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Syntheses, Structures, and Characterization of Three New Complexes Constructed From Triazolyl N-Heterocyclic Ligand

Qinqin Yuan ^a , Ming Zhao ^b , Songhe Zhang ^a , Hongwei Hou ^a , Jinpeng Li ^c , Shujun Zhu ^a , Xiaoli Gao ^a , Huan Sun ^a , Yaoting Fan ^a & Junbiao Chang ^{a c}

^a Department of Chemistry, Zhengzhou University, Henan, P. R. China

^b Experimental Management Centre, Zhongzhou University, Henan, P. R. China

^c School of Pharmaceutical Sciences , Zhengzhou University , Henan , P. R. China Accepted author version posted online: 22 Oct 2013.Published online: 21 Nov 2013.

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Syntheses, Structures, and Characterization of Three New Complexes Constructed From Triazolyl N-Heterocyclic Ligand

Qinqin Yuan,¹ Ming Zhao,² Songhe Zhang,¹ Hongwei Hou,¹ Jinpeng Li,³ Shujun Zhu,¹ Xiaoli Gao,¹ Huan Sun,¹ Yaoting Fan,¹ and Junbiao Chang^{1,3}

¹Department of Chemistry, Zhengzhou University, Henan, P. R. China ²Experimental Management Centre, Zhongzhou University, Henan, P. R. China

³School of Pharmaceutical Sciences, Zhengzhou University, Henan, P. R. China

Treatment of triazolyl ligand 3-(3-oxyphenyl)-5-(pyrazine-2yl)-1,2,4-triazole (opt) with Cu(NO₃)₂·3H₂O, Co(NO₃)₂·3H₂O or NiCl₂·6H₂O resulted in three new complexes, [Cu(opt)₂] (1), [Co(opt)₂(H₂O)₂] (2), [Ni(opt)₂(H₂O)₂] (3). Single-crystal X-ray crystallographic analyses reveal that all complexes 1–3 present mononuclear structures. Interestingly, various $\pi \cdots \pi$ interactions and hydrogen bonds interactions are discovered and extend these mononuclear structures to 3-D supramolecular networks. Notably, complex 1 presents the cavity construction with the approximate channel diameter 11.835 Å. Furthermore, the thermal analyses results are in reasonable agreement with the crystal structure analyses of complexes 1–3.

Keywords cavity constructure, crystal structure, $\pi \cdots \pi$ interaction, synthesis

INTRODUCTION

In recent years, the rational design and preparation of metallosupramolecular complexes have attracted intense interest for their unfamiliar architectures and potential applications.^[1–6] Various novel supramolecular architectures have been successfully built by the rational combination of preselected organic ligands and elaborately choosing metal ions with definite coordination geometry.^[7,8] In this field, the preselected organic ligand, to a certain extent, is crucial and usually the first choice for designing novel coordination complexes since it can adjust the coordination mode, flexibility of the molecular backbone, configurational preference, type and topology of the products by coordinating directly to the metal centers.^[9] While in various organic ligands, the derivatives of triazole are excellent nitrogen-heterocyclic ligands and often used to construct complexes with various configurations.^[10-12] More importantly, their aromatic rings attract our interest because of their importance in crystal engineering, which may form strong π - π stacking interactions, and may lead to variable π - π interactions modes and architectures. These interactions have great importance influence on controlling the conformation of molecules,^[13] crystal packing,^[14] molecular assembly into an organized supramolecular network,^[15-17] and the structure of proteins and DNA.^[18] Based on the foregoing reasons and as an extension of this research, we utilized the triazolyl ligand 3-(3-oxyphenyl)-5-(pyrazine-2-yl)-1,2,4-triazole (opt) to react with metal ions and prepared three new Cu(II), Co(II) and Ni(II) complexes. Herein, the synthesis, crystal structures, and thermal properties of the three complexes were reported.

EXPERIMENTAL

General Details

The ligand opt and other staring materials were of reagent grade quality and were obtained from commercial sources without further purification. Carbon, hydrogen and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm⁻¹ region. UV-vis absorption spectra were recorded on a Unico UV-2102 PC spectrometer. TG-DSC measurements were performed by heating the samples from 20–780°C for 1, 20–650°C for 2 and 3 at a rate of 10°C/min in air on a NETZSCH STA 409PC differential thermal analyzer.

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Address correspondence to Jinpeng Li, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China. E-mail: ljp-zd@zzu.edu.cn

Preparation of [Cu(opt)₂] (1)

The DMF (2 mL) solution of ligand opt (2.4 mg, 0.01 mmol) was added dropwise to a methanol solution (4 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (4.8 mg, 0.02 mmol). The resulting mixture was kept at room temperature. Four days later, the light blue crystals suitable for X-ray diffraction were obtained from the resultant green solution. Yield: 43%. Anal. Calcd. for $C_{108}H_{72}Cu_{4.5}N_{45}O_9$: C, 53.33; H, 2.96; N, 25.93. Found C, 50.04; H, 3.47; N, 24.28%. IR(cm⁻¹, KBr): 3017 (s), 2698(w), 1589(s), 1438(s), 1425(s), 1358(m), 1313(w), 1231(m), 1205(m), 1186(w), 1145(m), 1041(m), 1018(w), 885(m), 745(w), 684(w), 419(w).

Preparation of $[Co(opt)_2(H_2O)_2]$ (2)

The DMF (2 mL) solution of ligand opt (7.2 mg, 0.03 mmol) was added dropwise to the H₂O (5 mL) solution of Co(NO₃)₂·3H₂O (11.6 mg, 0.04 mmol). Then the mixture was sealed in 18 mL Teflon-lined stainless steel container, which was heated to 150°C under autogenously pressure for four days. After slow cooling to room temperature with the rate 10°C/h, the angered rod-like crystals suitable for X-ray diffraction were obtained. Yield: 56%. Anal. Calcd. for C₂₄H₁₈CoN₁₀O₄: C, 50.58; H, 3.16; N, 24.59. Found: C, 50.41; H, 3.02; N, 24.49%. IR (cm⁻¹, KBr): 3398(s), 1595(m), 1530(w), 1460(s), 1352(w), 1228(s), 1136(w), 883(m), 749(m), 679(w), 425(w).

Preparation of $[Ni(opt)_2(H_2O)_2]$ (3)

The DMF (2 mL) solution of ligand opt (7.2 mg, 0.03 mmol) was added dropwise to a mixture of NiCl₂·6H₂O (7.1 mg, 0.03 mmol) and H₂O (6 mL). Then the mixture was sealed in an 18 mL Teflon-lined stainless steel container, which was heated to 130°C under autogenously pressure for three days. After slow cooling to room temperature with the rate 10°C/h, the green crystals suitable for X-ray diffraction were obtained. Yield: 61%. Anal. Calcd. for C₂₄H₁₈N₁₀NiO₄: C, 50.60; H, 3.16; N, 24.60. Found: C, 50.44; H, 3.01; N, 24.52%. IR (cm⁻¹,KBr): 3423(s), 1596(m), 1533(w), 1464(s), 1422(w), 1371(w), 1353(s), 1229(s), 1193(w), 1140(w), 1039(m), 884(s), 864(w), 750(w), 685(w), 524(w), 430(w).

X-Ray Crystallography

The diffraction intensity data of **1**, **2** and **3** were collected at room temperature on a Rigaku RAXIS-IV and SATURN-724 imaging plate area detector with graphite monochromated Mo-*K* α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and expanded with Fourier techniques. 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 observed reflections and variable parameters. All calculations were performed using the SHELX-97 crystallographic software package.^[19] Crystallographic parameters and structural refinement are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

RESULTS AND DISCUSSION

TRANSITIONAL METAL COMPLEXES

Structural Description of [Cu(opt)₂] (1)

The structure determination of 1 reveals this molecule crystallizes in the space group R-3. A perspective view of the molecular structure with atom labeling scheme is shown in Figure 1. The Cu(II) center is tetracoordinated with four nitrogen atoms from two opt ligands. The bond lengths of Cu-N vary from 1.924(4) to 2.041(4) Å, which are in good accordance with the reported Cu(II) complexes with N donors.^[20] The N(1)-Cu(1)-N(1)#1 and N(5)#1-Cu(1)-N(5) angles in 1 are 179.996(1) and 179.997(1), respectively, which is very close to 180° . The other bond angles around Cu(II) vary from 81.31(18) to 98.70(18), respectively. The two opt ligands link one Cu(II) atom to form a quadrangular constructure. It should be pointed out that there are affluent aromatic ring systems in 1, which may form various $\pi \cdots \pi$ stacking interactions. Analysis of the crystal packing of **1** revealed that an infinite 1-D layered supramolecular array (Figure 1) was formed by the head-to-tail π - π stacking interactions between any two adjacent triazole rings with the interplanar separation of 3.240 Å (center-to-center separation: 3.932 Å).^[11,21,22] While between any adjacent triazole and pyrazine rings, the π - π interactions with the inter-planar separation of 3.298 Å (center-to-center separation: 4.069 Å) is slightly weaker than that of two adjacent triazole rings. Additionally, the intermolecular O.H.N hydrogen bonds are also observed in 1. The N^{\cdots}O distance of the hydrogen bonds is 2.753(6) Å and the bond angle around O. H. N is 164.4°, which further stabilizes the crystal structure and lead to the cavity constructure with the approximate channel diameter 11.835 Å in 1 (Figure 2). These aforementioned weak interactions result in an infinite 3-D supramolecular network (Figure 2). It is noteworthy that, from the actual elemental and thermogravimetric analysis of complex 1, there should be some water molecules in the cavities of 1. However, we cannot find them from its crystal structure analyses. This is because the skeleton of **1** is of high symmetry and porous nature, which led to water molecules being disordered.

Structural Description of $[Co(opt)_2(H_2O)_2]$ (2) and $[Ni(opt)_2(H_2O)_2]$ (3)

The X-ray diffraction analysis reveals that both complexes **2** and **3** crystallize in the monoclinic space group P21/n and exhibit similar mononuclear structures. Herein, we only describe the structure of complex **2** in detail. The Co(II) ion in **2** is six-coordinated in a slightly distorted octahedron geometry, which is provided by four N donor atoms from four opt ligands and two oxygen atoms from two coordinated water molecules (Figure 3). The four N donor atoms occupy the equatorial plane and two oxygen atoms take up the apical positions, which result in a mononuclear constructure. The bond length of Co-O is 2.1276(7) Å and the Co-N lengths vary from 2.0610(9) Å to 2.1022(9) Å, which are comparable to those reported cobalt(II) complexes [Co(plbbm)Cl₂]_n [plbbm = 1,1-(1,3-propylene)bis-1*H*-benzimidazole],^[23]

TABLE 1Crystallographic data for complexes 1–3

	1	2	3
Formula	C ₁₀₈ H ₇₂ Cu _{4.5} N ₄₅ O ₉	C ₂₄ H ₁₈ CoN ₁₀ O ₄	C ₂₄ H ₁₈ N ₁₀ NiO ₄
fw	2430.08	569.41	569.19
Temp (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal syst	Hexagonal	Monoclinic	Monoclinic
Space group	R-3	P21/n	P21/n
a (Å)	36.151(4)	8.4249(4)	8.5138(3)
<i>b</i> (Å)	36.151(4)	7.347(4)	7.303(2)
c (Å)	5.3013(11)	18.526	18.319
α (°)	90	90	90
β (°)	90	94.10	93.58
γ (°)	120	90	90
$V(Å^3)$	6000.0(16)	1143.8(6)	1136.9(3)
Z	1	2	2
$D_{\rm c} (\rm g \cdot \rm cm^{-3})$	1.345	1.653	1.663
<i>F</i> (000)	2474	582	584
θ range for data collection(deg) collection(deg)	1.13-25.00	2.98-26.36	3.00-26.36
Reflections collected /unique	19215 / 2345	5101 / 2327	5023 / 2315
Data / restraints / params	2345 / 0 / 177	2327 / 0 / 180	2315 / 0 / 180
Goodness-of-fit on F^2	1.052	1.021	1.034
Final R_1^{a} , wR_2^{b}	0.0597, 0.1521	0.0396, 0.0857	0.0363, 0.0871

 ${}^{a}R1 = ||F_{o}| - |F_{c}||/|F_{o}|. {}^{b}wR2 = [w(|F_{o}^{2}| - |F_{c}^{2}|)^{2}/w|F_{o}^{2}|^{2}]^{1/2}. w = 1/[\sigma^{2}(F_{o})^{2} + 0.0297P^{2} + 27.5680P], \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3.$

 TABLE 2

 Selected bond lengths (Å) and angles (°) for complexes 1–3

Complex 1					
Cu(1)-N(1)	1.924(4)	Cu(1)-N(1)#1	1.924(4)	Cu(1)-N(5)#1	2.041(4)
Cu(1)-N(5)	2.041(4)	N(1)-Cu(1)-N(1)#1	179.996(1)	N(1)-Cu(1)-N(5)#1	98.69(18)
N(1)-Cu(1)-N(5)	81.31(18)	N(1)#1-Cu(1)-N(5)#1	81.31(18)	N(1)#1-Cu(1)-N(5)	98.70(18)
N(5)#1-Cu(1)-N(5)	179.997(1)	N(2)-N(1)-Cu(1)	137.4(3)		
Complex 2					
Co(1)-N(1)	2.100(2)	Co(1)-N(1)#1	2.0999(19)	Co(1)-O(3)#1	2.1276(17)
Co(1)-O(3)	2.1276(17)	Co(1)-N(4)#1	2.154(2)	N(1)-Co(1)-N(1)#1	180
N(1)-Co(1)-O(3)#1	91.38(8)	N(1)#1-Co(1)-O(3)#1	88.62(8)	N(1)-Co(1)-O(3)	88.62(8)
N(1)#1-Co(1)-O(3)	91.38(8)	O(3)#1-Co(1)-O(3)	180	N(1)-Co(1)-N(4)	77.40(8)
N(1)#1-Co(1)-N(4)	102.60(8)	O(3)#1-Co(1)-N(4)	87.44(8)	O(3)-Co(1)-N(4)	92.56(8)
O(3)-Co(1)-N(4)#1	87.44(8)	O(3)#1-Co(1)-N(4)#1	92.56(8)	N(4)-Co(1)-N(4)#1	180
Complex 3					
Ni(1)-N(1)#1	2.0610(9)	Ni(1)-N(1)	2.0610(9)	Ni(1)-N(4)	2.1022(9)
Ni(1)-N(4)#1	2.1022(9)	Ni(1)-O(4)#1	2.1231(16)	Ni(1)-O(4)	2.1231(16)
N(1)#1-Ni(1)-N(1)	180	N(1)-Ni(1)-N(4)	79.01(7)	N(1)#1-Ni(1)-N(4)	100.99(7)
N(1)-Ni(1)-N(4)#1	100.99(7)	O(4)#1-Ni(1)-O(4)	180	N(4)-Ni(1)-N(4)#1	180
N(1)-Ni(1)-O(4)#1	91.50(7)	N(1)-Ni(1)-O(4)	88.50(7)	N(4)#1-Ni(1)-O(4)	87.11(7)
N(1)#1-Ni(1)-N(4)#1	79.01(7)	N(1)-Ni(1)-O(4)#1	91.50(7)	N(4)#1-Ni(1)-O(4)#1	92.89(7)

Symmetry transformations used to generate equivalent atoms:

For 3: #1 - x + 1, -y + 1, -z + 1.

For 1: #1 - x + 1/3, -y + 2/3, -z + 5/3.

For **2**: #1 –x, –y + 2, –z.



FIG. 1. (a) Perspective view of $[Cu(opt)_2]$ (1) with atom-labeling scheme; (b) One-dimensional layered supramolecular network of complex 1. The dashed lines represent the $\pi \cdots \pi$ stacking interactions between two adjacent aromatic rings (color figure available online).

For 2 and 3, there are the same aromatic ring systems as that in 1, in which they form similar π - π stacking interactions. Figure 3 reveals that an infinite 2-D layer of 2 (3) was formed by the π - π stacking interactions between two adjacent triazole and pyrazine rings with the interplanar separations of 3.334 Å (2) and 3.340 Å (3) [center-to-center separations: 3.874 Å (2) and 3.964 Å (3)], two adjacent triazole and benzene rings



FIG. 2. Top: the cavity with the approximate channel diameter 11.835 Å forming by hydrogen bonds and $\pi \cdots \pi$ stacking interactions along *c* axis; Bottom: the space-filling representation of 3-D supramolecular network of [Cu(opt)₂] (1) (hydrogen atoms omitted for clarity) (color figure available online).



FIG. 3. (a) ORTEP view with atom labeling of the mononuclear fragment for complexes 2 and 3 (M = Co for 2 and M = Ni for 3); (b) two-dimensional layered supramolecular network of complexes 2 or 3. The dashed lines represent the π - π stacking interactions between two adjacent aromatic rings (color figure available online).

with the inter-planar separations of 3.3715 Å and 3.417 Å (3) [center-to-center separations: 3.673 Å (2) and 3.549 Å (3)]. While between two adjacent pyrazine and benzene rings, the inter-planar separations of π - π stacking interactions are 3.367 Å for 2 and 3.489 Å for 3 [center-to-center separation: 3.776 Å (2) and 4.000 Å (3)]. Moreover, the intermolecular O⁻⁻H⁻⁻O and O⁻⁻H⁻⁻N hydrogen bonds are also observed in complexes 2 and 3, which further stabilize their crystal structures and lead to a 3-D supramolecular network (Figure 4). The O⁻⁻O and O⁻⁻N distances of the hydrogen bonds are 2.852(2) Å, 2.863(3) Å for 2 and 2.872(3), 2.883(3) Å for 3, the bond angles around O⁻⁻H⁻⁻O and O⁻⁻H⁻⁻N are 164.7°, 164.3° for 2 and 165.6°, 159.6° for 3. These foregoing facts specify that the π - π interactions are very important in all three complexes, where they contribute significantly to molecular self-assembly processes.

UV-Vis Spectra

Figure 5 presents the UV-/Vis absorption spectra of the free ligand opt and its corresponding complexes 1-3 in 2 \times 10⁻⁵

mol/L mol·L⁻¹ DMF solution. The UV-Vis spectra of the free ligand opt exhibit two intense absorption peaks at 264 nm and 295 nm, respectively. The absorption peak at 264 nm can be ascribed to the π - π^* transition of the benzene rings, while the absorption peak at 295 nm should be assigned to the intraligand n- π^* transition.^[29-31] In the spectra of complexes 1-3, the dominant absorption peaks are 265 and 296 nm for 1, 267 and 296 nm for 2, and 271, 300 and 355 nm for 3, which is basically coincident with that of opt ligand and only these peaks are red-shifted to a certain degree. The foregoing two absorption peaks can also be ascribed to the intraligand π - π^* or n- π^* transitions. Additionally, the latter absorption peak at 296 nm (3 for 300 nm) undergoes a gradual fall (from 1 to 3) when compared with that of the free ligand, indicating the coordination of Cu(II), Co(II), and Ni(II) atoms with opt ligand. While for complex 3, a newly-produced moderate absorption peak is observed at 355 nm, which probably arises from the transition of the bonding electrons between metal ion and opt ligand, namely arises from the metal to ligand charge transfer transition.[32,33]



FIG. 4. Packing of 2 and 3 viewed along b axis, showing the hydrogen bonds, $\pi \cdots \pi$ stacking interactions and three-dimensional supramolecular networks of 2 and 3 (hydrogen atoms omitted for clarity) (color figure available online).



FIG. 5. The UV-Vis absorption spectra of opt ligand and its corresponding complexes 1, 2 and 3 in 2×10^{-5} mol·L⁻¹ DMF solution (color figure available online).

Thermogravimetric Analysis (TGA)

To characterize the thermal stability of the different selfassemblies constructed by the same ligands and different metals, the complexes 1, 2, and 3 were investigated by the TG-DSC techniques. As shown in Figure 6, the TG-DSC of 1 is determined in the range 20-780°C in the air. The TG curve of complex 1 exhibits two continuous weight loss stages in the ranges of 77-192°C and 332-657°C, corresponding to the decompositions of the water molecule and opt ligand. Finally, a plateau region is observed from 660 to 780°C. A black residue of CuO (obsvd. 13.96%, calcd. 13.80%) was remained. There are two weak endothermic peaks (329.6°C and 391.0°C) and one strong exothermic peak (540.6°C) on the DSC curve of 1. The thermal decomposition behavior of complex 2 is similar to that of 3. On the DSC curve of 2 (or 3), there are one big exothermic peaks at $511.4^{\circ}C(2)$ [$512.2^{\circ}C(3)$] and two weak endothermic peaks at 222.4°C and 452.5°C (2) [240.7°C (3)], respectively. The TG curves of complexes 2 and 3 both exhibit two continuous weight loss stages in the ranges of 194-230°C and 334-530°C (2) $[197-262^{\circ}C \text{ and } 404-534^{\circ}C \text{ (3)}]$ corresponding to the concomitant release of the coordination water molecule and the



FIG. 6. The thermal decomposition curves of $[Cu(opt)_2] \mathbf{1}$ (a), $[Co(opt)_2(H_2O)_2] \mathbf{2}$ (b), and $[Ni(opt)_2(H_2O)_2] \mathbf{3}$ (c).

decomposition of opt ligand. Finally, in complex **2**, a plateau region is observed from 530 to 650° C. A brown amorphous residue of CoO (observed 14.44%, calculated 13.16%) was remained. While in complex **3**, the plateau region is between 534 and 650° C, the decomposition process was completed at 650° C giving dark green nickel oxide (NiO) as the final decomposition product (obsvd. 13.60%, calcd. 13.12%).

SUPPLEMENTARY MATERIALS

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with CCDC numbers 922394–922396 for **1–3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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