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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Syntheses, Crystal Structures and Thermal Decomposition Kinetics of Ni(II) and Cu(II) Complexes with dpa and dca: [Ni(dpa)₂(dca)₂] and [Cu(dpa)₂(dca)₂] (dpa=2, 2'-Dipyridylamine, dca=Sodium Dicyanamide) Ligands

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Syntheses, Crystal Structures and Thermal Decomposition Kinetics of Ni(II) and Cu(II) Complexes with dpa and dca: [Ni(dpa)₂(dca)₂] and [Cu(dpa)₂(dca)₂] (dpa = 2, 2'-Dipyridylamine, dca = Sodium Dicyanamide) Ligands

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The syntheses, crystal structures, luminescence properties and thermal decomposition kinetics of Ni(II) and Cu(II) complexes with dpa and dca, [Ni(dpa)₂ (dca)₂] (I) and [Cu(dpa)₂(dca)₂] (II) (dpa = 2, 2'-dipyridylamine, dca = sodium dicyanamide) are described. I crystallizes in Monoclinic cells with c2c space groups; the center metal ion Ni^{II} lies in a distorted octahedron environment, and the endmost nitrogen atom of dca with a "V" model coordinates to Ni^{II}. Though the chemical formula of II is similar to I, II crystallizes in triclinic cells with a Pī space group. The center Cu^{II} ion has an octahedral-coordinated environment.

Keywords synthesis, crystal structure, fluorescence property, non-isothermal kinetics of decomposition

INTRODUCTION

Recently, many researchers are focusing their attention on the construction of supramolecular architectures organized through coordinate covalent bonding or hydrogen bonding and π - π stacking interactions^[1] in organic-inorganic hybrid molecules because of potential applications as functional materials.^[2] Bidentate ligands containing pyridine units, especially, have attracted much attention.^[3] 2,2'-Dipyridylamine (dpa) as an

aromatic amine has the ability both to form a hydrogen bond network by active amine hydrogens (-NH-) and to show π - π interactions through pyridine planes. As far as our knowledge goes, many metal complexes with dpa are reported, including elements of metal, namely Co(II), Ni(II), Zn(II),^[4] Pt(II),^[5] Pd(II),^[6] Re(I),^[7] Ru(II),^[8] Au(I), Ag(I),^[9] Fe(II),^[10] Mn(II),^[11] Cu(II).^[12] In this work, we have reported the syntheses, crystal structures, fluorescence and thermal analysis properties of [Ni(dpa)₂(dca)₂] (I) and [Cu(dpa)₂(dca)₂] (II). Based on the result of thermal analysis, the kinetic parameters for the thermal decomposition of I and II have been calculated by the OFW method.

EXPERIMENTAL

Materials and Physical Measurements

The 2,2'-dipyridylamine, sodium dicyanamide and other chemicals employed (Zhengzhou Chemical Reagent Company) were commercial products and used without further purification.

Crystal structure was measured on a Rigaku-Raxis-IV X-ray diffractometer. Thermal analysis was measured on NETZSCH TG209 instrument. The IR spectrum was recorded on a Nicolet IR-470 spectrometer using KBr pellets in the range of $4000-400 \text{ cm}^{-1}$. Liquid fluorescence measurements were made with Hitachi F-4500 spectrophotometer at room temperature.

Preparation of the Complexes

Synthesis of [Ni(dpa)₂(dca)₂] (I)

10 mL acetonitrile solution containing 0.034 g (0.2 mmol) of dpa was added to the solution of 0.0242 g (0.1 mmol) of NiSO₄ \cdot 6H₂O in methanol (10 mL) and was stirred. The solution of 0.0178 g (0.2 mmol) NaN(CN)₂ in acetonitrile

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(10 mL) was added dropwise to the above-mentioned solution, again while stirring. The mixture was refluxed for 30 min, cooled to room temperature, and filtered. The filtrate was allowed to stand evaporation at the ambient temperature. The amethyst crystals of I were obtained after 2 months with the yields of 68%. IR (KBr, cm⁻¹): v(N-H) 3444 m; v(C=N) 1644 s, 1477 s; v(C=C) 1530 s, 1587 s; $v(N(CN)_2^-)$ 2165 m.

Synthesis of $[Cu(dpa)_2(dca)_2]$ (**II**)

Except for replacing 10 ml acetonitrile solution containing 0.0120 g (0.1 mmol) of Cu(CH₃COO)₂ · H₂O, the synthesis of **II** is similar to the procedure of **I**. The grass-green crystals of [Cu(dpa)₂(dca)₂] were obtained after 3 months with the yields of 62%. IR (KBr, cm⁻¹): v(N-H) 3429 m; v(C=N)1647 s, 1477 s; v(C=C) 1530 m, 1587 m; v(N(CN)₂⁻) 2135 s, 2238 m.

X-ray Crystallographic Analyses

An amethyst prismatic single crystal of I (0.20 mm \times $0.18 \text{ mm} \times 0.17 \text{ mm}$) and a grass-green prismatic single crystal of II (0.20 mm \times 0.18 mm \times 0.17 mm) were mounted on a Rigaku-Raxis-IV X-ray diffractometer using graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 291(2) K. 3880 reflections were measured over the ranges $1.90^{\circ} \le 2\theta \le 24.99^{\circ}, -10 \le h \le 8, -8 \le k \le 16, -25 \le 100$ $1 \le 25$, yielding 2185 unique reflections for **I**. 1793 reflections were measured over the ranges $2.24^{\circ} < 2\theta < 25.00^{\circ}$, $-8 \le h \le 8, -10 \le k \le 0, -11 \le l \le 10$, all of which being unique for II. The raw data were corrected and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full matrix least-squares calculations on F^2 were applied to the final refinement. The refinement converged at $R_1 = 0.0369$ and $wR_2 = 0.0895$ values for reflections with $I > 2\sigma(I)$ for **I**, and $R_1 = 0.1019$ and $wR_2 = 0.2648$ values for reflections with $I > 2\sigma(I)$ for **II**. The crystal data and data collection parameters of I and II are summarized in Table 1. Full atomic data are available as files in CIF format deposited with the Cambridge Crystallographic Data Center (CCDC 269645 and CCDC 250102, respectively).

Thermal Analysis

Thermal decomposition experiments in nitrogen atmosphere with the flow rate of 20 mL min⁻¹ were carried out using a NETZSCH TG 209 instrument. In these experiments the complexes I and II were pre-triturated. The employed heating rate for thermal decomposition was $10 \,^{\circ}\text{C} \cdot \text{min}^{-1}$, and the rates for kinetic analysis of I and II were 10, 20, $25 \,^{\circ}\text{C} \cdot \text{min}^{-1}$ and 15, 20, $30 \,^{\circ}\text{C} \cdot \text{min}^{-1}$ respectively.

RESULTS AND DISCUSSION

Structural Description of the Complexes I and II

Complex I crystallizes in a monocline cell with the c2c space group. Though the chemical formula of II is similar to

 TABLE 1

 Crystallographic data for complexes I and II

	111	II2
Empirical formula	C ₂₄ H ₁₈ N ₁₂ Ni	C ₂₄ H ₁₈ Cu N ₁₂
Formula weight	533.21	538.04
Crystal system	Monoclinic	Triclinic
Space group	C2C	Pī
Crystal size (mm)	$0.20 \times$	$0.20 \times$
	0.18×0.17	0.18×0.17
Temperature(K)	291.2	291.2
a/Å	8.6627(17)	7.5188(15)
b/Å	13.746(3)	8.6084(17)
c/Å	21.463(4)	9.5067(19)
$\alpha/^{\circ}$	90	72.86(3)
$\beta/^{\circ}$	94.23(3)	88.12(3)
$\gamma/^{\circ}$	90	80.01(3)
$V/Å^3$	2548.9(9)	579.0(2)
Z	4	1
$D_c/g \cdot cm^{-3}$	1.390	1.543
Reflens collected	3880/	1793/
	2185[R(int) =	1793[R(int)
	0.0285]	=0.0000]
Data/restraints	2185/0/173	1793/0/174
R1, wR2[I > 2σ (I)]	0.0369, 0.0895	0.1019, 0.2648
R1, wR2(all data)	0.0424, 0.0923	0.1106, 0.2778
Good of fit on F ²	1.062	1.181
$\Delta ho_{ m min,}\Delta ho_{ m max}/{ m e}~{ m \AA}^{-3}$	0.8761, 0.8565	0.8504, 0.8274

that of **I**, **II** crystallizes in a triclinic cell with the $P\bar{1}$ space group. Figures 1 and 2 show the ORTEP drawing and 2D network formed by the hydrogen bonds for **I**. Figures 3 and 4 show the ORTEP diagram, essentially a 1D double-chain helix



FIG. 1. X-ray crystal structure of **I** showing the structure unit (H atoms are not shown which have neither part nor lot in forming hydrogen bonding).



FIG. 2. Two-dimensional reticulate structure of the I by hydrongen bonding.

structure via hydrogen bonding for **II**. Selected bond distances and angles relevant to both the Ni coordination spheres for **I** and the Cu coordination spheres for **II** are given in Tables 2 and 3. The significant hydrogen bond parameters are shown in Table 4.

In **I**, the Ni^{II} atom was coordinated with six nitrogen atoms from two dpa and two dca in a distorted octahedron environment (shown in Figure 1), four N atoms (N1A, N3A, N4, N3) respectively come from one dca unit and two dpa units lay in the equatorial plane (mean deviation from plane is 0.0111 Å). One dca and one dpa respectively provided one N atom that occupied the trans axial sites (N4A, N1). All the six Ni-N bond lengths lie within a close range [2.0933(19)-2.123(2) Å]. These values are very similar to dpa complexes with Ni-N systems.^[13] The axial bond angle [N1-Ni1-N4A] is 175.828°, making it almost linear. The endmost N atom of the two dca ligands compound with Ni(II) in the form of



FIG. 3. X-ray crystal structure of **II** showing the structure unit (pyridine rings of hydration not shown).



FIG. 4. 1D double-chain helix structure by hydrogen bond in II.

"V," the center bond angle [C11-N5-C12] is 123.63°. The joined pyridine rings via the NH group are not planar, involving two dihedral angles (N1, C1 \rightarrow C5 and N3, C6 \rightarrow C10; N1A, C1A \rightarrow C5A and N3A, C6A \rightarrow C10A) of 26.2°, which are similar to other Ni(II) complex formats.^[13] There are two types of hydrogen bonds (shown in Figure 2) in the solid structure of I, one is the imine group and the endmost N atom of the dca in the other coordinate structure unit link by hydrogen bonding [N(2D)-H(2EG)...N(6A) = 2.916(3)Å, $\angle N(2D)$ -H(2EG) ... N(6A) = 178.3°], which form 1D chains. These 1D chains are connected with the 2D network through the other hydrogen bonding [C(1C)-H(1AE)...N(5AD) =3.396Å, $\angle C(1C)$ -H(1AE) ... N(5AD) = 154.4°] between the C-H group of the pyridine rings and the imine N atom of dca in proximate structure unit. Weak π - π interaction comes from between the pyridine planes.

The ORTEP drawing of **II** shows that Cu^{II} centers can be described as a octahedral (CuN₆) environment (show as Figure 3). Four N atoms (N3, N3A, N4, N4A) of the equatorial plane are provided by two dpa and the end-cap N atom of the two dca, respectively. The trans axial sites are occupied by two nitrogen atoms (N1, N1A) from two dpa, 2.2'-Dipyridylamine as a chelate ligand connect with Cu^{II} atom by *cis*-format, forming six-membered ring (Cu1, N1, C5, N2, C6, N3) of non-coplane (mean deviation from plane is 0.2362Å). The axial bond angle (N1-Cu1-N1A) [180.000(0)°] and two bond angles (N3-Cu1-N3A [180.000(1)°] and N4-Cu1-N4A [180.0 $(3)^{\circ}$) of the equatorial plane are linear. The two pyridine rings joined via the NH group are not planar, involving a dihedral angle of 139.6°. Two dihedral angles via the pyridine rings from different dpa in axial and in equatorial plane are all 0.0° . The Cu-N_{dpa} bond lengths are 2.0106Å and 2.0176Å, respectively. These values are very similar to dpa complexes with Ni-N systems.^[13] The Cu-N_{dca} bond length is 2.4807Å, which is longer than that of $M^{II}(dca)_2(M = transition metal).^{[14]}$

It is seen from Figure 4 that the ligand dca only forms one hydrogen bond (N2-H2E...N6 = 0.2956 nm) by a weak interaction from the end-cap N_{dca} and the imine (N2-H) group in adjacent structure unit. The hydrogen bond

beleeted bond lenguis (r) and angles () for r				
2.123(2)	Ni(1)-N(3A)	2.123(2)		
2.0933 (19)	Ni(1)-N(1A)	2.0933(19)		
2.103(2)	Ni(1)-N(4A)	2.103(2)		
94.45(11)	N(4)-Ni(1)-N(4A)	90.71(11)		
175.82(8)	N(1A)-Ni(1)-N(3A)	84.92(8)		
87.54(8)	N(1)-Ni(1)-N(3A)	95.50(8)		
87.54(8)	N(4)-Ni(1)-N(3A)	91.24(8)		
175.82(8)	N(4A)-Ni(1)-N(3A)	88.33(8)		
95.50(8)	N(1)-Ni(1)-N(3)	84.92(8)		
88.33(8)	N(4A)-Ni(1)-N(3)	91.24(8)		
179.39(12)				
	2.123(2) 2.0933 (19) 2.103(2) 94.45(11) 175.82(8) 87.54(8) 87.54(8) 175.82(8) 95.50(8) 88.33(8) 179.39(12)	2.123(2) Ni(1)-N(3A) 2.0933 (19) Ni(1)-N(1A) 2.103(2) Ni(1)-N(4A) 94.45(11) N(4)-Ni(1)-N(4A) 175.82(8) N(1A)-Ni(1)-N(3A) 87.54(8) N(1)-Ni(1)-N(3A) 175.82(8) N(4A)-Ni(1)-N(3A) 87.54(8) N(4A)-Ni(1)-N(3A) 95.50(8) N(1)-Ni(1)-N(3) 88.33(8) N(4A)-Ni(1)-N(3) 179.39(12) —		

 TABLE 2

 Selected bond lengths (Å) and angles (°) for I

Symmetry operations A: -x, y, -z + (3/2).

(N2-H2E... N6) makes Cu atoms into 1D double-chain helix structure. The distance (Cu... Cu) is 0.8608 nm in the chain. Face-to-face π - π weak interaction between pyridine rings results in the structure units forming a 3D continuum as a solid.

Luminescence Spectra

The luminescence spectra of the ligand dpa and I and II in DMF(1 × 10⁻⁵M) solution has been determined at room temperature (shown in Figure 5). 2, 2'-Dipyridylamine has been excited at 332 nm, an intense absorption appearing at 346.8 nm. The peak shape of I and II is almost the same as that of dpa, when it was have been excitated under each maximal wavelength, which indicate that the luminescence of I and II are assigned to the type of π - π^* (C==C)and π - π^* (C==N) of the ligand. The fluorescent absorption of the complexes I and II appeared to shift to length wave-length compared with dpa, which is due to the metallic ions perturbing

to the ligand types. Hydrogen bonding can enhance the intension of fluorescence so that complex I is stronger than complex I.

Thermal Analyses

The TG and DTG curve of **I** are shown in Figure 6. The thermal decomposition starts at 314.2 °C (on TG curve) and the main process ends before 500 °C. One maximum rate of weight loss appears at 341.2 °C(on DTG curve). Furthermore, the sub-process of the thermal decomposition appears between 500–600 °C, with the peak at 548.6 °C. The total mass loss up to 600 °C(on TG curve) is only 68.6%, which is due to the carbon deposition resulted products in N₂ atmosphere. The final product may be nickel.

The TG and DTG curve of **II** are shown in Figure 7. The thermal decomposition of **II** starts at 213.1 $^{\circ}$ C (on TG curve) and two similar transitions can be seen from the DTG curve. The two maximum rates of weight loss appear at 225.2 $^{\circ}$ C

 TABLE 3

 Selected bond lengths ($^{\circ}$) for **H**

beleeted bond lengths (1) and angles () for H				
Cu(1)-N(3)	0.2010(6)	Cu(1)-N(1)	0.2017(6)	
$Cu(1)-N(3)A^{1}$	0.2010(6)	$Cu(1)-N(1)A^{1}$	0.2017(6)	
$Cu(1)-N(4)A^2$	0.2480(7)	$Cu(1)-N(4)A^{3}$	0.2480(7)	
$N(3)-Cu(1)-N(3)A^{1}$	180.000(1)	$N(3)-Cu(1)-N(1)A^{1}$	94.2(2)	
N(3)-Cu(1)-N(1)	85.8(2)	$N(3)A^{1}-Cu(1)-N(1)$	94.2(2)	
$N(3)-Cu(1)-N(4)A^{2}$	92.7(2)	$N(3)A^{1}-Cu(1)-N(4)A^{2}$	87.3(2)	
$N(1)-Cu(1)-N(4)A^2$	90.2(2)	$N(3)-Cu(1)-N(4)A^{3}$	87.3(2)	
$N(1)-Cu(1)-N(4)A^{3}$	89.8(2)	$N(1)A^{1}-Cu(1)-N(4)A^{3}$	90.2(2)	
C(5)-N(1)-Cu(1)	121.0(4)	C(1)-N(1)-Cu(1)	121.1(5)	
C(10)-N(3)-Cu(1)	121.9(5)	$C(11)-N(4)-Cu(1)A^4$	136.5(7)	
$N(3)A^{1}-Cu(1)-N(1)A^{1}$	85.8(2)	$N(1)A^{1}-Cu(1)-N(1)$	180.000(0)	
$N(1)A^{1}-Cu(1)-N(4)A^{2}$	89.8(2)	$N(3)A^{1}-Cu(1)-N(4)A^{3}$	92.7(2)	
$N(4)A^2-Cu(1)-N(4)A^3$	180.0(3)	C(6)-N(3)-Cu(1)	120.3(5)	

Symmetry operations A^1 : -x, -y + 2, -z; A^2 : x, y + 1, z; A^3 : -x, -y + 1, -z; A^4 : x, y - 1, z.

TABLE 4 Hydrogen bond distances (Å) and angles (°)				
D-H A	$d(D\ldots A) \big/ \mathring{A}$	$^{\circ}$; DHA/ $^{\circ}$		
$C(1C)$ - $H(1A^1E) \dots N(5A^1D)(I)$	3.396	154.4		
$N(2)-H(2E)N(6)A^{2}(I)$	2.9163	178.3		
N(2)-H(2E) N(6) (II)	2.9569	172.5		

Symmetry operations A^1 : -x, -y + 2, -z; A^2 : (-x - 1)/2, (-y + 1)/2, -z + 1.

and 249.0 °C. The value of total mass loss is only 56.37% to 600 °C, the reasoning being the same as that of complex **I**. The final product may be copper.

Non-Isothermal Kinetics Studies

5000-

A series of dynamic scans with different heating rates results in a set of data that exhibits the same degree of conversion (σ) at different temperatures. Based on this, two methods are developed by Friedman as well as Ozawa-Flynn-Wall(OFW) to determine the kinetic parameters without having to



FIG. 5. The emission spectra of the complexes I, II and dpa.



FIG. 6. TG-DTG curves of I.



FIG. 7. TG-DTG curves of II.

presuppose a certain model. Figure 8 shows the TG curves of complex I decomposition from 200 to 450 °C with heating rates of 10, 20 and 25 °C \cdot min⁻¹. Figure 9 shows the TG curves of complex II decomposition from 120 to 320 °C with heating rates of 15, 20 and 30 °C \cdot min⁻¹. The base data



FIG. 8. TG curves of I with different heating rates (°C/min).



FIG. 9. TG curves of II with different heating rates (°C/min).



FIG. 10. The OFW analysis of I.

 (β, σ, T) taken from the TG curves of the complexes I and II are used in the equations that follow.

The Friedman equation^[15] is

$$\ln(d\alpha/dt)_{\alpha=\alpha j} = \ln[A \bullet f(\alpha)_j] - \frac{E}{RT}$$
(1)

where $d\alpha/dt$ is the rate of conversion, and $f(\alpha)$ mechanism function, E activation energy, A pre-exponential factor and R gas constant.

The Ozawa-Flynn-Wall equation^[16,17] is

$$\ln \beta = \ln \left(\frac{AE}{R}\right) - \ln f(\alpha) - 5.3305 - 1.052 \cdot \frac{E}{RT} \qquad (2)$$

where β is the heating rate, *a* the degree of conversion.

It is seen from Eqs (1) and (2) that the graphs $\ln(d\alpha/dt)$ versus 1/T and $\ln\beta$ versus 1/T both show straight lines with slopes $m_{(1)} = -(E/R)$ and $m_{(2)} = -1.052 E/R$. The slopes

of these straight lines are directly proportional to the reaction activation energy (*E*). Figure 10 shows these lines at different α by means of OFW method for **I** and the calculated results using both Eq. (1) and Eq. (2) are shown in Table 5. Table 6 shows the calculated results using both Eq. (1) and Eq. (2) of complex **II**.

From Table 5 it is seen that the values of *E* and IgA calculated by using different methods are comparable, which indicates that the kinetic parameters thus obtained are reasonable. Table 5 shows that the activation energy is not a constant and two maximums appear at a = 0.05 and 0.9, which indicates that the thermal decomposition of complex I is not a one-step reaction.^[18,19] Furthermore, the two methods obtained activation energies and pre-exponential factors which are of good pertinence. Kinetic parameters of this reaction can be estimated from the maximums of the Friedman method or OFW method or also from averaging

TABLE 5Parameters Ea (kJmol⁻¹) and lgA (s⁻¹) for the thermal decomposition of I

Partial mass loss	Ozawa-Flynn-Wall analysis		Friedman analysis	
	$Ea (\text{kJmol}^{-1})$	$lgA(s^{-1})$	$Ea (\text{kJmol}^{-1})$	$lgA(s^{-1})$
0.02	64.73 ± 107.30	2.38	142.82 ± 45.24	9.93
0.05	185.26 ± 56.01	13.99	179.05 ± 34.84	13.27
0.10	190.82 ± 39.52	14.39	191.38 ± 37.83	14.31
0.20	198.38 ± 40.68	14.97	210.41 ± 45.07	15.90
0.30	203.91 ± 42.77	15.40	208.19 ± 44.11	15.66
0.40	204.06 ± 40.86	15.37	199.75 ± 35.85	14.90
0.50	203.42 ± 36.57	15.28	199.51 ± 24.59	14.84
0.60	205.93 ± 31.10	15.46	213.54 ± 13.81	15.95
0.70	214.48 ± 23.71	16.14	227.55 ± 6.33	17.03
0.80	216.92 ± 8.70	16.27	196.37 ± 31.00	14.35
0.90	199.63 ± 16.39	14.68	206.84 ± 52.07	14.84
0.95	317.36 ± 89.31	23.73	457.60 ± 116.41	33.78
0.98	873.14 ± 304.02	65.68	1168.10 ± 318.20	86.93

	Ozawa-Flynn-Wa	Ozawa-Flynn-Wall analysis		Friedman analysis	
Partial mass loss	$Ea (\text{kJmol}^{-1})$	$lgA(s^{-1})$	$Ea~(kJmol^{-1})$	$lgA (s^{-1})$	
0.02	90.25 ± 12.03	6.66	112.24 ± 7.01	9.07	
0.05	119.06 ± 3.04	9.90	141.04 ± 9.11	12.27	
0.10	124.08 ± 2.30	10.48	114.74 ± 1.53	9.56	
0.20	109.44 ± 2.72	8.95	69.77 ± 14.53	4.94	
0.30	94.69 ± 6.08	7.42	57.27 ± 20.58	3.69	
0.40	86.42 ± 8.27	6.57	72.65 ± 16.23	5.27	
0.50	87.86 ± 8.19	6.74	109.67 ± 13.29	8.99	
0.60	94.35 ± 7.22	7.43	108.38 ± 17.26	8.89	
0.70	94.66 ± 7.32	7.49	82.43 ± 10.48	6.39	
0.80	89.94 ± 7.04	7.04	63.55 ± 6.79	4.58	
0.90	81.22 ± 5.76	6.18	47.41 ± 4.03	2.96	
0.95	69.86 ± 2.86	5.01	34.34 ± 4.71	1.46	
0.98	54.76 ± 3.95	3.41	32.42 ± 9.06	1.11	

TABLE 6Parameters Ea (kJmol⁻¹) and lgA (s⁻¹) for the thermal decomposition of **II**

values from each of the two methods.^[20] According to OFW method, the activation energies and pre-exponential factors of thermal decomposition of I are, $\bar{E}_1 = 203.77 \pm 32.29 \text{ kJmol}^{-1}$, $1gA_1 = 154.28 \text{ s}^{-1}$; $E_{2\text{max}} = 873.14 \pm 304.02 \text{ kJmol}^{-1}$, $1gA_2 = 65.68 \text{ s}^{-1}$, respectively.

From Table 6 it can be seen that the values of lgA calculated by using Friedman method (0.02 < a < 0.98) are smaller than the values of lgA calculated by using OFW method (0.02 < a < 0.98), and the values of *E* calculated by using Friedman method are very different, which may be due to the analytic method effected in the experiment. According to OFW method, the activation energies and pre-exponential factors of thermal decomposition of **II** are, $E_{1\text{max}} = 124.08 \pm 2.30 \text{ kJmol}^{-1}$, lgA=10.48 s⁻¹; $\bar{E}_2 =$ 90.00 \pm 7.28 kJmol⁻¹, lgA = 6.99 s⁻¹, respectively.

The analytic results show that the activation energy of **II** is smaller than that of complex **I**, which may be because structure **I** is more stable due to the two types of hydrogen bond action.

SUPPLEMENTARY MATERIAL

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 269645 for complex I and 273706 for complex II. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 - 1223 - 336 - 033; E-mail: deposit@ccdc.cam. ac.uk or (www:http://www.ccdc.cam.ac.uk)).

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