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Two Novel Supramolecules Built by Dimethylphenyl Imidazole Dicarboxylate: Syntheses, Structures, and Thermal Properties[1]

X. S. Lin[a] and Y. L. Sang[a, *]

[a]*College of Chemistry and Chemical Engineering, Chifeng University, Chifeng, Neimenggu, 024000 P.R. China*

**e-mail: sangyali0814@126.com*

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Abstract—By solvothermal reactions of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ with 2-(3,4-dimethylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (3,4-DMPhH_3IDC), respectively, two supramolecular complexes, $[Zn(3,4\text{-}DMPhHIDC)_2(H_2O)_2]_n$ (**I**) and $[Ni(3,4\text{-}DMPhHIDC)_2(H_2O)_2]_n$ (**II**) have been successfully prepared and structurally characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1440305 (**I**) and 1440316 (**II**)), elemental analyses, and IR spectroscopy. The results show that ligand 3,4-DMPhH_3IDC in the two complexes has quite strong coordination ability, and the 3D solid-state supramolecular structures of **I** and **II** involve intermolecular hydrogen bonds. The thermal properties of the complexes have also been investigated and discussed.

Keywords: imidazole dicarboxylate, supramolecule, crystal structure, thermal property

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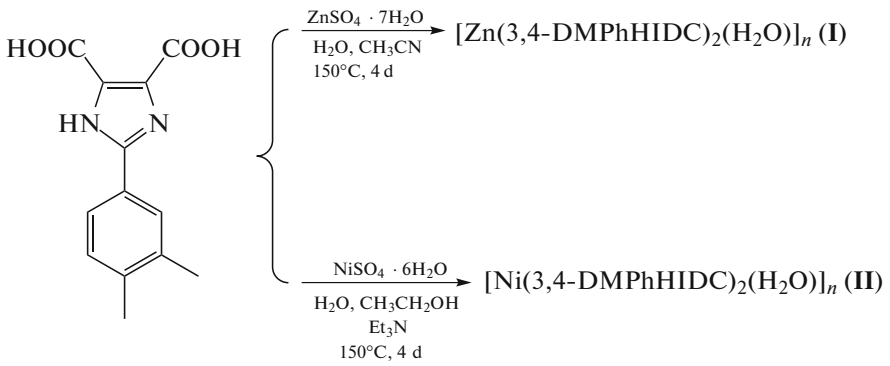
INTRODUCTION

At present, by the frequent development of coordination chemistry, more and more useful supramolecules are applied in catalyzing some organic pigments, luminescent materials, molecular transport and so on. [1–4]. However, it is still a challenging subject how to improve the design of the charming supramolecules with specific functions. To obtain such complexes, there are two key points: one is the choice of metal ions, another is the design of the multifunctional organic ligands. The choice of metal ions is usually based on its inherent characteristic, for example, some metal ions were often chose to design the complexes showing good luminous performance, such as Zn^{2+}, Cd^{2+}, or some rate earth metals, Eu^{3+} and Tb^{3+}. Considering the radius of the metal ions and the affinity to ligating atoms, the choice of organic ligands is abundant.

According to the literatures, one of the most effective and facile approach for the construction of coordination frameworks with desired properties is to adopt organic ligands containing N and O donors, which usually show various coordination modes and satisfy many central metal coordination preferences. In numerous organic ligands, 4,5-imidazole dicarboxylic acid (H_3IDC) has one imidazole ring and two carboxylate groups indicating complicated and changeable coordination fashions [5], which has been proved as an outstanding ligand not only for the possession of six coordination sites but also for its potential ability as hydrogen-bonding donors and acceptors [6, 7]. Summarizing the literature, the most of derivatives of H_3IDC are adipose substitutes, for example, methyl, ethyl and aromatic substitutes [8, 9]. Some groups have researched the organic ligands bearing 2-position aromatic groups in the imidazole ring of H_3IDC, such as phenyl group and so on [10–14].

In this context, the research of the dimethylphenyl substituted imidazole dicarboxylate ligand 2-(3,4-dimethylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (3,4-DMPhH_3IDC) are very limited. Thus, we surveyed the reaction conditions and successfully obtained two novel supramolecular complexes, $[Zn(3,4\text{-}DMPhHIDC)_2(H_2O)_2]$ (**I**) and $[Ni(3,4\text{-}DMPhHIDC)_2(H_2O)_2]$ (**II**) (Scheme 1). Their crystal structures and thermal properties have also been investigated.

[1] The article is published in the original.



Scheme 1.

EXPERIMENTAL

Materials and methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The C, H and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Thermal gravimetric (TG) measurements were performed by heating the crystalline sample from 20 to 850°C at a rate of 10°C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer.

The organic ligand 3,4-DMPhH_3IDC was prepared according to literature procedure [15]. The product is gray powder with productivity being 51%.

For $C_{13}H_{12}N_2O_4$

Anal. calcd., %	C, 59.00	H, 4.62	N, 11.37
Found, %	C, 59.38	H, 4.37	N, 11.08

IR (KBr; ν, cm^{-1}): 3420 m, 3100 w, 2968 s, 1631 m, 1595 s, 1558 m, 1500 s, 1482 s, 1390 m, 1271 w, 1096 w, 890 w, 772 w, 653 w, 492 w, 440 w.

Synthesis of I. A mixture of $ZnSO_4 \cdot 7H_2O$ (14.4 mg, 0.1 mmol), 3,4-DMPhH_3IDC (26.0 mg, 0.1 mmol), CH_3CN–H_2O (3 : 4, 7 mL) were sealed in a 25 mL Teflon-lined bomb and heated at 150°C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10°C/h. The pale yellow crystals of **I** were collected, washed with distilled water and dried in air (58% yield based on Zn).

For $C_{30}H_{28}N_6O_{10}Zn$

Anal. calcd., %	C, 51.58	H, 4.01	N, 12.0
Found, %	C, 51.25	H, 3.95	N, 11.79

IR (KBr; ν, cm^{-1}): 3259 m, 1713 m, 1669 w, 1500 s, 1543 s, 1492 s, 1387 s, 1283 m, 1219 w, 1024 w, 771 w, 730 s, 642 w, 512 w, 446 w.

Synthesis of II. A mixture of $NiSO_4 \cdot 6H_2O$ (26.3 mg, 0.1 mmol), 3,4-DMPhH_3IDC (26.0 mg, 0.1 mmol), CH_3CH_2OH–H_2O (3 : 4, 7 mL), Et_3N (0.1 mL) were sealed in a 25 mL Teflon-lined bomb and heated at 150°C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10°C/h. Green virgulate crystals of **II** were collected, washed with distilled water and dried in air (51% yield based on Ni).

For $C_{26}H_{24}N_4NiO_{10}$

Anal. calcd., %	C, 51.05	H, 3.93	N, 9.16
Found, %:	C, 51.15	H, 4.01	N, 9.22

IR (KBr; ν, cm^{-1}): 3587 w, 3207 s, 1717 s, 1588 s, 1544 s, 1493 s, 1392 s, 1282 m, 1109 w, 1022 m, 899 w, 829 m, 733 s, 646 w, 514 w, 445 w.

X-ray crystallography. Crystallographic data of **I** and **II** were collected on a Bruker smart APEXII CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Single crystals of **I** and **II** were selected and mounted on a glass fiber. All data were collected at a temperature of 291(2) K using the ω–2θ scan technique and corrected for Lorenz-polarization effects. Furthermore, a correction for secondary extinction was applied. The two structures were solved by the direct methods and expanded using the Fourier technique. They were refined on F^2 by full matrix least-squares using SHELXTL [16]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 3455 observed reflections and 223 variable parameters for **I**, and 2314 observed reflections and 202 variable parameters for **II**.

The crystallographic data experimental details for the two compounds are contained in Table 1. The selected bond lengths and angles are listed in Table 2.

Supplementary material for the structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1440305 (**I**) and 1440316 (**II**); deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data and structure refinement for compounds **I** and **II**

Parameter	Value	
Temperature, K	293(2)	296(2)
Fw	697.97	611.18
Crystal system	Triclinic	Monoclinic
Crystal size, mm	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18
Space group	$P\bar{1}$	$P2_1/c$
a, Å	7.3183(13)	5.746(5)
b, Å	9.1715(16)	13.258(11)
c, Å	13.265(2)	17.650(14)
α, deg	97.873(2)	90
β, deg	103.665(2)	98.632(12)
γ, deg	786.2(2)	90
V, Å^3	786.2(2)	1329.3(19)
ρ_{calcd}, mg m^{-3}	1.474	1.527
Z	1	2
μ, mm^{-1}	0.848	0.795
Reflections collected/unique (R_{int})	4784/3455 (0.0188)	6219/2314 (0.0605)
Reflections with $I > 2\sigma(I)$	3082	2058
Data/restraints/parameters	3455/3/223	2314/32/202
GOOF on F^2	1.087	1.089
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0479$, $wR_2 = 0.1384$	$R_1 = 0.0801$, $wR_2 = 0.1254$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.1479$	$R_1 = 0.0949$, $wR_2 = 0.1489$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, *e* Å^{-3}	0.671 and −0.477	1.760 and −1.420

RESULTS AND DISCUSSION

The zinc and nickel supramolecules were synthesized by solvothermal reactions of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ with the 3,4-DMPhH_3IDC ligand, respectively. The synthetic routes are shown in Scheme 1, and the organic ligands in both complexes have the similar coordination modes as shown in Fig. 1. As we all know, some factors could influence the supramolecular assembly process, which can be concluded as follows: the pH value, temperature, templates, solvent system, counterions, reaction time and molar ratio of the reactants. The pH value is one key factor for preparation of the complexes. In most cases, the pH value influences the deprotonation of the organic acids and finally affects the resultant structures of compounds. Compound **I** was synthesized under the pH value of ~7, while the compound **II** was prepared under the pH value of 8–9, the reactions of metal salts and related ligands in a molar ratio of 1 : 1 and 1 : 1, respectively, have produced the crystals of **I** and **II** successfully, which are centrosymmetric. Through lots of parallel experiments in the synthesis process of coordination compound **II**, lightly excessive Et_3N would cause a failure, once the reaction conditions were slightly changed, the yields were low or only unidentified precipitates were isolated. We have also attempted to set the temperature at 150°C in the syntheses of **I** and **II**. Additionally, complexes **I** and **II** exhibit good stability under ambient conditions and are insoluble in water and common organic solvents.

A single-crystal X-ray diffraction study shows that compound **I** is a mononuclear structure. The asymmetric unit of **I** consists of one crystallographically independent Zn^{2+} ion, two 3,4-DMPhHIDC^{2-} anions, and two water ligands. The 3,4-DMPhHIDC^{2-} unit exhibits one kind of coordination mode, namely η-*k*N, O mode (Fig. 1). The geometry around the Zn(II) center is best portrayed as a slight distorted [ZnO_4N_2] octahedral environment, which is defined by two imidazolate N(1), N(1a) atoms and two carboxylate O(1), O(1a) atoms from two individual 3,4-DMPhHIDC^{2-} anions, and the remaining two sites are occupied by two O(5), O(5a) atoms from two coordination water molecules (Fig. 2a). The Zn–O(1) and Zn–O(5) bond lengths are 2.110(2) and 2.066(2) Å, respectively, while the Zn–N(1) distance is 2.176(2) Å, which are comparable to those reported imidazole dicarboxylate-based Zn(II) complexes [17].

Table 2. Selected bond distances (Å) and angles (deg) for the complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
		I			
N(1)–Zn(1)	2.176(2)	O(1)–Zn(1)	2.1101(19)	O(5)–Zn(1)	2.066(2)
O(5)–H(1*w*)	0.81	O(5)–H(2*w*)	0.81		
		II			
Ni(2)–O(2)	2.049(6)	Ni(2)–O(3)	2.095(8)	Ni(2)–N(13)	2.166(8)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
		I			
O(5)Zn(1)N(1)	87.24(1)	O(5)Zn(1)O(1)	90.49(9)	O(1)Zn(1)N(1)	78.62(7)
		II			
O(3)Ni(2)N(13)	89.9(3)	O(2)Ni(2)O(3)	91.5(3)	O(2)Ni(2)N(13)	80.8(3)

The bond angles of OZnN are in the range of 78.62(7)° to 101.38(7)°.

Within the organic ligand, two weak twists present between the imidazole and two carboxylate rings with the dihedral angles of 2.4(3)° and 5.4(3)°, respectively, what is more, the dihedral angle between aromatic phenyl and imidazole ring is 33.0(1)° indicating a strong twist. It should be pointed that water molecules all participate in the formation of hydrogen bonds. There are two types of intermolecular hydrogen bonds: O(5)–H(1*w*)···O(4), O(5)–H(2*w*)···O(4) (Table 3). There are four hydrogen bonds forming a diamond between four Zn(3,4-DMPh-H_2IDC)$_2$-(H_2O)$_2$ units forming a 2D layer (Fig. 2b). Furthermore, from the *b* direction, the layers are interlinked to produce a 3D polyporous framework by weak π···π stacking interactions of the phenyl rings which are crossed each other (Fig. 2c). The distance of the two phenyl rings which have the strong conjugation effect are 3.991 and 3.619 Å. Notably, the hydrogen bonding interactions further stabilize the supramolecular network. As far as we know, the ligand 3,4-DMPhH_3IDC is used to synthesize the Zn complex for the first time.

Supramolecular complex **II** is one unique Ni^{2+} ion, two 3,4-DMPhHIDC^{2-} anions, and two water ligands. The 3,4-DMPhHIDC^{2-} unit exhibits one kind of coordination mode, namely η-*k*N, O (Fig. 1). As depicted in Fig. 1b, the Ni(II) center is in a six-coordinated environment, the coordination atoms are O(2a), O(3a), O(2), O(3), N(13a), N(13), which can be best described as an octahedral geometry [NiO_4N_2]. The coordination sphere of Ni(II) consists of two carboxylate O(2), O(2a) atoms from two individual 3,4-DMPhHIDC^{2-} anions, two O(3), O(3a) atoms from two coordination water molecules, and two imidazolate N(13), N(13a) atoms (Fig. 3a). The Ni–O lengths are 2.049(6) and 2.095(8) Å, respectively. And the distance of Ni–N bond is 2.166(8) Å, which are compared to those reported values [17]. The ONiN bond angles vary from 80.8(3)°–99.2(3)°.

Table 3. Geometric parameters of hydrogen bond distances (Å) and angles (deg) for the complexes **I** and **II**

D–H···A	Distance, Å		Angle DHA, deg
	H···A	D···A	
	I		
O(5)–H(1*w*)···O(4)	1.98	2.770(3)	170
O(5)–H(2*w*)···O(4)	1.93	2.741(2)	174
	II		
O(14)–H(14)···O(18)	1.72	2.534(2)	172
N(24)–H(6)···O(36)	1.82	2.839(3)	170
O(3)–H(3)···O(18)	1.97	2.731(2)	148

Interesting, in this supramolecular complex, two types of intramolecular hydrogen bonds, (O(14)–H(14)···O(18), O(3)–H(3)···O(18)) (Table 3), and one type of intermolecular hydrogen bond (N(24)–H(6)···O(36)) play a key role in the process of accumulation. Neighbor [Ni(3,4-DMPhHIDC)$_2$(H_2O)$_2$] units are joined by the N–H···O hydrogen bonds to form 1D straight chains (Fig. 3b). Furthermore, from the *b* direction, the layers are interlinked to produce a 3D polyporous framework by weak π···π stacking interactions of the phenyl rings which are crossed each other (Fig. 3c). Also, the hydrogen bonds stabilize the supramolecular network.

The distance of the two phenyl rings which have the strong conjugation effect is 6.011 Å, within the organic ligand, two weak twists present between the imidazole ring and two carboxylate plans with the dihedral angles of 5.4(7)° and 5.0(7)°, respectively, what is more, the dihedral angle between aromatic plane and the imidazole ring is 17.9(3)° indicating a week twist. To our astonished, the complex [Ni(3,4-DMPhHIDC)$_2$-(H_2O)$_2$]$_n$ is the first complex based on the newly designed ligand, the successful formations of supramolecules **I** and **II** supply more chance for the subsequent study of imidazole dicarboxylate ligands.

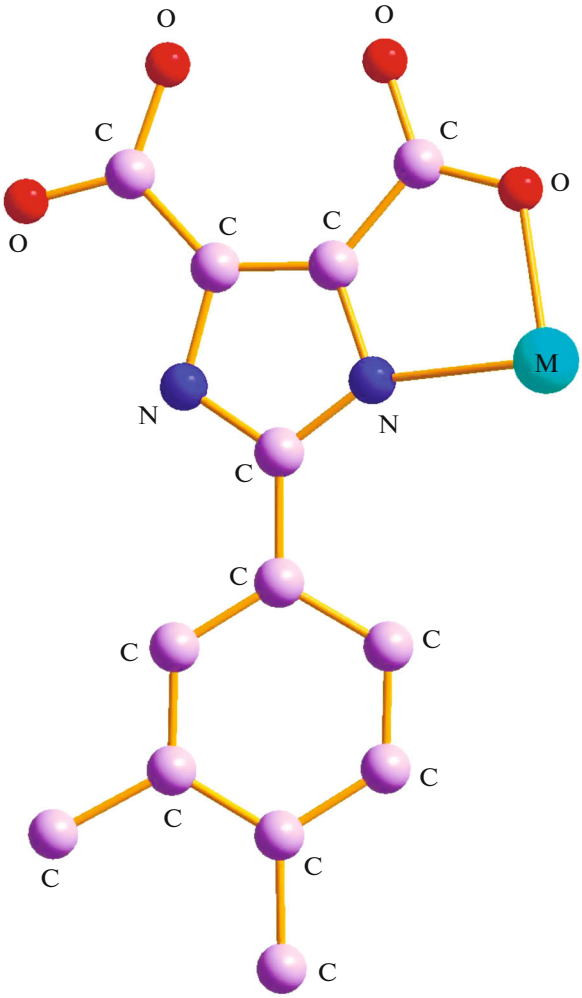


Fig. 1. Coordination modes of 3,4-DMPhHIDC^{2-} anions in complexes **I** and **II**.

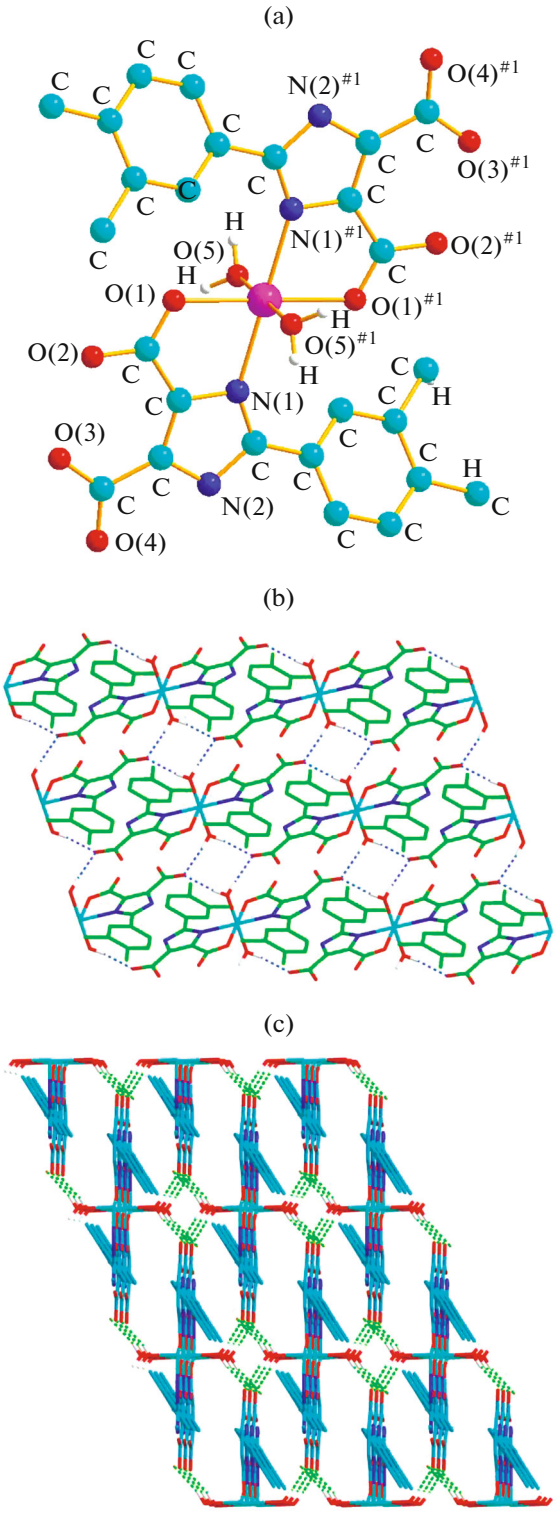


Fig. 2. Coordination environments of the Zn(II) with atomic labels in **I** (a); view of the layer of complex **I**, containing intramolecular hydrogen bonds (b); crystal packing diagram of **I** along the *c* direction showing the π···π stacking between the chains, containing intramolecular hydrogen bonds (c).

Compounds **I** and **II** indicate strong and broad absorption bands in the range of 3100–3600 cm^{-1}, which indicate the presence of the ν(N–H) and the ν(O–H) stretching frequencies of imidazole ring and water molecules. The asymmetric and symmetric vibrations of carboxyl group in the complexes appeared at ~1713 and ~1544 cm^{-1} for **I**, ~1717 and ~1588 cm^{-1} for **II**, which can indicate the existence of free and coordinated carboxyl groups. The frame vibration of phenyl ring is observed at 1492 and 1493 cm^{-1} for **I** and **II**, respectively. The characteristic IR band of the methyl at 1380–1400 cm^{-1} due to δ(=C–H) vibrations, which can be found at 1386 and 1391 cm^{-1} for **I** and **II**. Moreover, the absorption in the range of 1000–1300 cm^{-1} attributed to C=N and C=C vibrations. In conclusion, IR spectra 400–4000 cm^{-1} display characteristic absorption bands for water molecules, carboxylate, imidazolyl units, and phenyl

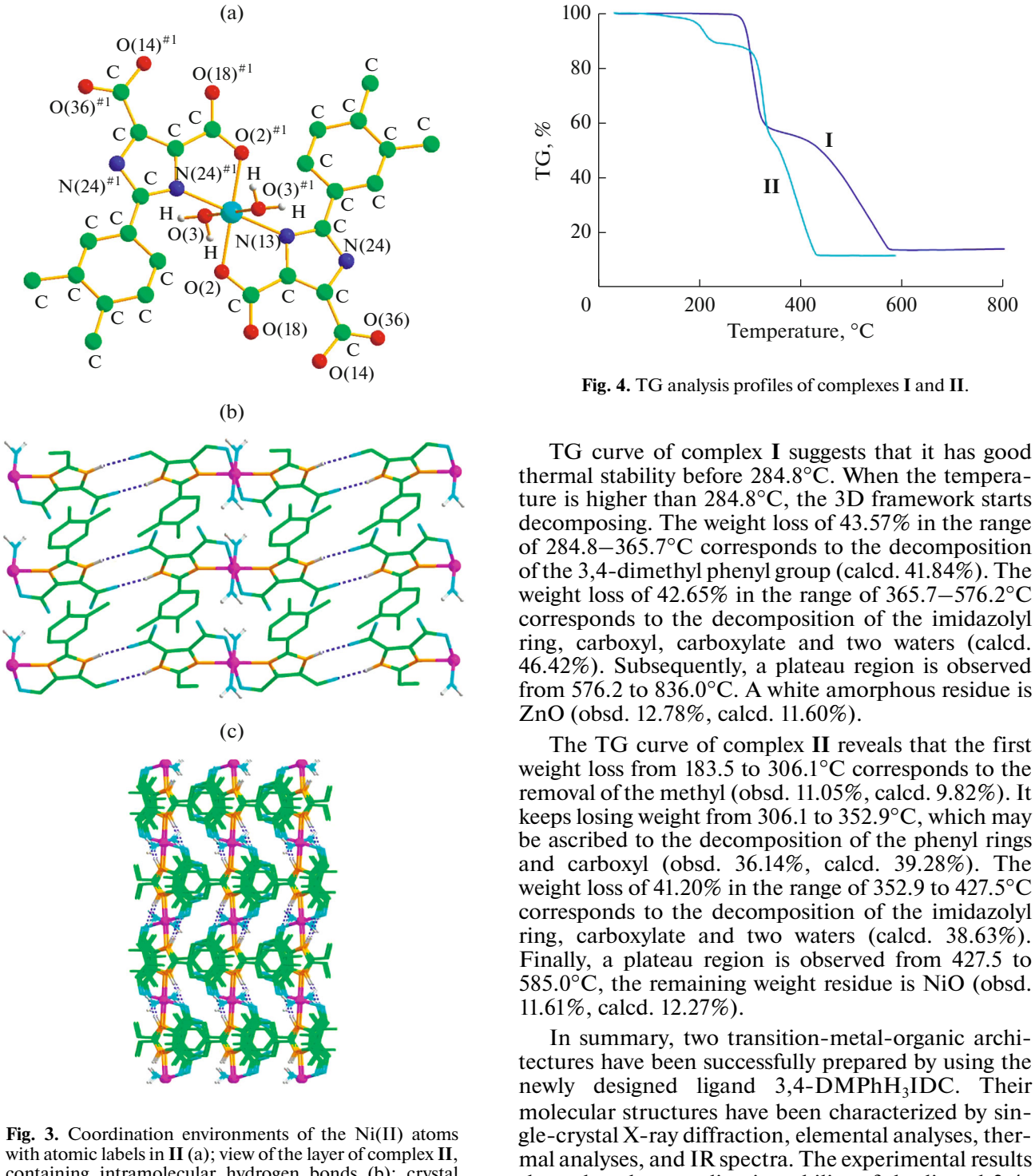


Fig. 3. Coordination environments of the Ni(II) atoms with atomic labels in **II** (a); view of the layer of complex **II**, containing intramolecular hydrogen bonds (b); crystal packing diagram of **II** along the *c* direction showing the π···π stacking between the chains, containing intramolecular hydrogen bonds (c).

Fig. 4. TG analysis profiles of complexes **I** and **II**.

units, which are accordant with the result of the X-ray diffraction analyses.

In order to estimate the thermal stabilities of the complexes, TG analyses of **I** and **II** were carried out in the air (Fig. 4).

TG curve of complex **I** suggests that it has good thermal stability before 284.8°C. When the temperature is higher than 284.8°C, the 3D framework starts decomposing. The weight loss of 43.57% in the range of 284.8–365.7°C corresponds to the decomposition of the 3,4-dimethyl phenyl group (calcd. 41.84%). The weight loss of 42.65% in the range of 365.7–576.2°C corresponds to the decomposition of the imidazolyl ring, carboxyl, carboxylate and two waters (calcd. 46.42%). Subsequently, a plateau region is observed from 576.2 to 836.0°C. A white amorphous residue is ZnO (obsd. 12.78%, calcd. 11.60%).

The TG curve of complex **II** reveals that the first weight loss from 183.5 to 306.1°C corresponds to the removal of the methyl (obsd. 11.05%, calcd. 9.82%). It keeps losing weight from 306.1 to 352.9°C, which may be ascribed to the decomposition of the phenyl rings and carboxyl (obsd. 36.14%, calcd. 39.28%). The weight loss of 41.20% in the range of 352.9 to 427.5°C corresponds to the decomposition of the imidazolyl ring, carboxylate and two waters (calcd. 38.63%). Finally, a plateau region is observed from 427.5 to 585.0°C, the remaining weight residue is NiO (obsd. 11.61%, calcd. 12.27%).

In summary, two transition-metal-organic architectures have been successfully prepared by using the newly designed ligand 3,4-DMPhH_3IDC. Their molecular structures have been characterized by single-crystal X-ray diffraction, elemental analyses, thermal analyses, and IR spectra. The experimental results show that the coordination ability of the ligand 3,4-DMPhH_3IDC is strong and the coordination modes are flexible.

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