internal standard. Elemental analyses were performed on a Carlo-Erba-1106 instrument. $[\text{Pt}(\text{phen})\text{Cl}_2]$ and 4,5-bis(2'-cyanoethylsulfanyl)-4',5'-dipropylthiotetrathiafulvalene were prepared according to the literature procedures [17,18].

2.2. Synthesis of **1**

4,5-Bis(2'-cyanoethylsulfanyl)-4',5'-dipropylthiotetrathiafulvalene (523 mg, 1 mmol) was dissolved in anhydrous THF (30 ml). The solution obtained was degassed by nitrogen bubbling. Then 2.2 equivalents of cesium hydroxide monohydrate were dissolved in a minimum of anhydrous methanol and added drop-wise. The resultant mixture was stirred for 1 h before 1 equivalent of $[\text{Pt}(\text{phen})\text{Cl}_2]$ (446 mg, 1 mmol) was added. The resulting solution was stirred under nitrogen for additional 3 h. The solvent was then evaporated under vacuum and the residue was purified by chromatography on neutral alumina ($\text{CH}_2\text{Cl}_2/\text{EtOAc} = 10:1$) to afford the analytical pure complex (0.35 g, 44%): ^1H NMR (300 MHz, $\text{DMSO}-d_6$): $\delta = 9.18$ (d, $J = 5.5$ Hz, 2H), 8.97 (dd, $J = 1.0$ Hz, $J = 8.3$ Hz, 2H), 8.26 (s, 2H), 8.05 (dd, $J = 5.5$ Hz, $J = 8.3$ Hz, 2H), 2.85 (t, $J = 4.6$ Hz, 4H), 1.58 (m, 4H), 0.97 (t, $J = 5.1$ Hz, 6H); IR (KBr, cm^{-1}): $\nu = 2955, 2924, 2865, 1632, 1449, 1431, 1414, 1234, 915, 832, 769, 707$; Calc. for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{PtS}_8$: C, 36.49; H, 2.81; N, 3.55. Found: C, 36.51; H, 2.74; N, 3.31%. Suitable crystals were obtained as dark-brown plates by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{hexane}$ solution of **1**.

2.3. Crystallography

A dark-brown crystal of **1** was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was performed at -100 °C using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 180^\circ$ and with the crystal oscillating through 1° in φ . The resolution was $D_{\text{max}}-D_{\text{min}}$: 12.45–0.81 Å. The structure was solved by direct methods using the program SHELXS-97 [19] and refined by full matrix least squares fitting on F^2 with SHELXL-97 [20]. A partial disorder has been found for one of the propyl groups. Accordingly, the atom positions C7, C8, C9 and C7a, C8a and C9a have been refined with 50% occupancies. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using DIFABS (PLATON03 [21], $T_{\text{min}} = 0.257$, $T_{\text{max}} = 0.712$). The crystallographic data are summarized in Table 1.

2.4. Cyclic voltammetry

Cyclic voltammetric measurements were conducted on a Metrohm VA-Stand 663 electrochemical analyzer. All oxidation

potentials were determined under N_2 in CH_2Cl_2 versus Ag/AgCl at room temperature. Measurements were performed at a scan rate of 100 mV s^{-1} using 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as electrolyte and a Pt-disk as working electrode.

2.5. Steady-state absorption and emission spectroscopy

UV-Vis absorption spectra were recorded on a Cary 5000 spectrophotometer. Steady-state emission spectra were recorded on a Fluorolog 3 spectrophotometer. The preparation of samples in different solvents was started from the initial concentrated solution with a concentration of 2.0×10^{-3} M in CH_2Cl_2 , and diluted with the respective solvent to a concentration of around 2.0×10^{-5} M. Thus the volume proportion of dichloromethane was around 1% in all of the tested solution samples.

Solution samples with proper concentrations were prepared by dilution for steady-state photoluminescence experiments ($\text{OD} < 0.1$ at the excitation wavelength) and deoxygenated for 30 min in a 1 cm path-length quartz cell prior to measurements. Precautions were taken to limit exposure of the photosensitive complexes to light in between measurements and during bubbling. The temperatures during the emission experiments in frozen $n\text{-BuCN}/\text{MeCN}$ (4/1) solution were controlled by a closed cycle cryostat (Oxford Instruments CCC1204) achieving a base temperature of 10 K.

2.6. Spectroelectrochemistry

Spectroelectrochemical experiments were performed under an argon flow in deoxygenated CH_2Cl_2 using 0.1 M Bu_4NPF_6 as supporting electrolyte. All these measurements were carried out in a three-compartment electrolytic cell, where a platinum mesh was used as the working electrode, a platinum mesh as the auxiliary electrode, and potentials were referenced to an Ag wire pseudo reference electrode.

Concerning the evolution of UV-Vis-NIR spectra of **1** after successive addition of FeCl_3 aliquots, the experiments were carried out on a Cary 5000 spectrophotometer using a solution of **1** (2.0×10^{-5} M) in CH_2Cl_2 and a solution of FeCl_3 (2.0×10^{-3} M) in CH_3CN .

Table 1
Crystallographic data for **1**.

Complex	1
Molecular formula	$\text{C}_{24}\text{H}_{22}\text{N}_2\text{PtS}_8$
Molecular weight	790.01
Crystal dimensions (mm)	$0.40 \times 0.30 \times 0.10$
Temperature (K)	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
<i>a</i> (Å)	12.1732(12)
<i>b</i> (Å)	15.851(2)
<i>c</i> (Å)	14.5371(16)
β (°)	107.693(12)
<i>V</i> (Å ³)	2672.4(5)
<i>Z</i>	4
D_{calc} (g cm^{-3})	1.964
Absorption coefficients (mm^{-1})	5.895
R_{int}	0.0854
Measured reflections	21011
Independent reflections	5233
Reflections with $I > 2\sigma(I)$	3671
R_1 (observed)	0.0480
wR_2 (all data)	0.0514
Goodness-of-fit (GOF)	0.848

Download English Version:

<https://daneshyari.com/en/article/1338426>

Download Persian Version:

<https://daneshyari.com/article/1338426>

[Daneshyari.com](https://daneshyari.com)