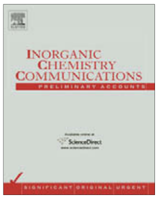
Inorganic Chemistry Communications 12 (2009) 1227–1230

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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



Novel 3-dimensional sixfold interpenetrating diamondoid networks of copper(I) coordination polymers of polypyridyl ligands – Syntheses, characterization and crystal structures

Anindita Mukherjee [a], Rajesh Chakrabarty [b], Goutam Kumar Patra [a,*]

[a] Department of Chemistry, Vijoygarh Jyotish Ray College, Jadavpur, Kolkata 700 032, India
[b] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

ARTICLE INFO

Article history:
Received 30 June 2009
Accepted 28 September 2009
Available online 1 October 2009

Keywords:
N-donor ligands
Coordination polymer
3D polymer
Copper(I) complexes
Sixfold interpenetration
Diamondoid networks
Crystal structures

ABSTRACT

Two new coordination polymers $[Cu(\mathbf{L^1})_2]_n(ClO_4)_n \cdot 2nH_2O$ (**1**), $[Cu(\mathbf{L^2})_2]_n(ClO_4)_n \cdot 2nH_2O$ (**2**) of polydentate imine/pyridyl ligands, $\mathbf{L^1}$ and $\mathbf{L^2}$ with Cu(I) ion have been synthesized and characterized by single crystal X-ray diffraction studies, elemental analyses, IR′ UV–vis and NMR spectroscopy. They represent 3-dimensional, sixfold interpenetrating diamondoid network structures having large pores of dimension, 35×21 Å^2 in **1** and 38×19 Å^2 in **2**, respectively.

Construction of coordination polymers based on polydentate ligands is rapidly growing [1–10] area of current research. Polydentate 4,4′-bipyridyl type of ligands with varied spacer length between the pyridyl moieties are one of the most attractive building blocks not only because of their intriguing structural motifs [11–15] but also of their potential applications in host–guest chemistry [16], catalysis [4,17], molecular absorption [18], magnetism [19], non-linear optics [20], luminescence [21] and molecular sensing [22]. Organic ligands play crucial roles in the design and construction of diverse frameworks, as even small change in flexibility, length and symmetry of the ligands can result in a remarkable versatility of architecture and functions [2,3,9,12,13]. The length of the organic moiety has a great impact on the polymer networking especially on the size of the pores or channels and whether the structure is interpenetrating or non-interpenetrating [23–25]. Thus the prospect of regulating the properties of metal–organic frameworks through a systemic change of organic ligands provides an impetus for further search on metal–organic supramolecular building blocks. To obtain the desired architecture of coordination polymers held together only by coordination bonds, constructed by organic ligands and metal ions is still a continuing challenge to the chemists due to difficulty in prediction of either the compositions or the structures of the reaction products of mainly the flexible polydentate ligands. Moreover, the ligand *N,N′*-bis-pyridin-4-yl-methylene hydrazine is being known as an antitumor precursor as well as an analytical reagent for the determination of Fe^{2+} concentration in solution [26,27].

Cu(I) ion is a well suited cation because of its labile coordination modes with coordination number 2–5. It is well known that metal–organic polymeric compounds of Cu(I) exhibit the photoluminescence properties and have the potential applications in optoelectronic devices, fluorescent sensors and probes [28–31]. Cu(I) salts catalyze many organic transformations like aryl guanidinylation [32], amination [33], photocycloaddition [34], oxidation of adrenaline [35], ferrocytochrome c oxidation [36], etc. Coordination chemistry of copper(I) complexes with polydentate ligands is particularly relevant to the search for model compounds those can mimic or even ideally duplicate some of the important physical and chemical properties of Cu(I) containing proteins [37].

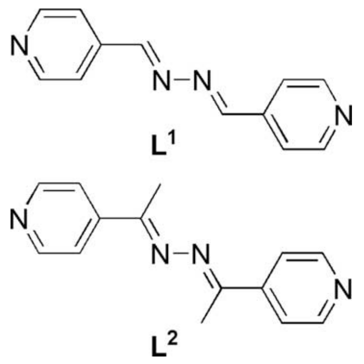
This study is part of our ongoing effort to design and characterize an extensive series of coordination polymers and oligomers tailored by polypyridyl/imine ligands and metal ion building blocks [6,9,13]. In this paper we report the syntheses, characterization and X-ray crystal structures of two novel 3-D coordination polymers of the ligands *N,N′*-bis-pyridin-4-yl-methylene hydrazine ($\mathbf{L^1}$) and *N,N′*-bis-(1-pyridin-4-yl-ethylidene)-hydrazine ($\mathbf{L^2}$). Ligands are shown in Scheme 1.

The ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ were synthesized [2,38] as yellow crystalline solids by condensing hydrazine hydrate with

---

* Corresponding author. Tel.: +91 33 24124082.
E-mail address: patra29in@yahoo.co.in (G.K. Patra).

1387-7003/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2009.09.027



Scheme 1. Chemical structures of polydentate imino-pyridyl ligands $\mathbf{L^1}$ and $\mathbf{L^2}$.

4-pyridinecarboxaldehyde and 4-acetyl pyridine respectively in 1:2 molar ratio in dehydrated methanol. These are characterized by an approximate C_2 symmetry. They were designed to contain readily accessible multiple imino nitrogen donor in the inner sites and also pyridyl nitrogens in the periphery of the molecular framework. They thus provide excellent building blocks for the formulation of coordination polymers with the Cu(I) ions. Cu(I) complexes **1** and **2** of the ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ were prepared [39] as reddish crystals in good yield by reacting the ligands with $[Cu(CH_3CN)_4]ClO_4$ [40] in 2:1 molar ratio in room temperature in inert atmosphere. Those red crystalline solids **1** and **2** were extremely stable in air both in solid state and in solution (CH_3CN and DMF).

Strong IR bands corresponding to –C=N– were observed at 1631 and 1608 cm^{-1} for $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively. No shift in –C=N– stretching frequencies were noticed upon complexation indicating the non-involvement of the –C=N– nitrogen in coordination. Strong well resolved bands around 1080 cm^{-1} in both the complexes **1** and **2** indicated the existence of the non-coordinating nature of the ClO_4^-. The absorption band with the variable intensity in the frequency range 1415–1542 cm^{-1} corresponds to ring vibrations of the pyridyl moiety of the ligands.

The ^1H NMR spectra of the ligand $\mathbf{L^1}$ in DMSO-D_6 showed a singlet at δ 8.71 ppm due to (HC=N) proton. For the ^1H NMR spectra of the ligand $\mathbf{L^2}$, the methyl protons resonated at δ 2.29 ppm. Slight upfield shift of the signals were observed in **1** and **2** upon complex formation. These protons appear at δ 8.53 and 2.22 ppm in the complexes **1** and **2**, respectively. There are not much shifts in the ^{13}C NMR spectra between the ligands and their corresponding metal complexes [39]. The electronic absorption spectra of the ligands and the corresponding Cu(I) complexes were recorded in acetonitrile solution. In absorption spectra of the free ligands a band observed at 285 nm (ε = 34 500) in $\mathbf{L^1}$ and 270 nm (ε = 28 200) in $\mathbf{L^2}$ are due to π–π^* transition. In the spectra of the complexes **1** and **2** no *d*–*d* transitions are expected [Cu(I), d^{10} system], the UV–Vis band observed at 370 nm (ε = 8420) in case of **1** and 362 nm (ε = 7560) in case of **2** were assigned to metal ligand charge transfer (MLCT) or ligand centred π–π^* transition [41]. The fluorescence spectra of the ligands ($\mathbf{L^1}$ and $\mathbf{L^2}$) and their Cu(I) complexes **1** and **2** were studied at room temperature in acetonitrile and DMF and they showed non-luminescent behavior. The redox behavior of the Cu(I) complexes **1** and **2**, examined by cyclic voltammetry in acetonitrile at platinum and glassy carbon working electrodes under dry N_2 atmosphere revealed ill-defined redox couple.

The single crystal X-ray diffraction studies on complexes **1** and **2** reveals that both the complexes feature sixfold interpenetrated 3D network built from Cu(I) and ligands $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively. While the complex **1** crystallizes in triclinic $P\bar{1}$ space group having one formula unit in the asymmetric unit, complex **2** crystallizes in tetragonal $P\bar{4}b2$ space group with half formula unit included in the asymmetric unit [42]. The Cu(I) atom in both the complexes adopts a slightly distorted tetrahedral geometry generated by the binding of one of the pyridyl nitrogens of the ligands (Fig. 1). The average Cu–N bond distances around the Cu(I) ion in **1** and **2** are 2.042 and 2.038 Å and are consistent [13,43]. The N–Cu–N angles lies within the range of 102.6(4)°–113.3(4)° in **1**, while in **2** it ranges between 100.8(5)° and 119.8(6)° indicating distortion from the ideal tetrahedral system.

The structures of the complexes appear on initial examination consisting of 3D polymeric chains bridging the tetra-coordinated Cu(I) metal centre. The building blocks $[Cu(\mathbf{L^1})_2]$ in **1** and $[Cu(\mathbf{L^2})_2]$ in **2** self-assemble to give rise diamondoid layers having large pores of dimension ca. 35 × 21 Å^2 and 38 × 19 Å^2 in **1** (Fig. 2) and **2**, respectively. The two pyridyl rings of ligand $\mathbf{L^1}$ are coplanar in **1**, while in **2** the said rings of ligand $\mathbf{L^2}$ form a dihedral angle of 27.57°.

But a closer inspection and topological calculations [44] revealed that these undulating diamondoid layers in both **1** and **2** stack in three dimensions to form a sixfold interpenetrating network. Fig. 3 shows the sixfold interpenetrating network in complex **2**. The accessibility of the pores of the full three-dimensional structures is drastically reduced by interpenetration and presence of perchlorate as well as solvent water molecules in the pores. Although longer flexible ligands in principle should favour the for-

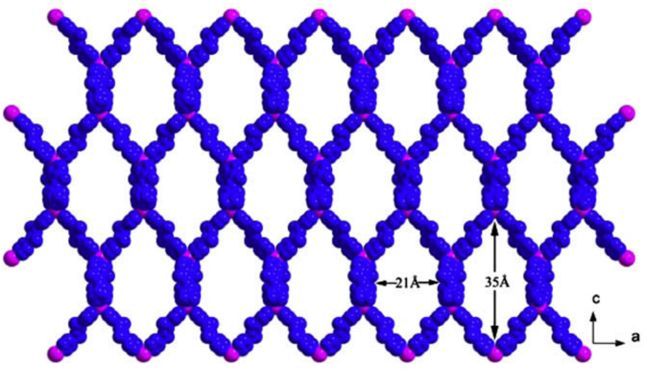


Fig. 2. View of diamondoid grid layers down crystallographic *b* axis in **1**. Perchlorate ions, solvent water molecules and hydrogen atoms are omitted for clarity.

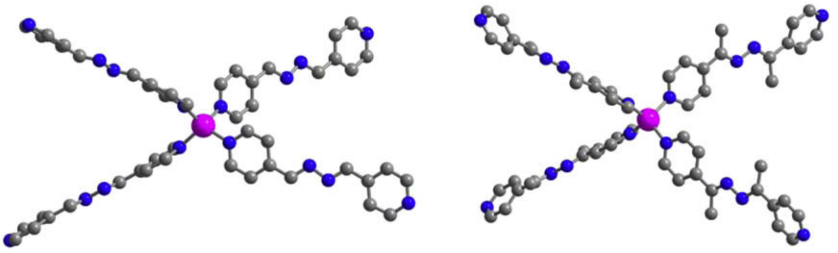


Fig. 1. Molecular building blocks of $[Cu(\mathbf{L^1})_2]_n(ClO_4)_n \cdot 2nH_2O$ (**1**) (left), $[Cu(\mathbf{L^2})_2]_n(ClO_4)_n \cdot 2nH_2O$ (**2**) (right).