Inorganica Chimica Acta 376 (2011) 694–698

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

Note

Metallosupramolecular silver complexes with ligands of 4,4′-di(2-pyridyl-4-pyrimidinyl) disulfide and 4,4′-di(3-pyridyl-4-pyrimidinyl) disulfide: Syntheses, structures and luminescent properties

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ARTICLE INFO

Article history:
Received 2 April 2011
Received in revised form 7 June 2011
Accepted 25 July 2011
Available online 5 August 2011

Keywords:
Disulfide
Macrocycle
Helical chain
Ag–S bond
Luminescence

ABSTRACT

Reaction of 4,4′-di(3-pyridyl-4-pyrimidinyl) disulfide (**3-PPDS**) with $AgNO_3$ leads to a unique 2D extended structure $\{[Ag(\mathbf{3\text{-}PPDS})(NO_3)]\}_n$ (**1**) based on $[Ag_2(\mathbf{3\text{-}PPDS})_2]$ macrocycle units, of which 1D inorganic $[Ag(NO_3)]_n$ helical chains are generated. By contrast, definite Ag–S bonding interactions associated with the disulfide function have been established in $\{[Ag(\mathbf{2\text{-}PPDS})]ClO_4\}_n$ (**2**), which is assembled of 4,4′-di(2-pyridyl-4-pyrimidinyl) disulfide (**2-PPDS**) with $AgClO_4$. Solid state luminescent properties of complexes **1** and **2** are also examined.

1. Introduction

Over the past few years, heterocyclic disulfides as organic building blocks have received more and more attention in the field of crystal engineering, among which 4,4′-dipyridyldisulfide (**4-dpds**) and 2,2′-dipyridyldisulfide (**2-dpds**) have been much studied [1–5]. Their structural characteristics include (1) semi-rigid conformation with the C–S–S–C torsion angle of approximately 90° even when coordinated to metal ions; (2) axial chirality with *P*- and *M*-enantiomers, which is of particular interest in terms of chiral crystal engineering. Furthermore, diverse *in situ* reactions of the disulfide function (–S–S–) are becoming a promising tool towards fascinating metallosupramolecular architectures [6]. Besides, despite the fact that the disulfide function is labile to coordinate with soft metal ions (e.g. Ag^+, Cu^+) under suitable conditions, examples concerning this issue remain scarce hitherto [7]. Considering the potential function of organic–metal–sulfur compounds such as electrical conductivity and photoluminescent properties [8–10], metal–disulfide complexes bearing metal–sulfur bonds should be deserved more attention.

We have focused on the coordination chemistry of 4,4′-di(*n*-pyridyl-4-pyrimidinyl) disulfide (***n*-PPDS**, *n* = 2, 3, 4) (Chart 1) in recent years. In this context, we have described the structures of metallosupramolecular Zn(II) and Fe(II) complexes with **4-PPDS** [11] and uncovered versatile *in situ* reactions of **2-PPDS** triggered by metal coordination [12,13]. As continuation of our work, we have investigated the self-assembly of **2-PPDS** and **3-PPDS** with AgX salts ($X = NO_3^-$, ClO_4^-) to further understand their coordination chemistry.

2. Experimental

2.1. General procedure

All chemicals and solvents were in analytical grade and used as commercially available. **2-PPDS** and **3-PPDS** ligands were prepared according to our previous work [12]. All procedures for syntheses and measurements of the silver (I) complexes were conducted in the dark unless otherwise stated. Elemental analyses for C, H and N were performed on a CHN–O-Rapid analyzer and an Elementar Vario MICRO analyzer. Infrared spectra were performed on a Nicolet 200 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer.

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doi:10.1016/j.ica.2011.07.038

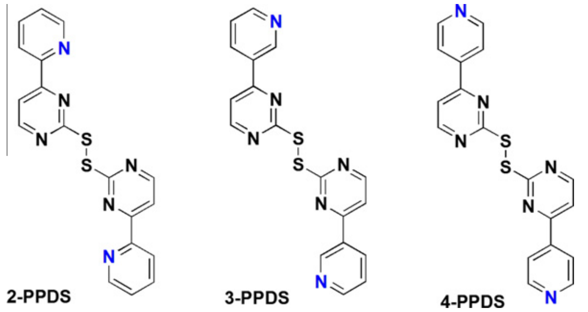

Chart 1. Schematic representation of ***n*-PPDS** ($n = 2, 3, 4$).

2.2. Preparation of [Ag(**3-PPDS**)(NO_3)]$_n$ (**1**) and [Ag(**2-PPDS**)(ClO_4)]$_n$ (**2**)

A colorless solution of $AgNO_3$ (0.017 g, 0.1 mmol) in CH_3CN (5 mL) was carefully layered above a solution of **3-PPDS** (0.039 g, 0.1 mmol) in CH_2Cl_2 (5 mL). After 3 days light-yellow crystals were produced. Yield 61% (based on $AgNO_3$). *Anal.* Calc. for $C_{18}H_{12}AgN_7O_3S_2$: C, 39.57; H, 2.21; N, 17.95. Found: C, 39.52; H, 2.39; N, 17.75%. ν_{max}/cm^{-1} 3069m, 1593s, 1564s, 1537m, 1481m, 1430s, 1338s, 1203s, 1181s, 1038m, 1027m, 824s, 811s, 719s, 701s, 641s, 503w.

The preparation of complex **2** is similar to complex **1** but by reaction of $AgClO_4$ with **2-PPDS**. Yield 21% (based on $AgClO_4$). *Anal.* Calc. for $C_{18}H_{12}AgClN_6O_4S_2$: C, 37.03; H, 2.07; N, 14.40. Found: C, 37.21; H, 2.19; N, 14.35%. ν_{max}/cm^{-1} 3067m, 1590m, 1565s, 1540m, 1470m, 1445m, 1412s, 1349s, 1257m, 1182s, 1092s, 1006m, 819w, 793m, 759m, 715s, 646m, 622s.

2.3. X-ray crystallography

Diffraction intensities for complexes **1** and **2** were collected at 298(2) K on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected using SMART and reduced by the program SAINT [14]. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2_{obs} by using SHELXTL-PC software package [15]. All non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic data for complexes **1** and **2** are listed in Table 1. Selected bond lengths and angles are given in Supplementary material.

Table 1
Crystallographic data for complexes **1** and **2**.

	1	**2**
Formula	$C_{18}H_{12}AgN_7O_3S_2$	$C_{18}H_{12}AgClN_6O_4S_2$
M_r	546.36	583.80
T (K)	298(2)	298(2)
Crystal system	monoclinic	monoclinic
Space group	$P21/n$ (no. 14)	$P21/n$ (no. 14)
a (Å)	15.196(1)	14.204(8)
b (Å)	8.5636(6)	15.139(9)
c (Å)	16.733(1)	9.541(5)
β (°)	113.271(1)	94.263(5)
V (Å^3)	2000.3(2)	2046(2)
Z	4	4
D_{calc} (g cm^{-3})	1.814	1.895
F(0 0 0)	1088	1160
Dimension (mm)	0.20 × 0.18 × 0.15	0.12 × 0.07 × 0.05
Reflections collected/unique (R_{int})	11474/4432 (0.020)	11900/3388 (0.132)
Goodness-of-fit (GOF) on F^2	1.01	1.16
R_1, wR_2 [$I > 2\sigma(I)$]	0.0303, 0.0758	0.1006, 0.1622
R_1, wR_2 (all data)	0.0442, 0.0830	0.2104, 0.1817
Residuals (e Å^{-3})	−0.55, 0.27	−0.61, 0.70

3. Results and discussion

3.1. Structure description of complexes **1** and **2**

Macrocycle structures have been obtained by assembling **4-dpds** with several metal ions (e.g. Pt, Ir, Co, Ni) [16–18], but Ag(I)-based macrocycles are still less known. Interestingly, assembly between $AgNO_3$ and **3-PPDS** generated complex **1** containing 2:2 M:L macrocycle units, of which each Ag atom is five-coordinated by three O atoms from two NO_3^- anions and two N atoms from two **3-PPDS** ligands (Fig. 1(a)). Both Ag–O and Ag–N bond lengths are within the normal range, and the C–S–S–C torsion angle (89.55°) is comparable to that of the free **3-PPDS** ligand (81.33°) as expected [19]. Moreover, the macrocycle cavity has its dimension of 7.34 × 13.01 Å measured by Ag···Ag and S–S···S–S separations. As most examples in literatures [1], complex **1** also crystalizes in a non-chiral space group ($P2/1$) due to the presence of 1:1 macrocycle enantiomers.

Remarkably, each macrocycle unit is further linked to four neighboring ones to give a 2D extended structure through μ-2 bridging NO_3^- anions. More strikingly, 1D right- and left-handed purely inorganic [Ag(NO_3)]$_n$ helical chains are alternatively arrayed along b axis (Fig. 1(b)), which are generated from μ-2 NO_3^- anions bridging Ag(I) atoms. The helicity of [Ag(NO_3)]$_n$ inorganic chains is believed to be conferred by the intrinsic axial chirality of **3-PPDS** ligands. Finally, it is noted that both helix and macrocycle motifs present in a single structure are rarely described as far as we know.

As aforementioned, the disulfide function tends to coordinate to soft metal ions according to HSAB theory (HSAB = hard-soft acid–base). However, there is only one example describing such bonding interactions, which is involved with **2-dpds** and $CuClO_4$ [7]. If taking into account structural difference between **2-dpds** and **4-dpds**, it may be inferred that the close proximity between N and S atoms in **2-dpds** promote metal–disulfide interactions. With this in mind, we choose **2-PPDS** as the candidate given that the N,N-chelation of **2-PPDS** may restrict the Ag atom in space close to the disulfide function. In our previous study, we have noticed that **2-PPDS** is readily subject to *in situ* S–S reactions induced by metal coordination. Consequently, we first examined the stability of **2-PPDS** in the presence of AgX salts (X = NO_3^-, ClO_4^-, BF_4^-) with our reported method [13], and found that **2-PPDS** can remain intact. Unfortunately, growing single crystals are only achieved in the case of $AgClO_4$ largely because of the rapid reaction between **2-PPDS** and AgX.

Albeit its poor quality, X-ray diffraction analysis unambiguously indicates that Ag–S bonding interactions have been established in complex **2**. As depicted in Fig. 2, each Ag(I) atom is bound to two set of NNS donor atoms from two **2-PPDS** ligands with Ag–S bond distances of 2.753(4) and 2.729(3) Å, which are far shorter than the sum of Van der Waals radius of Ag and S atoms (3.52 Å). Compared with the free **2-PPDS**, the S–S distance (2.016(4) Å) of **2-PPDS** in complex **2** is almost unchanged while the C–S–S–C torsion angle is altered significantly from 82.7° to 99.7° [12]. Particularly, complex **2** has two types of five-membered chelated rings (CNAgNC and CNAgSS) sharing one common Ag–N edge. If treating the two fused five-membered rings as the repeating unit, the linkage between adjoining units could be classified into two types (1) sharing one common S–S edge with the Ag–S–S–Ag torsion angle of approximately 115.5°; (2) sharing one common Ag vertex with the S–Ag–S angle of 95.8°. Alternative use of two linkages produces a 1D extended structure, of which a unique Ag···S–S···