

Metallophilic interactions in polymeric group 11 thiols



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ABSTRACT

Three polymeric group 11 transition metal polymers featuring metallophilic interactions were obtained directly via self-assembly of metal ions and 4-pyridinethiol ligands. In the cationic $[\text{Cu}_2(\text{S-pyH})_4]_n^{2+}$ with $[\text{ZnCl}_4]_n^{2-}$ counterion (**1**) and in the neutral $[\text{Ag}(\text{S-py})(\text{S-pyH})]_n$ (**2**) 4-pyridinethiol (S-pyH) and its deprotonated form (S-py) are coordinated through the sulfur atom. Both ligands are acting as bridging ligands linking the metal centers together. In the solid state, the gold(I) polymer $[\text{Au}(\text{S-pyH})_2]\text{Cl}$ (**3**) consists of the repeating cationic $[\text{Au}(\text{S-pyH})_2]^+$ units held together by aurophilic interactions. Compound **1** is a zig-zag chain, whereas the metal chains in the structures of **2** and **3** are linear. The protonation level of the thiol ligand had an impact on the crystallization of polymers. Both nature of the metal center and reaction conditions affected the polymerization. QTAIM analysis confirmed direct metal-metal contacts only in polymers **1** and **3**. In polymer **2**, no theoretical evidence of argentophilic contacts was obtained even though the $\text{Ag}\cdots\text{Ag}$ distance was found to be less than sum of the Bondi's van der Waals radius of silver.

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1. Introduction

Metallopolymers is a class of compounds that covers a wide range of metal containing polymeric systems [1]. The structures vary from mainly organic polymers with metal centers in the main or side chain, to systems with direct covalent metal-metal bonds [2a,b,c,d], and non-covalent metallophilic assemblies of metal species [2e,f,g,h]. The motivation for preparation of metallopolymers lie in their versatile properties, such as conductivity [2i] and photophysical properties [3] as well as their magnetic [4] and catalytic [5] behavior. These properties determined applications of metallopolymers such as photovoltaic cells, catalysts and light emitting devices [1–5].

In most cases, the key properties arise from the interactions between metal centers [6a,b,c]. These interactions can be achieved by linking metal centers together with a suitable (usually conjugated) ligands and building coordination polymers [6d]. Another approach is to exploit direct metal-metal contacts. These contacts can either be covalent metal-metal bonds or non-covalent metallophilic contacts [6e]. Polymeric transition metal systems that have

only covalent metal-metal bonds between the repeating units are relatively rare [2b,d]. More commonly, metal-metal contacts are further supported by suitable multidentate ligands that can force metal centers close to each other. Multidentate nitrogen ligands are widely used supporters [6f, g,h,2h]. However, metals can also be brought together by single atom bridges. Simple bridging ligands such as halides, pseudo halides or sulfur containing ligands can be used in this type of systems [7]. In metal thiols and closely related coordination compounds, the soft sulfur atom is readily available for coordination and capable to act as bridging atom through its free electron pairs [8a–d]. Usually, thiol ligands can be relatively easily modified to adjust their electronic and steric properties. Because of this adjustability, thiols are excellent components for coordination chemistry [8e–i]. Heterocyclic thiols provide particularly versatile group of thiol ligands [9–12].

The 4-pyridine thiol is one of the commonly used heterocyclic thiol ligand. It can exist in different tautomeric forms, thiol (**A**), thione (**B**) and zwitterionic (**C**) forms (Fig. 1).

Removal of the NH proton from 4-pyridinethiol opens up a possibility to use both of softer sulfur and harder nitrogen for coordination. Therefore, pyridinethiols have drawn attention as potential ambidentate ligands [13] exhibiting interesting spectroscopic [14a] and electrochemical [14b] behavior. Due to exocyclic sulfur and heterocyclic nitrogen donor, pyridine thiols

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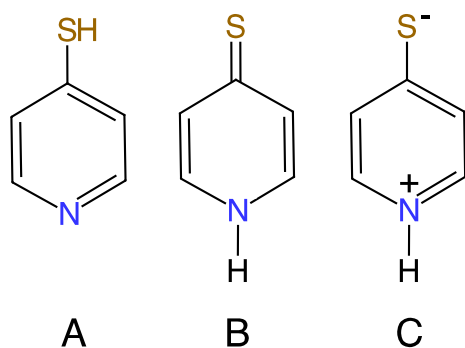


Fig. 1. Schematic representation of tautomeric forms of 4-pyridinethiol.

have also been successfully exploited as ditopic ligands [15] for oligomeric and polymeric metal systems. Polynuclear species combining different metals by thiols have been used for example in catalytic [16a], pharmaceutical [16b], biochemical [16c], luminescent [16d], and magnetic [16e] materials and also as precursors for silver chalconides [16f]. One of the potential applications of thiols is to use them as supporting single-atom linking ligands in metallophilic polymers.

Metallophilicity can be described as attraction between closed shell or pseudo closed shell d^{10} or d^8 transition metal cations [17a]. Strength of a metallophilic interaction is typically comparable to hydrogen bonds and it is clearly stronger than van der Waals interactions [17a]. Metallophilic interactions have been widely studied by the means of spectroscopic techniques [17a,6c], computational chemistry [17b–e] and structural studies [17f,g]. Metallophilicity is considered to be mainly a dispersion force with electron correlation effects [18]. Structurally metallophilicity can favor formation of various extended polynuclear structures including dimers, 1D chains, 2D sheets, 3D networks or molecular aggregates [19].

In this paper, we describe generation of linear and pseudolinear group 11 metallopolymers supported by sulfur coordinated 4-pyridinethiols. The primary goal was generation of novel metallophilic interactions due to application of the thiols that serve as

molecular staples bringing together two metal atoms. The impact of the metal center and reaction conditions to the formation of polymers and their solid state structures are also briefly discussed.

2. Materials and methods

2.1. General remarks

Reagents were used as received. Acetonitrile and methanol were HPLC grade. Purity of ethanol and dichloromethane were 99.5%. NMR spectra were recorded with a Bruker 500 MHz NMR with BBFO probe under ambient conditions. Mass spectra were measured on an ABSciex QSTAR Elite ESI-Q-TOF MS.

2.2. X-ray structure determinations

The crystals of $[\text{Cu}_2(\text{S-pyH})_4]_n [\text{ZnCl}_4]_n$ (**1**), $[\text{Ag}(\text{S-py})(\text{S-pyH})]_n$ (**2**), and $[\text{Au}(\text{S-pyH})_2]\text{Cl}$ (**3**) were immersed in cryo-oil, mounted in a MiTeGen loop and measured at 120–170 K. The X-ray diffraction data were collected on an Agilent Technologies Supernova or a Bruker AXS KappaApex diffractometers using $\text{Cu K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) or $\text{Mo K}\alpha$ radiation ($\lambda = 0.70173 \text{ \AA}$). The CrysAlisPro [20] or Denzo/Scalepack [21] program packages were used for cell refinements and data reductions. The structures were solved by charge flipping method using the SUPERFLIP [22] program or by direct methods using SHELXS-2014 [23] program. An empirical absorption correction based on equivalent reflections (CrysAlisPro [20] or SADABS [24]) was applied to all data. Structural refinements were carried out using SHELXL-2014 [23] with the Olex2 [25] and SHELXLE [26] graphical user interfaces. In **1**, the NH and OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atoms, with $U_{\text{iso}} = 1.5 U_{\text{eq}}$ (parent atom). In **3**, the NH hydrogens were located from the difference Fourier map and refined isotropically. All other hydrogens were positioned geometrically and constrained to ride on their parent atoms, with $\text{C-H} = 0.98\text{--}1.00 \text{ \AA}$, $\text{N-H} = 0.88 \text{ \AA}$, and $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}$ (parent atom). The crystallographic details are summarized in Table 1.

Table 1
Crystal data for **1–3**.

	1	2	3
empirical formula	$\text{C}_{22}\text{H}_{26}\text{Cl}_4\text{Cu}_2\text{N}_4\text{O}_1\text{S}_4\text{Zn}$	$\text{C}_{10}\text{H}_9\text{AgN}_2\text{S}_2$	$\text{C}_{10}\text{H}_{10}\text{AuClN}_2\text{S}_2$
Fw	824.96	329.18	454.74
temp (K)	123 (2)	170 (2)	120 (2)
λ (\AA)	1.54184	0.71073	1.54184
cryst syst	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/n$	lbam	$P2_1/c$
a (\AA)	10.0163 (3)	12.1624 (6)	16.9203 (6)
b (\AA)	10.0845 (3)	13.7874 (10)	11.3649 (5)
c (\AA)	29.8809 (13)	6.3879 (4)	6.7730 (3)
α (deg)	90	90	90
β (deg)	95.051 (3)	90	99.647 (4)
γ (deg)	90	90	90
V (\AA^3)	3006.54 (19)	1071.17 (12)	1284.02 (10)
Z	4	4	4
ρ_{calc} (Mg/m^3)	1.823	2.041	2.352
μ ($\text{Mo K}\alpha$) (mm^{-1})	8.656	2.234	26.271
No. reflns.	12623	7680	5014
Unique reflns.	6128	849	2585
GOOF (F^2)	1.022	1.126	1.072
R_{int}	0.0926	0.0640	0.0961
$R1^a$ ($I \geq 2\sigma$)	0.0347	0.0253	0.0381
$wR2^b$ ($I \geq 2\sigma$)	0.0878	0.0615	0.0918
Largest diff. peak and hole $\text{e}\text{\AA}^{-3}$	0.589/–0.633	0.457/–0.517	1.811/–1.340

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

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