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SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENT PROPERTIES OF TWO COMPLEXES BASED ON ISO-CYANURIC ACID

Xifeng Lu,[a,b] Jing Gao,[a,b] Ligang Gai,[c] Deliang Cui,[a,*] and Qilong Wang[b]

a State Key Lab of Crystal Materials, Shandong University, Jinan 250100, P. R. China
b School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China
c School of Chemical Engineering, Shandong Institute of Light Industry, Jinan 250100, P. R. China
∗Corresponding author. Tel./fax: +86-531-88361856
E-mail:cuidl@sdu.edu.cn.

Abstract – Two new complexes, $[Cu_2(C_3N_3O_3H_2)_4]\cdot H_2O$, I, and $[Zn(C_3N_3O_3H_2)_2(H_2O)_4]\cdot C_3N_3O_3H_3\cdot H_2O$, II, have been synthesized by the reactions of cyanuric chloride ($C_3N_3Cl_3$), melamine ($C_3N_6H_6$) with $CuCl_2\cdot 2H_2O$ and $ZnCl_2$, respectively, through hydrothermal route. They were characterized by single crystal diffraction, elemental analysis, thermalgravimetry analysis. Furthermore, the photoluminescent properties of both I and II were studied. In complex (I), the Cu(II) is two coordinated in a linear fashion by two nitrogen atoms. The Zn(II) atom in complex (II) is surrounded by two nitrogen atoms and four oxygen atoms to complete a six-coordinate environment. The combination of hydrogen bonds and π···π stacking interactions extends complex (I), (II) into three-dimension architectures.

INTRODUCTION

The field of crystal engineering is of great interest currently, for example, in the design of materials with desired physical and chemical properties. It has been known that hydrogen bonding[1,2] and π···π stacking[3,4] are important tools to generate supramolecular networks from simple building blocks, which have been used by chemists in the fields of self-assembly, host-guest chemistry and crystal engineering. The hydrogen bonds and π-interaction have attracted ever increasing attention over the past decade.[5,6] Melamine has three ring N atoms and three amine functionalities which can function both as hydrogen bond donors and acceptors and hence useful for the construction of supramolecular networks. So tremendous efforts have been devoted to the rational design and synthesis of their coordination complexes.[7,8]

1,3,5-Triazine derivatives have shown their great potential in the emerging area of material chemistry, both for their π-interaction abilities,[9] and for their aptitudes to be involved in intricate hydrogen-bond networks.[10] Sophisticated s-triazine derivatives can be easily prepared from the cheap, readily available cyanuric chloride,[11] which is definitely an excellent synthon for the straightforward preparation of highly structured multitopic molecules[12] and a crucial intermediate for the synthesis of a variety of organic compounds. The importance of melamine and cyanuric chloride prompts us to prepare complexes of transition-metal ions using them as coordination building unit by means of coordination and/or hydrogen bonds. In the present work, we report the synthesis of two types of coordination complexes of iso-cyanuric acid under the cooperation of cyanuric chloride and melamine, which self-assemble into a three-dimension structure by hydrogen bonding and π····π stacking.

RESULTS AND DISCUSSION

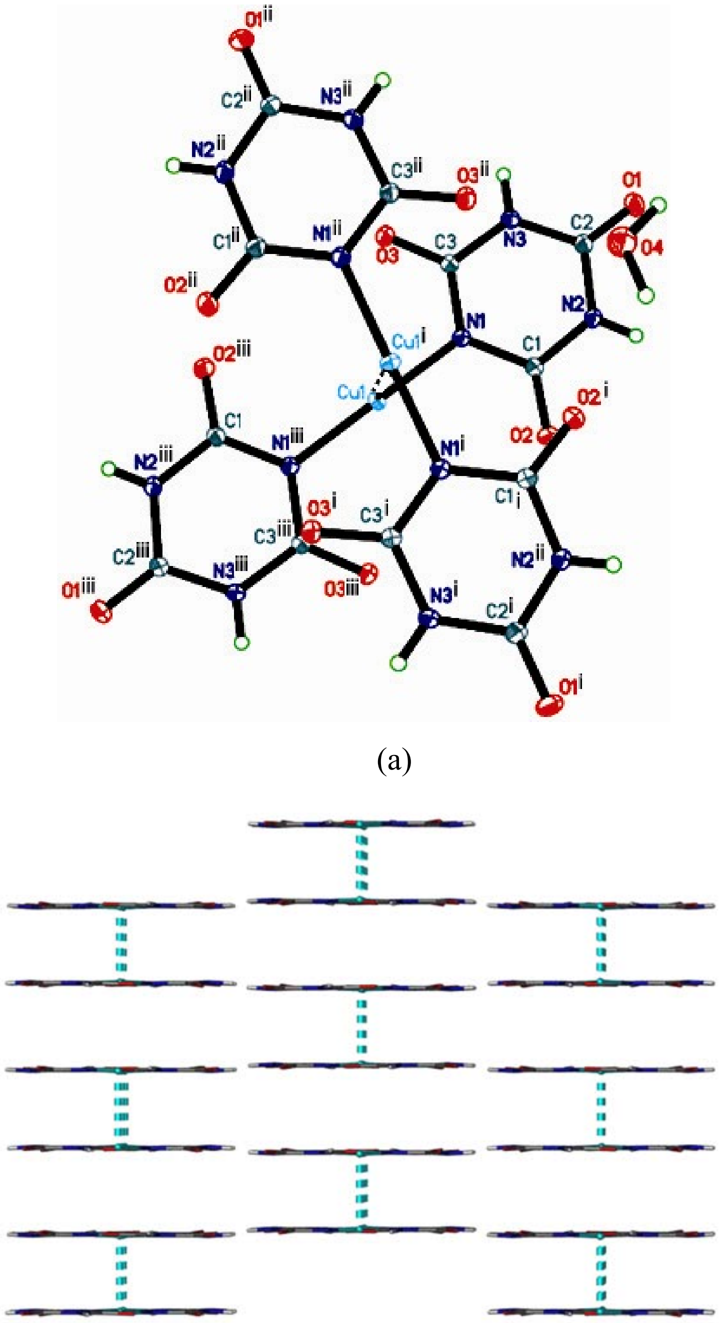
Crystal Structure descriptions

$[Cu_2(C_3N_3O_3H_2)_4]\cdot H_2O$ (I)

Single-crystal X-ray diffraction analysis indicates that complex (I) crystallizes in the orthorhombic space group of *Fddd* (No.70) with the formula $[Cu_2(C_3N_3O_3H_2)_4]\cdot H_2O$. As shown in Figure 1a, each unit contains two central copper ions and four iso-cyanuric acid ligands. Both copper ions are coordinated in a linear fashion by two nitrogen atoms from two different iso-cyanuric acid, with an angle N-Cu-N being 177.08(10)° and with the average Cu-N distance being 1.8898(18) Å. The nearest distance of Cu····Cu is 2.8850(14)Å, which is a little longer than the van der Waals contact distance 2.80 Å, illustrating the lack of direct metal-metal contact between Cu(II) ions. Cu-Cu weak interactions make up the unsupported dinuclear building block. It is noted two coordinated Cu(II) compounds are very rare. Compared to the four coordinated Cu(II) complex Diaqua-bis(cyanuric acid-N)-copper,[13] the Cu-N distance in I is shorter. This probably can be a consequence of two- coordination. Selected bond lengths and angles are shown in Table 2.

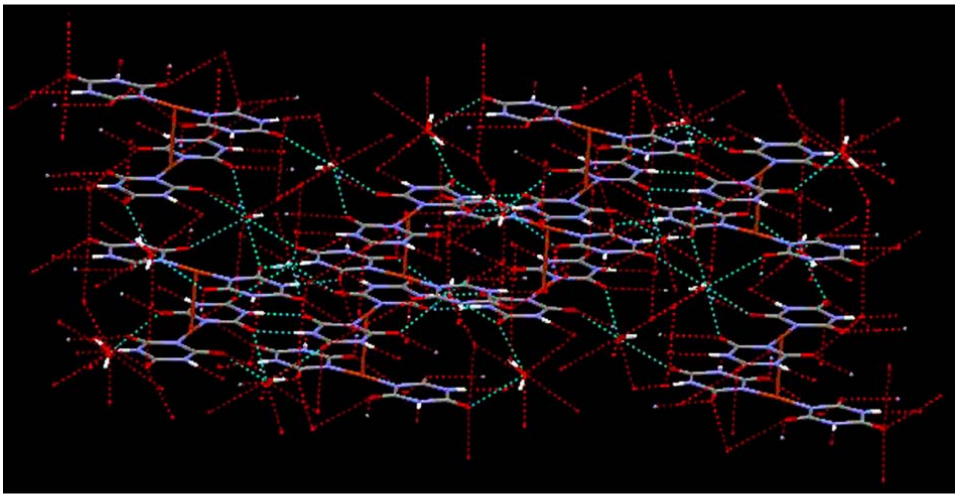
In each layer, there are dominant hydrogen bonds involving the iso-cyanuric acid ligand (Figure 1c). The donor-acceptor (O····H) distances around 1.925 Å and the angles about 179.24° (O···H-N) indicate that the hydrogen bond interactions are strong (Table 4). In addition, the water molecules also contribute significantly for the hydrogen bond interactions, which fill the layers by the hydrogen bonds with iso-cyanuric acid. The iso-cyanuric acid as both acceptors and donors for hydrogen bonds link further with each other to generate a two dimensional supramolecular network. Aside from hydrogen bonding, π····π interaction is another powerful organizing force in supramolecular assembly.[14] In I, two iso-cynauric acid in different layers are involved in an offset π····π stacking (along the *c* axis) with a perpendicular distance of 2.88 Å between the iso-cyanuric acid rings.

Hydrogen-bonds and π····π interactions result the complex a three-dimensional supramolecular architecture (Figure 1b), causing the complex to have remarkable thermal stability.



(a)

(b)



(c)

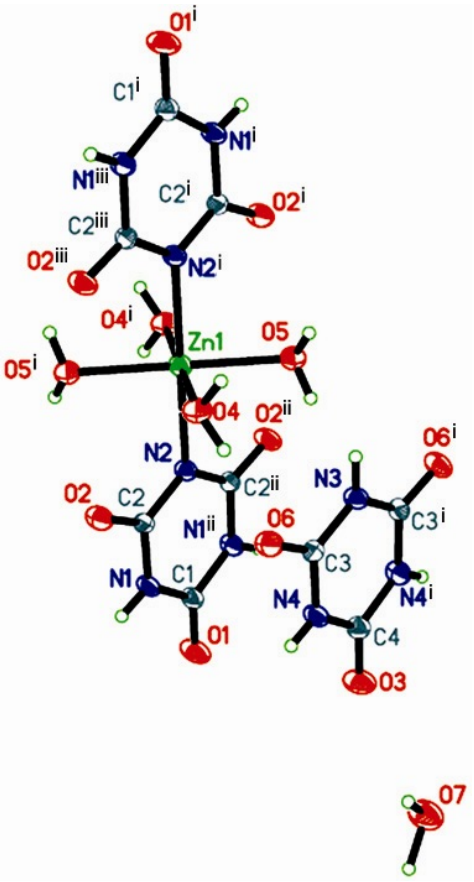
Figure 1. (a) ORTEP plot of coordination environments of Cu(II) in I. Thermal ellipsoids are given at 50% probability. Symmetry codes: (i) 5/2-x, 1/2-y, z; (ii) x, 1/2-y, 1/2-z; (iii) 5/2-x, y, 1/2-z. (b) Packing diagram of I (along the c axis) showing the 3D supramolecular structure. Hydrogen atoms and water molecules are omitted for clarity. (c) Hydrogen bonds (Dashed lines).

$[Zn(C_3N_3O_3H_2)_2(H_2O)_4]\cdot C_3N_3O_3H_3\cdot H_2O$ (II)

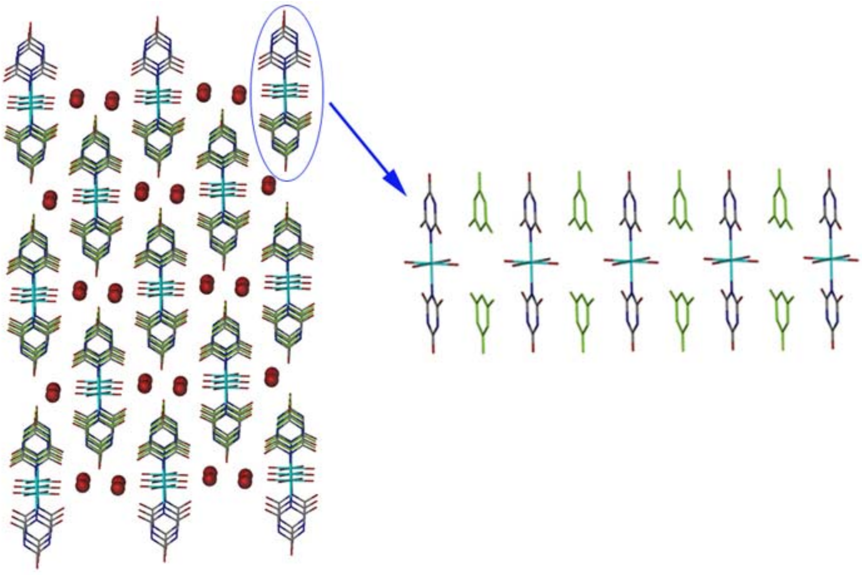
Complex (II) crystallizes in the monoclinic, space group C2/m (No.12) with the formula $[Zn(C_3N_3O_3H_2)_2(H_2O)_4]\cdot C_3N_3O_3H_3\cdot H_2O$. Figure 2a shows the local coordination of the zinc center in II. The Zn(II) ion is coordinated by two nitrogen atoms of the cyanuric acid ligands (Zn-N = 2.2093(19) Å), and four oxygen atoms of coordinated water molecules. The bond length of Zn-O ranges from 2.1382(19) Å to 2.1524(19) Å. Selected bond lengths and angles are shown in Table 3.

Three kinds of hydrogen bonds are observed in II (Figure 2c): a) hydrogen bonds between uncoordinated cyanuric acid, which make them form one-dimensional polymeric chain along *a* axis; b) hydrogen bonds between coordinated cyanuric acid oxygen atoms and the free water molecules; and c) hydrogen bonds between coordinated cyanuric acid, which make them 1D chain structure. Two types of 1D chain structure form layered structure. Table 4 lists the bond lengths and angles.

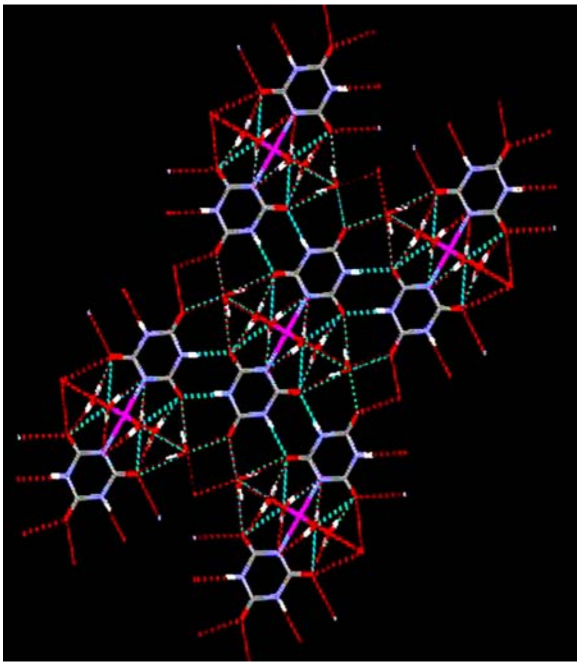
A π····π stacking interaction is also evident, which is shown in Figure 2b. The rings of coordinated iso-cyanuric acid and free cyanuric acid stack on top of each other (the arrow denotes), along the *c* axis with a face-to face distance of 3.415 - 3.502 Å. The hydrogen bonds and π····π interactions make them extend to 3D supermolecular structure.


O1^{i}
C1^{i}
N1^{i}
N1^{iii}
C2^{i}
O2^{i}
C2^{iii}
O2^{iii}
N2^{i}
O4^{i}
Zn1
O5
O5^{i}
O4
O2^{ii}
N2
C2^{ii}
O6^{i}
N3
O2
C2
N1^{ii}
O6
C3^{i}
C3
N1
C1
N4
N4^{i}
C4
O1
O3
O7

(a)



(b)



(c)

Figure 2. (a) ORTEP plot of coordination environments of Zn(II) in II. Thermal ellipsoids are given at 50% probability. Symmetry codes: (i) –x, -y, -z; (ii) –x, y, z; (iii) x, -y, z; (iv) –x, y, 1-z. Hydrogen atoms are omitted for clarity. (b) Packing diagram (along the *c* axis) of II showing the 3D supramolecular structure. Red balls denote water molecules. (c) Hydrogen bonds (Dashed lines).

Thermal properties

Thermal gravimetric analysis (TGA) for complex (I) and (II) was carried out in a air stream (100 mL/min) at a heating rate of 10 °C/min. As shown in Figure 3 I, almost no weight loss occurs until 330 °C, indicating good thermal stability. An abrupt weight loss of 75.89 % occurs in the temperature range of 330 - 419 °C and 424 - 463 °C is due to the loss cyanuric acid ligands per formula unit (Calcd. 77.93 %). A stable residue is formed up to 466 °C. The TGA curve shows that II is stable up to 113 °C. A total weight loss of 12.69 % occurred in the temperature range 113 - 286 °C, mainly corresponding to the removal of the four coordinated water molecules per formula unit (Calcd. 13.33 %). The abrupt weight loss of 48.50 % occurs between the temperature of 306 - 356 °C, which is attributed to the removal of the two cyanuric acid ligands (Calcd. 47.37 %). A appeasement weight loss of 24.62 % occurred in the temperature range 358 - 567 °C, consistent with the removal of cyanuric acid molecules (Calcd. 23.87 %). It is noted that the high thermal stability of the two complexes can be indicative of the fact that the lattice water is strongly H-bonded and hence removed at a very high temperature. The stable residue of them are tentatively assigned to the formation of CuO and ZnO.

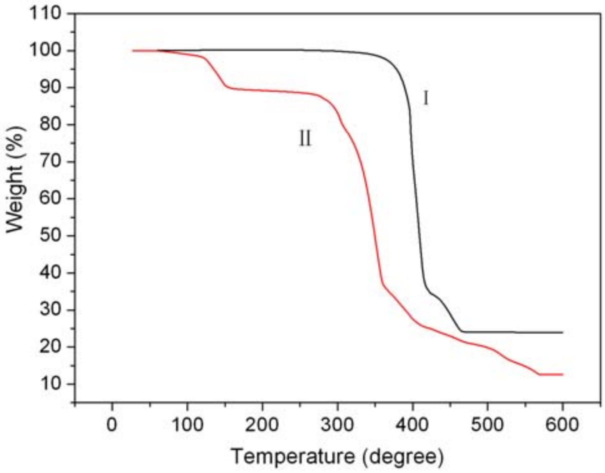


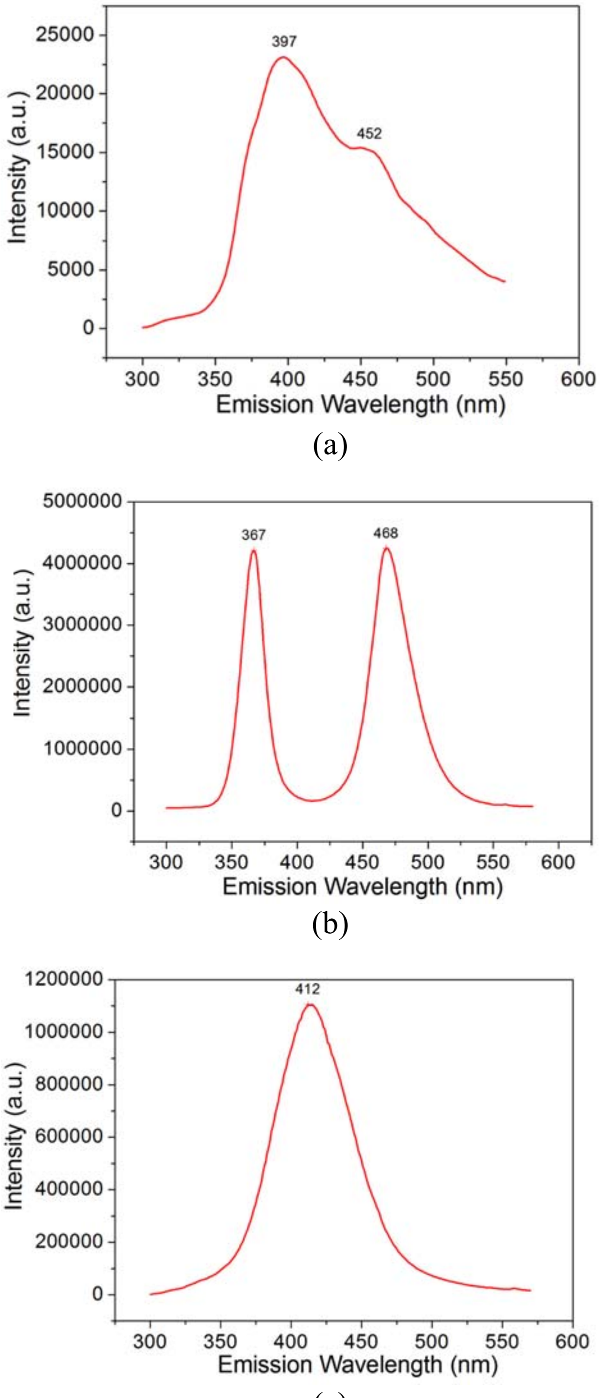
Figure 3. TGA curves of I and II.

Photoluminescent properties

The photoluminescent properties of complex (I) and (II) in the solid state at room temperature have also been studied (Figure 4). Upon excited at 290 nm, complex (I) shows intense photoluminescence centered at 367 nm and 468 nm; complex (II) exhibits an intense emission band with emission maxima at 412 nm. In order to get to know the nature of photoluminescent mechanism, as shown in the Figure 4a, photoluminescence measurement of the ligand was carried out. The spectrum shows a main peak at 397 nm and a shoulder at about 452 nm, indicating that it is also photoluminescent.

Compared to the ligand emission, very intense emission peaks are observed for I (Figure 4b), which is red-shifted to 468 nm and blue-shifted to 367 nm. Possible assignment for emission phenomena of I is intraligand transitions (ILCT). In addition, low-energy LMCT and high-energy MLCT transitions can also mix with intraligand transitions, which add more complexity to the assignment. Complex (II) indicates a red shift ($\Delta\lambda$ = 15 nm) in comparison with that 397 nm of the free iso-cyanuric acid ligand (Figure 4c). The emission band is tentatively assigned to intraligand charge transfer (ITCT) and ligand-to-metal charge transfer (LMCT).

The emission intensity of them is significantly higher than that of the free ligand, which may be attributed to the influence of coordination linkage, π-π interactions and hydrogen bonding[15-17] resulting in the nonradiative decay of intraligand excited states. The two complexes may be used as potential materials for blue-light-emitting device, providing a new entry to the design of advanced emissive materials.



(a)

(b)

(c)

Figure 4. A room-temperature PL emission spectrum of a) ligand excitated b) complex (I), and c) complex (II) at 290 nm.

CONCLUSION

In summary, the present study shows that two new complexes by the combination of coordination bonds, hydrogen bonds and π-π interactions via hydrothermal method can be obtained. More important, this may provide researchers an opportunity to the rational design and preparation of other coordination compounds of iso-cyanuric acid.

EXPERIMENTAL

General

All the starting materials were purchased commercially as reagent grade and used without further purification. FTIR spectra were recorded on a Nicolet NEXUS-670 infrared spectrometer using KBr pellets. Elemental analyses (C, H, and N) were measured with an Elemental Vario III elemental analyzer. Thermalgravimetry analyses were performed on SDTQ 600 Instrument. Fluorescence spectra were measured at room temperature on an Edinburgh FLS 920 fluorescent spectrometer.

Synthesis of the complexes

In a typical synthesis of I**,** a mixture of $C_3N_3Cl_3$ (1.91 g, 0.01 mol), $C_3N_6H_6$ (1.30 g, 0.01 mol), $CuCl_2{\cdot}2H_2O$ (1.77 g, 0.01 mol), and distilled water (95 mL) was sealed in a 135 mL Teflon-lined stainless steel autoclave, which was then heated to 250 °C for 8 h. After cooling the sample to room temperature, white platelike crystals of complex (I) were obtained with a yield of 65 %. A similar procedure was carried out using $ZnCl_2$ (1.42 g, 0.01 mol) in place of $CuCl_2{\cdot}2H_2O$, resulting in crystals of complex (II) with rodlike morphology in 70 % yield. The crystals were filtered and washed thoroughly with de-ionized water. Elemental microanalysis showed (Found/Calcd, wt %): C, 21.92/21.98; H, 1.54/1.61; N, 25.57/25.51 for I (MW = 657.44); and C, 19.99/19.94; H, 3.18/3.40; N, 23.32/23.22 for II (MW = 540.74). IR spectrum (cm^{-1}): 3480(w), 3250(w), 2978(m), 2828(m), 1789(w), 1710(m), 1651(m), 1608(m), 1476(s), 1433(s), 1389(s), 857(s), 769(s) for I; 3450(w), 2833(m), 1735(m), 1697(w), 1625(m), 1477(s), 1392(s), 826(s), 776(s) for II.

X-Ray crystallograhpy

Suitable single crystals of each complex were carefully selected under a microscope and glued to a thin glass fiber with silicone grease. Data collections were performed on a Bruker APEX2 CCD diffractometer with graphite monochromated X-ray source (Mo Kα radiation, $\lambda = 0.71069$ Å) at 293(2) K.

The structures were solved by direct methods and all calculations were performed using the SHELXL package,[18] and refined by full matrix least squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms belonging to the iso-cyanuric acid were found in the difference electron density map and refined isotropically, and the other H atoms were generated geometrically and treated as riding model. The crystallographic data are summarized in Table 1, while selected bond lengths and bond angles of I and II, and selected hydrogen-bond interaction observed in I and II are listed in Tables 2, 3 and 4, respectively.

Table 1. Crystal Data and Structure Refinement Parameters for I and II

	I	II
Chemical formula	$C_{12}H_{10}N_{12}O_{13}Cu_2$	$C_9H_{17}N_9O_{14}Zn$
Formula weight	657.44	540.74
Crystal size (mm)	0.265× 0.296× 0.377	0.175× 0.184× 0.466
Crystal system	orthorhombic	monoclinic
Space group	*Fddd* (No.70)	*C2/m* (No.12)
T (K)	293(2)	293(2)
a (Å)	9.362(5)	11.833(5)
b (Å)	12.585(5)	16.115(5)
c (Å)	36.724(5)	7.004(5)
α (deg)	90.000(5)	90.000(5)
β (deg)	90.000(5)	116.274(5)
γ (deg)	90.000(5)	90.000(5)
V (Å^3)	4327(3)	1197.6(11)
Z	8	4
ρ_{calc} (g /cm^{-3})	1.774	1.794
$\lambda_{\text{MoK}\alpha}$ (Å)	0.71069	0.71069
μ (mm^{-1})	2.980	2.086
F(000)	2280	648
θ Range (deg)	2.22 - 27.48	2.30 - 27.51
Index ranges	$-8 \leq h \leq 12$, $-16 \leq k \leq 13$, $-47 \leq l \leq 38$	$-15 \leq h \leq 14$, $-20 \leq k \leq 20$, $-9 \leq l \leq 8$
Reflns collected /unique	4833/1240 [R(int) = 0.0181]	4714/1418 [R(int) = 0.0146]
completeness to θ =	27.48°, 99.8 (%)	27.51°, 99.6 (%)
Refinement method	Full-matrix least squares	Full-matrix least squares
Data / restraints / params	1240 / 0 / 101	1418 / 0 / 128
GOF on F^2	1.192	0.931
Final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0320,	R1 = 0.0298,

	wR2 = 0.0801	wR2 = 0.0958
R indices (all data)^b	R1 = 0.0338,	R1 = 0.0303,
	wR2 = 0.0813	wR2 = 0.0968
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (eÅ^{-3})	0.585, -0.585	0.714, -0.815

$^aR_1 = \sum||F_0|-|F_c||/\sum|F_0|$, $^bwR_2 = [\sum w(F_0^2-F_c^2)^2/w(F_0^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_0)^2+(aP)^2 + bP]$, where $a = 0.0385$, $b = 15.78$ for (I) and $a = 0.1000$, $b = 0.00$ for (II)

Table 2. Selected Bond Distances and Bond Angles for I

Moiety	Distance (Å)
C(1)-O(2)	1.231(3)
C(1)-N(1)	1.367(3)
C(1)-N(2)	1.381(3)
C(2)-O(1)	1.217(3)
C(2)-N(2)	1.363(3)
C(2)-N(3)	1.368(2)
C(3)-O(3)	1.242(3)
C(3)-N(1)	1.355(3)
C(3)-N(3)	1.378(3)
Cu(1)-N(1)	1.8898(18)
Cu(1)-N(1)^{i}	1.8898(18)
Cu(1)-Cu(1)^{ii}	2.8850(14)
N(2)-H(3)	0.85(3)
N(3)-H(1)	0.86(3)
O(4)-H(4)	1.0596
Moiety	Angle (deg)
O(2)-C(1)-N(1)	122.20(18)
O(2)-C(1)-N(2)	119.60(18)
N(1)-C(1)-N(2)	118.18(18)
O(1)-C(2)-N(2)	123.4(2)
O(1)-C(2)-N(3)	122.6(2)
N(2)-C(2)-N(3)	114.01(18)
O(3)-C(3)-N(1)	121.86(18)
O(3)-C(3)-N(3)	119.14(19)

N(1)-C(3)-N(3)	118.99(17)
N(1)-Cu(1)-N(1)^{i}	177.08(10)
N(1)-Cu(1)-Cu(1)^{ii}	91.46(5)
N(1)^{i}-Cu(1)-Cu(1)^{ii}	91.46(5)
C(3)-N(1)-C(1)	120.01(17)
C(3)-N(1)-Cu(1)	119.48(13)
C(1)-N(1)-Cu(1)	120.50(14)
C(2)-N(2)-C(1)	124.58(18)
C(2)-N(2)-H(3)	117.4(19)
C(1)-N(2)-H(3)	117.8(19)
C(2)-N(3)-C(3)	124.12(18)
C(2)-N(3)-H(1)	115.0(19)
C(3)-N(3)-H(1)	121(2)

Symmetry codes: (i) -x+9/4, y, -z+1/4; (ii) -x+9/4, -y+1/4, z.

Table 3. Selected Bond Distances and Bond Angles for II

Moiety	Distance (Å)
Zn(1)-O(4)^{i}	2.1382(19)
Zn(1)-O(4)	2.1382(19)
Zn(1)-O(5)^{i}	2.1524(19)
Zn(1)-O(5)	2.1524(19)
Zn(1)-N(2)^{i}	2.2093(19)
Zn(1)-N(2)	2.2093(19)
O(1)-C(1)	1.229(3)
O(6)-C(3)	1.2406(19)
O(2)-C(2)	1.2319(19)
O(3)-C(4)	1.224(3)
C(3)-N(3)	1.3511(18)
C(3)-N(4)	1.385(2)
N(1)-C(1)	1.3596(17)
N(1)-C(2)	1.390(2)
N(4)-C(4)	1.3677(18)

N(3)-C(3)^{ii}	1.3511(18)
C(4)-N(4)^{ii}	1.3677(18)
C(2)-N(2)	1.3650(17)
N(2)-C(2)^{iii}	1.3650(17)
C(1)-N(1)^{iii}	1.3596(17)

Moiety	Angle (deg)
O(4)$^{i-}$Zn(1)-O(4)	180.00(15)
O(4)^{i}-Zn(1)-O(5)^{i}	84.74(8)
O(4)-Zn(1)-O(5)^{i}	95.26(8)
O(4)^{i}-Zn(1)-O(5)	95.26(8)
O(4)-Zn(1)-O(5)	84.74(8)
O(5)^{i}-Zn(1)-O(5)	180.00(6)
O(4)^{i}-Zn(1)-N(2)^{i}	90.000(7)
O(4)-Zn(1)-N(2)^{i}	90.000(7)
O(5)^{i}-Zn(1)-N(2)^{i}	90.000(4)
O(5)-Zn(1)-N(2)^{i}	90.000(4)
O(4)^{i}-Zn(1)-N(2)	90.000(7)
O(4)-Zn(1)-N(2)	90.000(7)
O(5)^{i}-Zn(1)-N(2)	90.000(4)
O(5)-Zn(1)-N(2)	90.000(4)
N(2)^{i}-Zn(1)-N(2)	180.0
O(6)-C(3)-N(3)	122.47(16)
O(6)-C(3)-N(4)	117.95(13)
N(3)-C(3)-N(4)	119.59(14)
C(1)-N(1)-C(2)	124.26(13)
C(4)-N(4)-C(3)	123.55(14)
C(3)-N(3)-C(3)^{ii}	119.38(19)
O(3)-C(4)-N(4)^{ii}	122.84(10)
O(3)-C(4)-N(4)	122.84(10)
N(4)^{ii}-C(4)-N(4)	114.3(2)
O(2)-C(2)-N(2)	123.48(15)
O(2)-C(2)-N(1)	117.27(13)
N(2)-C(2)-N(1)	119.24(13)

C(2)-N(2)-C(2)^{iii}	118.78(19)
C(2)-N(2)-Zn(1)	120.61(9)
C(2)^{iii}-N(2)-Zn(1)	120.61(9)
O(1)-C(1)-N(1)	122.89(9)
O(1)-C(1)-N(1)^{iii}	122.89(9)
N(1)-C(1)-N(1)^{iii}	114.21(19)

Symmetry codes: (i) -x, -y, -z; (ii) -x, y, -z+1; (iii) -x, y, -z.

Table 4. Selected Hydrogen-Bond Interaction Observed in I and II

D-H	d(D-H) (Å)	d(H···A) (Å)	<DHA (deg)	d(D···A) (Å)	A
Compound I					
N3-H1	0.862	1.925	179.24	2.787	O3^{i}
N2-H3	0.851	1.966	174.71	2.815	O2^{ii}
O4-H4	1.060	1.963	153.25	2.948	O1^{iii}
Compound II					
N3-H4	0.860	2.325	127.54	2.929	O5^{i}
N3-H4	0.860	2.325	127.54	2.929	O5^{ii}
N4-H6	0.767	2.067	174.14	2.832	O6^{iii}
O4-H7	0.826	1.970	169.07	2.786	O6^{iv}
N1-H8	0.840	2.039	171.50	2.872	O2^{v}
O5-H9	0.907	2.028	172.39	2.929	N3^{vi}
O7-H16	1.128	2.050	130.22	2.909	O2^{vii}
O7-H16	1.128	2.350	114.44	2.998	O5^{viii}

Symmetry codes in I: (i) -x-3/4, y, -z+1/4; (ii) -x, -y, -z; (iii) x+3/2, y+1/2, z. Symmetry codes in II: (i) x, y-1, z-1;(ii) -x+2, -y+1, -z+2;(iii) -x+5/2, -y+1/2, -z+1;(iv) x, y+1, z+1 ;(v) -x+5/2, -y+5/2, -z+2;vi -x+2, -y+1, -z+2;(vii) -x+3/2, -y+3/2, -z+2;(viii) x-1/2, y-1/2, z.

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