



# Pyridyldicarboxamide-based multinuclear complexes: Syntheses, structural characterizations, and magnetic properties

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## ABSTRACT

Using the pyridine dicarboxamide derivative *N,N'*-bis(1,3,4-thiadiazol-2-yl)-2,6-pyridinedi-carboxamide ( $H_2$ -btapca) as ligand, two novel polynuclear complexes: dimeric  $\{[Cu_2(\mu_2-O_2H)(btapca)_2] \cdot DMF \cdot H_2O\}$  (**1**) and tetrameric  $\{[Ni_4((\mu_2-O_2H)_2(btapca)_4)] \cdot DMF \cdot MeOH \cdot 3.5H_2O\}$  (**2**) were obtained. In complex **1**, two center Cu(II) ions are bounded by two btapca ligands and one aqueous molecule acting as a  $\mu_2$ - $H_2O$  bridge connect them together. Complex **2** is a tetrameric complex, in which the based backbone is an assumed  $Ni_4$  tetrahedron with two  $\mu_2$ - $O_2H$  bridges existing inside the tetrahedron forming a basic  $[Ni_2(\mu_2-O_2H)]_2$  core, which are surrounded by four btapca ligands. The magnetic properties of the two polynuclear complexes were determined, the results show that for both of the two complexes, the overall weak ferromagnetic exchange interactions between central metal ions are evident, the best fitting parameters are:  $J = 7.47 \text{ cm}^{-1}$  ( $g = 2.21$ ) for dimeric Cu(II) complex **1**, and  $2J_1 = 4.8 \text{ cm}^{-1}$ ,  $2J_2 = -0.00204 \text{ cm}^{-1}$  ( $g = 2.14$ ,  $zJ' = 0.00077 \text{ cm}^{-1}$ ) for tetrameric Ni(II) complex **2**.

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## 1. Introduction

The recent synthesis of polynuclear metal–organic complexes has afforded a fascinating array of MOFs which display a variety of unusual geometries and exhibit potential applications in some areas such as catalysis, electrical conductivity, molecular-based and host-guest chemistry [1–5]. So the synthetic strategies of such polynuclear complexes have received much attention. To obtain such complexes, multifarious functional ligands have been synthesized and used in the self-assembly process, among which pyridine carboxamide-containing derivatives, as one kind of excellent multidentate ligand, have drawn much attention by the coordination chemists in recent years, not only because of their own potential use in asymmetric catalysis, molecular receptors, dendrimer synthesis etc [6–8], but also because that the pyridine carboxamide derivatives can easily be synthesized [5]. As a kind of excellent linker, the presence of several N- and O-coordinated sites in the pyridine carboxamide moieties can make it particularly attractive for the preparation of polynuclear complexes, and these ligands also have the ability to stabilize metal ions in high oxidation states [9–11]. Up to now, lots of polynuclear complexes with interesting topologies constructed by pyridine carboxamide-based ligands have been prepared, and their biological, electrochemical, luminescent and magnetic properties have been widely investigated [4–15]. The behaviors of pyridine carboxamide derivatives towards the magnetic relevant d-block polynuclear complexes also have

attracted intense study since the magnetic interactions can be exchanged by the direct or indirect metal centers in the polynuclear systems. Inspired by these, we have synthesized and reported the structures and magnetic properties of several polynuclear Zn(II), Co(II), Ni(II) and Fe(II) complexes based on the pyridine carboxamide-based ligand [4].

Following our early research on the polynuclear complexes constructed by the pyridine carboxamide-based derivatives, we use *N,N'*-bis(1,3,4-thiadiazol-2-yl)-2,6-pyridinedi-carboxamide ( $H_2$ -btapca) as ligand to react with d-block metal ions Cu(II) and Ni(II), and result in two polynuclear complexes with different structures: dimeric complex  $\{[Cu_2(\mu_2-O_2H)(btapca)_2] \cdot DMF \cdot H_2O\}$  (**1**) and a tetrameric complex  $\{[Ni_4((\mu_2-O_2H)_2(btapca)_4)] \cdot DMF \cdot MeOH \cdot 3.5H_2O\}$  (**2**). In both of the two complexes, the aqueous molecules acting as  $\mu_2$ - $H_2O$  bridges connect the adjacent metal ions together. Determinations of the magnetic properties show that the overall weak ferromagnetic exchange interactions between central metal ions are evident for both of the two complexes. The results indicate that the M–M interactions mediated by the bridging aqueous molecules and M–O–M functions in the polynuclear systems lead to the dominant magnetic super exchange interactions between the metal centers.

## 2. Experimental

### 2.1. General

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental

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analyses (C, H, and N) were carried out on a Carlo-Erba 1106 elemental analyzer. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000  $\text{cm}^{-1}$  region. Ligand N,N'-bis(1,3,4-thiadiazol-2-yl)-2,6-pyridinedi-carboxamide ( $\text{H}_2$ -btapca) was prepared according to the literature method [4].

## 2.2. Syntheses of the complexes 1–2

### 2.2.1. Synthesis of $\{[\text{Cu}_2(\mu_2\text{-O}_2\text{H})(\text{btapca})_2]\cdot\text{DMF}\cdot\text{H}_2\text{O}\}$ (1)

5 mL MeOH/DMF mixture solution (1:1) of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.1 mmol, 0.0170 g) was added dropwise to a DMF solution (5 mL) of  $\text{H}_2$ -btapca (0.1 mmol, 0.0333 g). The mixture was kept at room temperature, after four days fine clubbed crystals suitable for X-ray analysis were produced. Yield: 52%. *Anal. Calc.* for  $\text{C}_{25}\text{H}_{17}\text{Cu}_2\text{N}_{15}\text{O}_7\text{S}_4$  (894.86): C, 33.52; H, 1.90; N, 23.47. Found: C, 33.45; H, 1.96; N, 23.38%. IR (KBr pellets): 3423w, 3090m, 1695w, 1641s, 1580m, 1540m, 1455s, 1371s, 1350m, 1305m, 1279m, 1232w, 1164m, 1080m, 1041m, 960w, 891m, 844mw, 762w, 721w, 721w, 685m, 623w  $\text{cm}^{-1}$ .

### 2.2.2. Synthesis of $\{[\text{Ni}_4(\mu_2\text{-O}_2\text{H})_2(\text{btapca})_4]\cdot\text{DMF}\cdot\text{MeOH}\cdot 3.5\text{H}_2\text{O}\}$ (2)

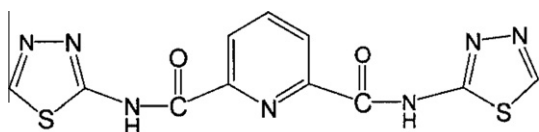
A MeOH solution (5 mL) of  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.0237 g) was added dropwise to a DMF solution (4 mL) of  $\text{H}_2$ -btapca (0.1 mmol, 0.0333 g), the mixture was heated at 60 °C for 30 min, then this mixture was placed under air, about a week later the light-blue fine crystals were obtained. Yield: 65%. *Anal. Calc.* for  $\text{C}_{48}\text{H}_{39}\text{Ni}_4\text{O}_{15.5}\text{S}_8$  (1761.40): C, 32.70; H, 2.21; N, 23.05. Found: C, 32.63; H, 2.18; N, 23.12%. IR (KBr pellets): 3400m (w), 2861m, 1639s, 1572s, 1530s, 1497s, 1470m, 1425m, 1372s, 1308s, 1269w, 1158m, 1074m, 1037w, 998w, 955m, 880m, 851w, 800w, 765w, 732m, 697m, 678m, 613w  $\text{cm}^{-1}$ .

## 2.3. Magnetic studies

Temperature-dependent magnetic susceptibility measurements on powdered solid sample was carried out on a SQUID magnetometer (MPMS Quantum Design) over the temperature range 1.8–300 K. The magnetic field applied was 2 kOe. The observed susceptibility data was corrected for underlying diamagnetism by using Pascal's constants [16].

## 2.4. X-ray crystallography

Crystal data collection and refinement parameters for complexes 1–2 are given in Table 1. All measurements were made on a Bruker APER CCD diffractometer with graphite monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Single crystals were selected and mounted on a glass fiber. The data were collected at a temperature of 291(2)K and corrected for Lorentz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the SHELXL-97 crystallographic software package [17]. Selected bond lengths and bond angles are tabulated in Table 2.



$\text{H}_2$ -btapca

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

	1	2
Formula	$\text{C}_{25}\text{H}_{17}\text{Cu}_2\text{N}_{15}\text{O}_7\text{S}_4$	$\text{C}_{48}\text{H}_{39}\text{Ni}_4\text{O}_{15.5}\text{S}_8$
Formula weight	894.86	1761.40
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	11.877(4)	14.784(4)
<i>b</i> (Å)	12.559(4)	15.564(4)
<i>c</i> (Å)	13.064(4) A	17.676(4) A
$\alpha$ (°)	102.767(6)	89.294(4)
$\beta$ (°)	93.074(7)	65.828(4)
$\gamma$ (°)	94.103(6)	73.503(4)
<i>V</i> (Å <sup>3</sup> )	1890.7(10)	3532.6(14)
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.572	1.724
<i>Z</i>	2	2
$\mu$ (mm <sup>-1</sup> )	1.408	1.369
Reflections collected/unique	9614/ 6386	16 679/11 543
<i>R</i> (int) = 0.0949		<i>R</i> (int) = 0.0317
Data/restraints/parameters	6386/26/479	11543/6/936
<i>F</i> (0 0 0)	900	1860
<i>R</i> <sub>1</sub> <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0917	<i>R</i> <sub>1</sub> = 0.0607
	<i>wR</i> <sub>2</sub> = 0.1614	<i>wR</i> <sub>2</sub> = 0.1577
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.926	1.000
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.719 and -0.782	1.100 and -0.551

$$R_1^a = \sum ||F_o| - |F_c|| / \sum |F_o|. WR = \sum [w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

## 3. Results and discussion

### 3.1. Crystal structure of $\{[\text{Cu}_2(\mu_2\text{-O}_2\text{H})(\text{btapca})_2]\cdot\text{DMF}\cdot\text{H}_2\text{O}\}$ (1)

Crystallographic analysis reveals that complex 1 crystallizes in the space group  $P\bar{1}$  and exhibits a dimeric structure as shown in Fig. 1. The two center Cu(II) ions are bounded by two btapca ligands and one  $\mu_2\text{-O}_2\text{H}$  bridge. Cu1 and Cu2 ions are penta-coordinated and form distorted  $[\text{N}_4\text{O}]$  donor sets, in which the Cu(II) ions are coordinated by three nitrogens from the two deprotonated carboxamides and the central pyridine, the other nitrogen atom comes from another btapca ligands' thiazole ring and one oxygen atom is from  $\mu_2\text{-O}_2\text{H}$  bridge. Due to the constraints of the ligand, the geometry around each pentacoordinated copper ion deviates from either square pyramidal or trigonal bipyramidal structure. To have an idea about the degree of distortion about each metal atom, we performed calculations based on the methods of Addison et al. [18]. The geometric parameter,  $\tau$ , for Cu1 is 0.148, and that for Cu2 is 0.135. The values indeed indicate that the geometry around the metal atom is closer to a square based pyramid. The atoms N3, N4, N5 and O5 around the Cu1 form a planar (derivation from the ideal plane 0.0216 Å), N13 atom locates in the axial position (the Cu1–N13 bond length is 2.239 Å). For Cu2 atom, N10, N11, N12 and O5 stay in the equatorial planar (derivation from the ideal plane 0.0389 Å), N2 atom exists in the axial position (the Cu2–N2 bond length is 2.202 Å). And the dihedral angle between the two planes around Cu1 and Cu2 is 103.0°.

The two btapca ligands are also nearly vertical to each other (dihedral angle is about 97.4° for the two planes Cu1–N3–N4–N5 and Cu2–N10–N11–N12 defined by the two different ligands, and the mean derivations of the two planes are 0.0532 and 0.0506 Å, respectively). The Cu–N distances range from 1.939 to 2.240 Å. The Cu1–O( $\mu_2\text{-O}_2\text{H}$ ) bond length is 1.910 Å, which is a little slightly shorter than the Cu2–O( $\mu_2\text{-O}_2\text{H}$ ) bond length of 1.970 Å, and both of them fall in the normal range of the Cu–O distances [19].

The N–Cu–N angles around the Cu(II) ions, among which the two nitrogen atoms are from different ligands, are in the range of 94.8°–97.7° for Cu1 and 89.9°–102.3° for Cu2, respectively, which further prove that the two btapca ligands are nearly vertical with each other. The Cu–O–Cu angle is 116.2°, and the Cu...Cu distance

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