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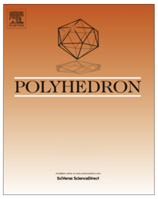

Syntheses, structural diversity and photo-physical properties of copper(I) and silver(I) coordination polymers based on the pyridine-4-amidoxime ligand

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ABSTRACT

Three new complexes, $[\{Cu(L)I\}_2]_n$ (**1**), $[Ag(L)]_n{\cdot}nClO_4$ (**2**) and $[\{Ag(L)(CF_3COO)\}_2]_n$ (**3**), have been synthesised and characterized by different physico-chemical methods with the aim of exploring the ligating properties of pyridine-4-amidoxime (L). Single crystal X-ray structure analysis reveals that **1** is a 2D coordination polymer, while **2** and **3** are wavy 1D chains in spite of the same coordination mode adopted by the ligand. The crystal structures also show that the coordination geometry of the metals is different in each complex, being tetrahedral in **1**, but distorted trigonal planar and distorted linear in **2** and **3**, respectively. The asymmetric units of **1** and **3** consist of two independent metal centres and each is associated with a counter anion of the metal salt used, while the asymmetric unit of **2** is cationic in nature, the perchlorate anion being non-coordinated. Structural diversities are also evident as the 2D structure of **1** is stabilized by O–H···I interactions, while several classical and non-classical hydrogen bonds lead to 3D supra-molecular structures for complexes **2** and **3**. The solid state fluorescence of L and of its complexes were studied revealing that both **1** and **2** show a broad emission band with a maxima at 525 and 522 nm, respectively, strongly red shifted when compared to the free ligand band (463 nm), while **3** is found surprisingly to be non-emissive.

1. Introduction

Metal organic frameworks have fascinated great interest not only for their prospective applications as materials in gas storage [1,2], non-linear optics [3], ion exchange [4], molecular sensing [5] and catalysis [6], but also for their rich structural diversities. A variety of functional coordination polymers can be obtained by tuning several factors, like the nature of the metal ions [7], pH of the medium [8], modes of metal–ligand binding [9] and counter anions [10]. Intriguing supramolecular assemblies are also generated using predesigned ligands and by varying the metal ion and consequently the coordination environment [11].

The chemistry of polymeric copper(I) and silver(I) complexes is an stimulating field of research not only for their interesting structural diversities, but also for their rich photo-luminescent properties and potential applications in materials [12] and medicinal sciences [13]. From a structural point of view, the silver(I) ion can exhibit more variations, such as linear [14], Y-shaped [15], square pyramidal [16], square-planar [17], tetrahedral [18] and octahedral [19] geometries, which widely differ from the copper(I) ion which mainly adopts tetrahedral [20] and trigonal planar [21] geometries. On the other hand, both metal ions have a high affinity for nitrogen and oxygen atoms, leading to new structural motifs [22,23].

Among the varieties of organic ligands used in constructing coordination polymers, oxime and its derivatives share a sizeable area due to their versatile coordination abilities to bind different kinds of (soft/hard) metal ions with diverse coordination (chelating/bridging) modes [24,25]. They can also act as very useful tools to construct different kinds of polynuclear complexes with rational applications including the fields of magnetism and catalysis. Different first row transition metals together with oxime or its derivatives result in different kinds of single molecular magnets [26,27]. The role of pyridine-2-aldoxime may be mentioned in this regard since it produces various kinds of homo- and heterometallic

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clusters [28,29], while its isomers, pyridine-3-aldoxime and pyridine-4-aldoxime are much less explored [30,31]. As a continuation of the exploration in this field, the aldoxime hydrogen atom is here replaced by an amino group, which results in a new class of amidoxime ligands [(py)C(NH_2)NOH]. The presence of the amine functionality not only enhances the coordination abilities of the ligand but also improves the potentiality for hydrogen bonding in comparison with that of the corresponding parent oximes. Thus pyridine-2-amidoxime as a ligand was explored in a number of complexes in the recent past [32]. However, unlike pyridine-2-amidoxime, the ligating abilities of pyridine-3-amidoxime and pyridine-4-amidoxime has not been explored to date.

Herein we have explored the ligating properties of pyridine-4-aldoxime for the first time and have successfully synthesized three copper(I)/silver(I) complexes, which have been characterized by elemental analysis, FT-IR and electronic (solid state) spectroscopic methods. The single-crystal X-ray diffraction analysis revealed that, in spite of same bridging mode adopted by the pyridine-4-aldoxime ligand in these complexes, the metal centre presents different geometries. The diverse dimensionality exhibited by the complexes is primarily the combined effect of the counter ion, nature of the metal ions and various weak interactive forces. The photo-physical properties of these complexes have been studied and compared to those of the ligand: the emission band appears strongly red shifted for complexes **1** and **2** in comparison to that of the free ligand, while **3** is found surprisingly to be non-emissive.

2. Experimental

2.1. Materials

4-Cyanopyridine, copper(I) iodide, silver(I) perchlorate and silver(I) trifluoroacetate were purchased from Sigma Aldrich and used as received. Hydroxylamine hydrochloride and sodium carbonate monohydrate were purchased from E. Merck, India. All other chemicals and solvents used for the syntheses were of AR grade and used without any further purification. Pyridine-4-amidoxime was prepared following the literature procedure [33].

Caution! Perchlorate salts in the presence of organic compounds are potentially explosive. Although we did not encounter any problems, these materials should be handled in small quantities with great caution!

2.2. Syntheses of the complexes

2.2.1. Synthesis of $[\{Cu(L)I\}_2]_n$ (**1**)

To a 20 mL acetonitrile solution of copper (I) iodide (0.5 mmol, 0.095 g), pyridine-4-amidoxime (0.5 mmol, 0.069 g) was added and stirred gently at room temperature for an hour. A greenish-yellow coloured solid precipitated. The reaction mixture was filtered and the filtrate was left undisturbed at room temperature for slow evaporation. Plate shaped greenish-yellow crystals of **1** were collected after 15 days. Yield: 40%, 0.065 g. *Anal.* Calc. for $C_{12}H_{14}Cu_2I_2N_6O_2$: C, 22.00; H, 2.15; N, 12.83. Found: C, 22.03; H, 2.18; N, 12.80%.

2.2.2. Synthesis of $[\{Ag\,(L)]_n \cdot nClO_4$ (**2**)

Pyridine-4-amidoxime (0.5 mmol, 0.069 g) was added to a stirred acetonitrile solution (20 mL) of silver(I) perchlorate (0.5 mmol, 0.101 g). The reaction mixture was stirred for half an hour. The solution turned a pale yellow colour and was filtered. The filtrate was kept in dark for slow evaporation. Colorless rod shaped single crystals of **2** were obtained after 25 days. Yield: 60%, 0.102 g. *Anal.* Calc. for $C_6H_7AgClN_3O_5$: C, 20.92; H, 2.05; N, 12.20. Found: C, 20.87; H, 2.01; N, 12.23%.

2.2.3. Synthesis of $[\{Ag(L)(CF_3COO)\}_2]_n$ (**3**)

Complex **3** was synthesized according to the same procedure as that adopted for **2**, except silver(I) trifluoroacetate (0.5 mmol, 0.110 g) was used instead of silver(I) perchlorate. Block shaped colourless crystals of **3** were obtained by slow evaporation of solvent after 15 days. Yield: 70%, 0.125 g. *Anal.* Calc. for $C_{16}H_{14}Ag_2F_6N_6O_6$: C, 26.84; H, 1.97; N, 11.74. Found: C, 26.80; H, 1.93; N, 11.71%.

2.3. Physical measurements

Elemental analyses (C, H, N) were carried out using a Perkin-Elmer 2400 II elemental analyzer. X-ray powder diffraction data were collected in a Bruker D8 Advance powder diffractometer using monochromatic Cu Kα radiation (λ = 1.5406 Å) selected with an incident beam germanium monochromator. The infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin-Elmer RX I FT-IR spectrometer with a KBr pellet. UV-Vis absorption spectra were recorded on a Specord 205 (Analytik Jena) spectrometer. Steady state emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrometer working with a continuous 450 W Xe lamp. For measurements in the solid state, the spectrometer was fitted with a Quanta-Φ integrating sphere from Horiba. Detection was performed with a Hamamatsu R928 photomultiplier. All spectra were corrected for the instrumental functions. When necessary, a 399 nm cut off filter was used to eliminate the second order artefacts. The solid state luminescence quantum yield was measured using the integrating sphere according to the literature procedures [34,35]. The luminescence quantum yield Φ is given by:

$$\Phi = \frac{E_i(\lambda) - (1 - A)E_0(\lambda)}{L_e(\lambda)A} \tag{1}$$

where

$$A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)} \tag{2}$$

in which $E_i(\lambda)$ is the integrated luminescence of the sample caused by direct excitation, $E_0(\lambda)$ is the integrated luminescence of the sample caused by illumination from the sphere, A is the absorbance of the sample, $L_e(\lambda)$ is the integrated excitation profile from the empty integration sphere (without the sample), $L_0(\lambda)$ is the integrated excitation profile when the sample is diffusively illuminated by the integration sphere and $L_i(\lambda)$ is the integrated excitation profile upon direct excitation of the sample by the incident beam. The integrated spectra were corrected for the wavelength sensitivity of the photomultiplier and the spectral response of the sphere using correction functions furnished by the supplier. The ligand emission lifetime in ethanol solution was measured in the time-resolved mode, by monitoring the decay at the maximum of the emission spectrum using a Jobin Yvon FluoroHub single photon counting controller, fitted with a 303 nm Jobin Yvon NanoLED. The decays were analyzed with DataStation v2.4. The same set up was used for solid state lifetime measurements using a 2 mm inner diameter quartz tube and the front face configuration of the instrument.

2.4. X-ray crystallography

A diffraction quality plate shaped greenish-yellow crystal of **1** and a rod shaped colourless crystal of **2** were mounted on a Bruker APEX-II CCD and a Bruker SMART 1000 CCD diffractometer, respectively, equipped with graphite monochromated Mo Kα radiation