Coordination Chemistry Reviews 355 (2018) 240–270

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

d^{10} coinage metal organic chalcogenolates: From oligomers to coordination polymers

Oleksandra Veselska, Aude Demessence *

Univ Lyon, Université Claude Bernard Lyon 1, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), UMR 5256 CNRS, 2 av. Albert Einstein, 69626 Villeurbanne, France

ARTICLE INFO

Article history:
Received 15 June 2017
Received in revised form 7 August 2017
Accepted 17 August 2017
Available online 12 October 2017

Dedicated to Prof. Pierre Braunstein on the occasion of his 70th birthday.

Keywords:
d^{10} metals
Organic chalcogenolates
Metal thiolates
Oligomers
Coordination polymers

ABSTRACT

Neutral d^{10} coinage Metal Organic Chalcogenolates (MOCs) exist as oligomeric species and coordination polymers with the formula $[M(ER)]_n$, where M = Cu(I), Ag(I), Au(I) and ER = $^{-}$SR, $^{-}$SeR, $^{-}$TeR. They have been known for a long time for their applications in pharmaceuticals, for their structural analogy to metaloproteins and as crucial intermediates in the synthesis of functionalized nanoparticles. These hybrid materials exhibit high potential as tunable compounds in terms of dimensionality of the network and functionality of the organic part to tailor their electronic, conductive and photophysical properties. This review reports the synthesis, structure and properties of the 40 neutral MOCs and 3 anionic monometallic species, $[M(ER)_2]^{-}$. A total of 23 oligomers, 13 1D and 4 2D coordination polymers are described, and presence of weak interactions such as hydrogen bonds and metalophilic interactions are discussed.

Contents

1. Introduction

One of the most important interfaces in material science is the metal-chalcogenolate interaction. This M–ER bond allows the formation of metal chalcogenolate-based materials, divided into three main families, namely (i) the Self-Assembled Monolayers (SAMs), (ii) the functionalized nanoparticles and clusters, and (iii) the molecular complexes and coordination polymers [1]. The metals commonly used in these families are of the coinage type (Cu, Ag, Au) due to their favorable soft base–soft acid interaction. These metal chalcogenolate-based materials are of tremendous

* Corresponding author.
E-mail address: aude.demessence@ircelyon.univ-lyon1.fr (A. Demessence).

http://dx.doi.org/10.1016/j.ccr.2017.08.014
0010-8545/

importance in various fields of science, such as nanotechnology, surface science, and molecular and coordination chemistry; thus understanding this interface at the atomic level is fundamental to design and target their specific properties [1]. In case of the SAMs, the grafting of chalcogenolates on metallic supports affords functionalized surface found in electronic devices or sensors, but the precise mode of their interaction with the metallic atoms is still under debate due to limited characterization techniques [2]. For chalcogenolate-based nanoparticles, the presence of organic molecules is crucial to control the formation and the size of the particles, to protect them and to bring some functionalization for applications in medicine, nanophotonics, optics and catalysis. In recent years, given the knowledge of the crystallographic structures of some clusters such as metal chalcogenolate clusters $[M_x(ER)_y]$ (M = Cu, Ag, Au) [3] or metal(I) chalcogenide/chalcogenolate clusters $[M_x(E)_y(ER)_z(L)_n]$ (M = Cu, Ag) [4], the interaction between the organic chalcogenolates and the coinage metals are perfectly identified with a rich variety of coordination modes. The last family of chalcogenolate-based materials are the molecular complexes or coordination polymers [5], which can be sub-divided into two families: (i) the metal(I) chalcogenolate-based complexes with additional linkers L: $[M_x(ER)_y(L)_z]_n$, and (ii) the neutral metal(I) chalcogenolate compounds: $[M(ER)]_n$. In analogy to Metal Organic Frameworks (MOFs) [6], which are also identified as coordination polymers or hybrid solids, and recently introduced by N.A. Melosh et al. [7] these $[M(ER)]_n$ compounds are named Metal Organic Chalcogenolates (MOCs). MOCs, as oligomeric species or coordination polymers, have been extensively studied for many years through coordination chemistry for their biological and pharmaceutical uses, diverse physical properties as well as catalytic activities [5]. In addition, metal thiolate compounds occur naturally through the coordination of the thiolate groups from the amino acid cysteine to various metals, including copper and silver. Their activity in biological systems is due to their relevance to the metal sites of metaloproteins (copper and silver), in a variety of redox and catalytic reactions [8]. Metal thiolates are also important in nanotechnology because they are the intermediates in the synthesis of functionalized nanoparticles and clusters [9,3b]. Moreover, some gold thiolates are of great importance as drugs, particularly in arthritis therapy for which they have been commercialized for many years [10]. Finally, d^{10} metal-based materials are intensively used as light-emitting self-assembled materials and their high potential as optical sensors or hybrid luminophores [11].

Chalcogenol ligands react rapidly with coinage metals; thus MOC oligomers are soluble and recrystallization techniques have been used to obtain single crystals. Nevertheless, the neutral MOC polymeric species are mostly insoluble due to their non-molecular structure, and the formation of large enough single crystals has been challenging. Owing to new synthetic methods to get crystalline compounds and the use of powder X-ray diffraction for crystallographic structure determination, new functional MOCs have emerged as coordination polymers in the last few years.

The aim of this review is to report all the structures, syntheses, characterizations and physical properties of neutral MOCs $[M(ER)]_n$, where M is a d^{10} coinage metal, ER^- an organic chalcogenolate and n is a defined number for oligomers or is infinite for polymers. Compounds with mixed ligands are not presented; hence, all the extended families of phosphine-based and thiolate complexes are not reported [12,5d]; also, the compounds with heterotopic thiolate ligands are shown only if the second function is not coordinated to the metal; finally, the charged MOCs are not exposed, only the monometallic $[M(ER)_2]^-$ species are included. The paper is divided into three parts according to the metals: Cu(I), Ag(I) and Au(I); then each part deals with the oligomeric $[M(ER)]_n$ species, the 1D and finally the 2D coordination polymers. Based on the unique capability of organic chalcogenolate ligands for their coordination to metals as monodentate, the μ_2-, μ_3- or μ_4-bridging pattern, the volume and functionality of the R substituent and the presence of weak interactions (hydrogen bonds or metalophilic interactions), this review points out the rich variety of the MOC structures and their physical properties.

2. Neutral Copper(I) organic chalcogenolates

Copper is the second most abundant metal in biological systems after iron. Thus, copper thiolate coordination chemistry is of significant interest to provide analogies for cysteine-rich copper(I) proteins such as "blue" copper proteins or metalothioneins [13]. Cuprophilic interaction, the attractive force between closed-shell d^{10} copper(I) atoms, requires Cu–Cu distances shorter than the orbital interaction radius (the van der Waals radius of Cu is 1.4 Å). Nevertheless, the existence of a weak bonding interaction between Cu(I) atoms still remains controversial. Some studies suggest that short copper–copper distances do not automatically imply the establishment of metal–metal bonds [14]. On the other hand, the presence and the distances of cuprophilic interactions are also known to imply rich photophysical properties in polynuclear copper(I) complexes [15]. Here, the shortest Cu–Cu distances are reported.

2.1. 0D Copper(I) organic chalcogenolates

Three mononuclear two-coordinate negatively charged copper (I) thiolate complexes have been reported: $[NEt_4][Cu(SC(CH_3)_3)_2]$ [28], $[N(n\text{-}Pr)_4][Cu(SC_{10}H_{13})_2]$ [29] and $[NEt_4][Cu(SAd)_2]$ [16] (AdS^-: adamantane thiolate anion). While white crystals of $[N(n\text{-}Pr)_4][Cu(SC_{10}H_{13})_2]$ are obtained from the reaction between $Cu(MeCN)_4BF_4$ and $[N(n\text{-}Pr)_4]Br$ with $LiSC_{10}H_{13}$ in ethanol, the two-coordinate complex, $[NEt_4][Cu(SAd)_2]$ (**1**) was synthesized by the direct addition of the sodium thiolate (NaSAd) to a solution of $Cu(MeCN)_4PF_6$ with Et_4NCl in methanol at room temperature for 30 min. Colorless single crystals were obtained by recrystallization in acetonitrile. The three anions, $[Cu(SR)_2]^-$, have a linear coordination structure (S–Cu–S angle between 176.7 and 180.0°) with crystallographic C_2 symmetry (Fig. 1). Compound **1** exhibits an absorption band centered at 253 nm and a luminescence peak

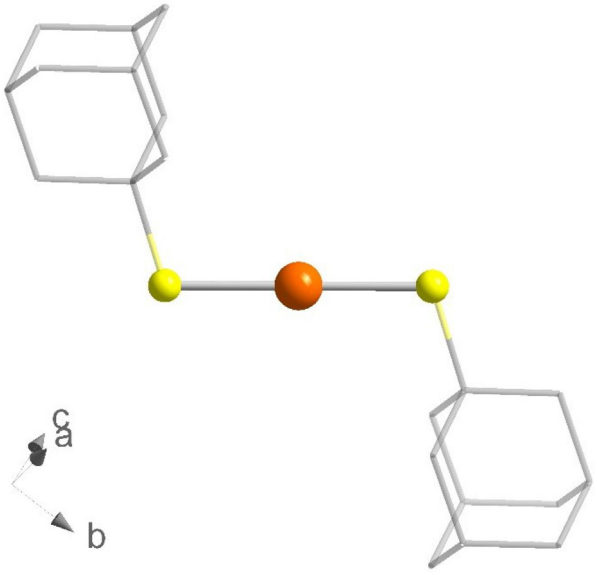

Fig. 1. Structure of $[NEt_4][Cu(SAd)_2]$ (**1**). Orange, Cu; yellow, S; gray, C. Hydrogen atoms and $[NEt_4]^+$ are omitted for clarity.