

Functional tetranuclear square grids synthesized by in situ oxidation of ligand



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ABSTRACT

Tetranuclear square grids, namely, $[\text{Cd}_4(\text{L}-\text{O})_4] \cdot 1.5\text{DMF}$ (**1**), $[\text{Ni}_4(\text{L}-\text{O})_4] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Zn}_4(\text{L}-\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**3**), $[\text{Zn}_4(\text{L}-\text{O})_4]$ (**4**), $[\text{Cu}_4(\text{L}-\text{O})_4] \cdot \text{H}_2\text{O}$ (**5**), and $\{[\text{Cu}_4(\text{L}-\text{O})_4][\text{Cu}_4(\text{L}-\text{O})_4]\} \cdot 2.5\text{DMF} \cdot 1.5\text{H}_2\text{O}$ (**6**) (DMF = *N,N*-dimethylformamide, $\text{H}_2\text{L}-\text{O} = 2,6\text{-bis}(\text{pyrazine-2-carboxamido})\text{pyridine-N-oxide}$), formed by the reactions of M ions (M = Cd^{II} , Ni^{II} , Zn^{II} and Cu^{II}) with pyridyldicarboxamide ligands 2,6-bis(pyrazine-2-carboxamido)pyridine (H_2L), was fully characterized. Notably, the central pyridines of ligands H_2L were oxidized into pyridine-N-oxides under air conditions, producing the new anionic ligands $(\text{L}-\text{O})^{2-}$ to fabricate those grids. In those square grids every octahedrally coordinated metal node is chelated by two doubly deprotonated ligands $(\text{L}-\text{O})^{2-}$ in the *mer* configuration, and each ligand $(\text{L}-\text{O})^{2-}$ acts as a rigid bis(tridentate) linker with the $\text{N}_{\text{carboxamide}}$ and one $\text{N}_{\text{pyrazine}}$ in each arm chelating metal ions plus the O atom in the pyridine-N-oxide group bridging the two bound M ions. The Cd^{II} and Zn^{II} grids show uncommonly-excellent thermal stabilities and interesting green emissions. Magnetic studies upon grid $[\text{Ni}_4(\text{L}-\text{O})_4]$ suggest an antiferromagnetic coupling between the adjacent Ni^{II} mainly exchanged through $\mu-\text{O}$ with a coupling constant of $J = -15.06 \text{ cm}^{-1}$.

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1. Introduction

Polynuclear complexes formed by predesigned ligands and judiciously selected metal centers have drawn much current attentions owing to their appealing structural innovation and wide exploration for molecule-based materials [1]. Amongst which the conformationally rigid tetranuclear complexes such as molecular squares [2] and grids [3] have been extensively investigated. For the molecular square it typically has a capping ligand on the corners. In contrast, all donors from the ligands are used to form the grid. Most recently, molecular grids have attracted wide interest with respect to their unusual properties in luminescence [4], redox activity [5], and magnetism [6].

Over recent decades, increasing interest has been centered on the supramolecular chemistry of pyridylcarboxamides [7], especially of U-shaped symmetric bis(amidopyridine) ligands (Fig. 1) [8]. Those polytopic pyridylcarboxamide ligands have been intentionally used to engineer functional metal-containing macrocycles [8a], nanocages [8b], and intriguing frameworks by us and others [8c–f], showing interestingly synergetic tunability to the architectures and properties of the resulted metal–organic

assemblies through the labile conformers, versatile binding modes, and multiple states related to the deprotonation of carboxamide $[-\text{C}(\text{O})\text{NH}-]$ group. Pyrazinamide analogues with antimycobacterial and antifungal activity have drawn special interest in bioorganic and medicinal chemistry [9], but the complexation of these types of ligands to metals has not yet been disclosed [10]. 2,6-Bis(pyrazine-2-carboxamido)pyridine (H_2L) is a typically U-shaped polydentate pyridine-containing pyrazinamide ligand (Scheme 1). Up to now, only a linear tricopper(II) complex of the multifunctional ligand H_2L has been reported by Woollins and co-workers [11]. In that complex, two doubly deprotonated H_2L ligands spanned three copper atoms with the internal metal centre being bound by the nitrogen atoms from the central pyridyls and the terminal metal centres being chelated by the carboxamide and pyrazine nitrogen atoms of each ligand arms (Scheme 2). Unluckily, no detailed discussion about the tricopper(II) complex had been given due to the poor crystal quality. In the same article, Woollins et al. also reported another isostructural tricopper(II) and a tetracopper(II) complexes of another U-shaped 2,6-bis(pyridine-2-carboxamido)pyridine ligand (H_2L^5 in Scheme 1). It was found that the coordination mode of the two doubly deprotonated H_2L^5 ligands in the later tricopper(II) complex are similar to those of ligands H_2L found in the former tricopper(II) complex. In the Woollins's tetracopper(II) square, two doubly deprotonated

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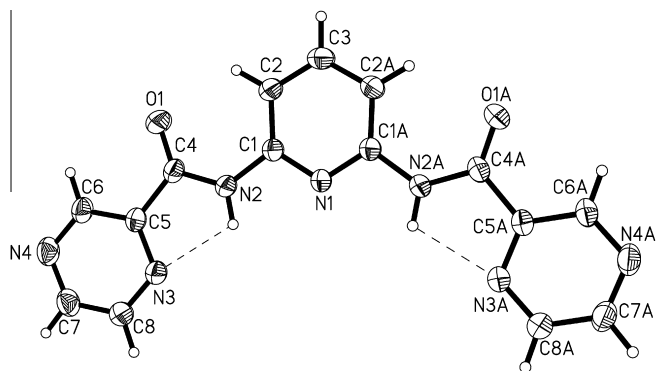


Fig. 1. View of planar structure of ligand H_2L .

H_2L^5 ligands bi-chelate the metal centers with the carboxamide and pyridine nitrogen atoms of each ligand arms while the other two doubly deprotonated H_2L^5 ligands whose central pyridines were oxidized into N-oxide through in situ reactions are plus the O atom in the pyridine-N-oxide group bridging the two bound M ions acting as bis(tridentate) linkers. An important feature of the work is that the pyridine group is oxidized very easily to the pyridine N-oxide during the synthesis. Generally, molecular oxygen cannot be used as the oxidant in this-sorted reaction because of its higher chemical stability, and the usually selected oxidant for the oxidation of pyridine into pyridine-N-oxide is peroxide. Notably, the very similarity both in the structure and binding domain around central pyridyl between H_2L and H_2L^5 seems to give a hint whether the oxidation of the central pyridine of H_2L into pyridine-N-oxide would occur in the preparation of metal complexes under aerobic condition.

In this context, ligand H_2L was deliberately synthesized and used by us to prepare polynuclear complexes with promising properties, and a series of functional tetranuclear square grids, namely,

$[Cd_4(L-O)_4] \cdot 1.5DMF$ (**1**), $[Ni_4(L-O)_4] \cdot H_2O$ (**2**), $[Zn_4(L-O)_4] \cdot 3H_2O$ (**3**), $[Zn_4(L-O)_4]$ (**4**), $[Cu_4(L-O)_4] \cdot H_2O$ (**5**), and $\{[Cu_4(L-O)_4][Cu_4(L-O)_4]\} \cdot 2.5DMF \cdot 1.5H_2O$ (**6**) (DMF = *N,N*-dimethylformamide, H_2L-O = 2,6-bis(pyrazine-2-carboxamido)pyridine-N-oxide) was synthesized and determined. Interestingly, the central pyridines of all ligands H_2L in the molecular grids were oxidized into pyridine-N-oxides under air conditions, producing the new anionic ligands $(L-O)^{2-}$ to fabricate those molecular grids (Scheme 2).

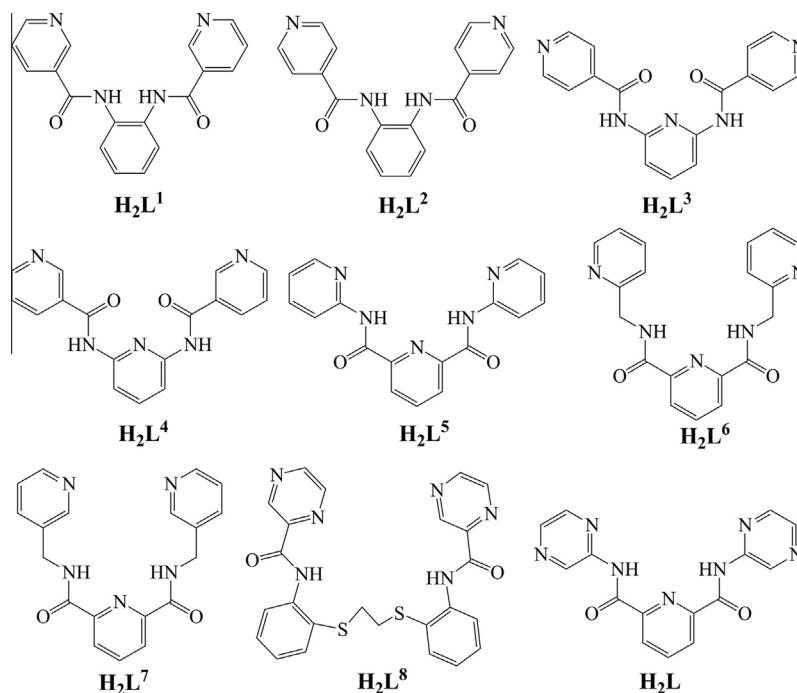
2. Experimental

2.1. General remarks

All commercial materials and solvents were of reagent grade or better, and used without further purification. Ligand H_2L was prepared by the method reported in the literature [11]. Element analyses were performed with a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Nicolet IR-470 spectrophotometer with KBr pellets in 400–4000 cm^{-1} region. Thermal analysis curves were scanned on a STA 409 PC thermal analyzer with air atmosphere. Fluorescence spectra were collected on a Hitachi F-4500 spectrophotometer. The powered X-ray diffraction (PXRD) pattern of the sample was recorded by a RIGAKU-DMAX2500 X-ray diffractometer with Cu-K α radiation. The temperature dependent magnetic measurements were determined on a Quantum Design SQUID-XL7 magnetometer.

2.2. Synthesis of $[Cd_4(L-O)_4] \cdot 1.5DMF$ (**1**)

A mixture of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.042 g, 0.1 mmol), H_2L (0.032 g, 0.1 mmol), DMF (5 mL) and ethyl acetate (10 mL) was refluxed for 6 h under air condition. The resultant yellow solution was allowed to naturally evaporate at room temperature. After a month, yellow block crystals **1** were collected, washed with DMF and ethanol, and dried naturally. Yield: 67%. Anal. Calc. for $C_{64.5}H_{46.5}Cd_4N_{29.5}O_{13.5}$: C, 40.77; H, 2.47; N, 21.74. Found: C, 40.35; H, 2.49; N, 21.89%. Selected



Scheme 1. Schematic representation of typically U-shaped pyridylcarboxamide and pyrazinamide ligands.

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