# Crystal Structure, Thermal Analysis and Theoretical Calculation of a One-dimensional Chain Complex [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

ZHANG, Rong-Lan[a](张荣兰)    ZHAO, Jian-She[*,a](赵建社)    GAO, Xin[b](高新)
SHI, Qi-Zhen[a](史启祯)    HE, Shui-Yang[a](何水样)

[a] *Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China*

[b] *Department of Chemical Engineering and Technology, College of Chemical Engineering, Northwest University, Xi'an, Shaanxi 710069, China*

A novel one-dimensional chain complex [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ was obtained when we tried synthesizing a mixed ligand supramolecular compound of Zinc(II) with dafo and *o*-phthalic acid. Its structure was determined by single-crystal X-ray diffraction analysis. The crystal belongs to triclinic system, *P*-1 space group. The crystallographic data: $a = 0.6989(4)$ nm, $b = 0.8281(5)$ nm, $c = 1.0231(5)$ nm, $\alpha = 94.934(5)°$, $\beta = 91.366(7)°$, $\gamma = 99.820(7)°$, $V = 0.5809(5)$ nm$^3$, $Z = 1$, $F(000) = 300$, $M_r = 589.78$, $D_c = 1.686$ g/cm$^3$, $\mu$(Mo K$\alpha$) $= 1.130$ mm$^{-1}$, $R_1 = 0.0521$, $wR_2 = 0.1096$. The analysis of the crystal structure indicates that the compound has a one-dimensional chain structure which is formed by hydrogen bonds. The constitutes of the title complex were proved by elemental analysis, IR spectra and thermal analysis. On the basis of the experimentation, the complex was calculated by DFT-B3LYP/LANL2DZ in Gaussian-98w also.

**Keywords**    one-dimensional chain structure, zinc(II) complex , crystal structure , thermal analysis, theoretical calculation

## Introduction

Molecular recognition and molecular self-assembly carried out by cooperation of the weak interactions (electrostatic reaction, hydrogen bonds, van der Waals force, short-range repulsive force, *etc*) are the common phenomena in nature. In recent years, the research on supramolecular complex has been a crossing focus of several subjects such as chemistry, physics, biology, material and information.[1] Supramolecular complex has a wide application foreground in material, catalysis, conductor, semiconductor, medicine and biotechnology, *etc*.[2-6] We attempted to synthesize supramolecular complex of Zn(II) with mixed ligands by the reaction of zinc(II) nitrate with dafo and *o*-phthalic acid. The anticipatory complex was not formed, accidentally, a complex [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ with one-dimensional chain supra- molecular structure was obtained. In this paper, the characterization, crystal structure and theoretical calculation of the title complex are reported.

## Experimental

### Apparatus and reagent

Elemental analysis was performed on a Germany Vario EL III CHNOS analyzer. IR spectra were measured on a Germany EQUINO×55 analyzer. Crystal structure was obtained on a Bruker Smart-1000CCD diffractometer. The thermal decomposition process was studied by using TG technique on a Germany NETZSCH STA449C thermal instrument. The theoretical calculations were carried out with Gaussian-98w package in windows system on a Legend computer (256MB, 60GB). All reagents were of A.R. grade. Dafo was prepared following the literature method.[7] *o*-Phthalic acid was obtained by hydrolysis of *o*-phthalic anhydride.

### Synthesis of compound [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

4,5-Diazafluorene-9-one (dafo) (0.3632 g 0.002 mol) dissolved in anhydrous ethanol (30 mL) was reacted with Zn(NO$_3$)$_2$ (0.2975 g 0.001 mol) dissolved in ethanol solution (3 mL). The mixture was refluxed for 1 h. Then a 95% ethanol solution of *o*-phthalic acid (0.166 g 0.001 mol) was added dropwise and the mixture was

refluxed for another 1 h. After standing at room temperature for 7 d, yellow crystals suitable for X-ray analysis were obtained from the reaction solution. m.p. 264—266 ℃. Anal. calcd for $C_{22}H_{16}ZnN_6O_{10}$: C 44.76, N 14.24, H 2.71; found C 44.60, N 13.78, H 2.72).

**Crystal data collection and refinement**

A single crystal with dimensions 0.30 mm×0.20 mm×0.15 mm was selected for data collection, using a Bruker Smart-1000CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda$=0.071073 nm). Data were collected by $\omega$-$2\theta$ scan technique. The total reflections of 2989 were collected, unique 1953 reflections could be observed [$R$(int)=0.0294] and used for structural analysis. The structure was solved by direct method. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of all non-H atoms were refined anisotropically with full-matrix least-squares on $F^2$. In the final difference map, the residuals are 379 e/nm$^3$ and −544 e/nm$^3$, respectively. The crystallographic data: triclinic system, space group $P$-1 with cell dimensions: $a$= 0.6989(4) nm, $b$=0.8281(5) nm, $c$=1.0231(5) nm, $\alpha$= 94.934(5)°, $\beta$=91.366(7)°, $\gamma$=99.820(7)°, $V$=0.5809(5) nm$^3$, $Z$=1, $F(000)$=300, $M_r$=589.78, $D_c$=1.686 g/cm$^3$, $\mu$(Mo Kα)=1.130 mm$^{-1}$, $R_1$=0.0521, $wR_2$= 0.1096.

# Results and discussion

## Crystal structure

The selected bond lengths and bond angles of the title complex are listed in Table 1. All of the data in brackets are standard deviation. The crystal structure, cell packing, one-dimensional chain structure and two-dimensional sandwich structure are shown in Figure 1—4, respectively. The structure unit cell of the complex consists of $[Zn(dafo)_2]^{2+}$, two $H_2O$ molecules, and two $NO_3^-$ anions. Zn(1) atom is in a six coordina-

tion environment, and at the center of an octahedron. From the data of the bond angles N(1A)-Zn(1)-N(1) (180.0°), N(1A)-Zn(1)-N(2) [99.02(12)°], N(1)-Zn(1)-N(2) [80.98(12)°], N(1A)-Zn(1)-N(2A) [80.98(12)°], N(1)-Zn(1)-N(2A) [99.02(12)°], N(2)-Zn(1)-N(2A) [180.0°] and the bond length Zn(1)—N(1A) [0.2202(3) nm], Zn(1)—N(1) [0.2202(3) nm], Zn(1)—N(2) [0.2278(3) nm], Zn(1)—N(2A) [0.2278(3) nm], we can conclude that N(1), N(2), Zn(1), N(1A) and N(2A) consist of a quadrangle in the same plane and the Zn(1) atom lies at the center of the quadrangule. The data of the bond angles O(5)-Zn(1)-N(1A) [89.32(13)°], O(5A)-Zn(1)-N(1A) [90.68(13)°], O(5)-Zn(1)-N(1) [90.68(13)°], O(5A)-Zn(1)-N(1) [89.32(13)°], O(5)-Zn(1)-N(2) [89.69(13)°], O(5A)-Zn(1)-N(2) [90.31(13)°], suggest that the two dafo molecules are in the same plane, that is, Zn(1) atom and the two dafo molecules are in the same plane. In addition, the bond angle of O(5)-Zn(1)-O(5A) is equal to 180.0°, which indicates that the bond Zn(1)—O(5) and bond Zn(1)—O(5A) are in the same straight line, and the line is vertical to the plane in which Zn(1) atom and the two dafo molecules lie in. The bond length data of Zn(1) atom with ligand atoms [N(1), N(2), N(1A), N(2A), O(5),O(5A)] respectively show that Zn(1) atom is at an octahedral center. The distance between O(5), O(9) and the nearest hydrogen atom are 0.1784 nm and 0.1828 nm, respectively, which is in the range of forming hydrogen bond. So the two coordination water molecules bond to the outside nitrate radical by hydrogen bond.

In Figure 2, the two hydrogen atoms of each water molecule in $[Zn(dafo)_2(H_2O)_2]^{2+}$ form hydrogen bonds with oxygen atoms of two $NO_3^-$ anions. The two oxygen atoms of each $NO_3^-$ anion form two hydrogen bonds with the hydrogen atoms of the water molecules which come from two different complex ions $[Zn(dafo)_2(H_2O)_2]^{2+}$. So there are not only intramolecular hydrogen bonds but also intermolecular hydrogen bonds in complex $[Zn(dafo)_2(H_2O)_2](NO_3)_2$. Because

**Table 1**  The selected bond lengths (nm) and bond angles (°) of the title complex

|  | Found | Calcd |  | Found | Calcd |
|---|---|---|---|---|---|
| Zn(1)—O(5) | 0.2066(4) | 0.2141 | O(5A)—Zn(1)—N(1A) | 90.68(13) | 90.02 |
| Zn(1)—O(5A) | 0.2066(4) | 0.2141 | O(5)—Zn(1)—N(1) | 90.68(13) | 89.99 |
| Zn(1)—N(1A) | 0.2202(3) | 0.2282 | O(5A)—Zn(1)—N(1) | 89.32(13) | 90.01 |
| Zn(1)—N(1) | 0.2202(3) | 0.2282 | N(1A)—Zn(1)—N(1) | 180.0 | 180 |
| Zn(1)—N(2) | 0.2278(3) | 0.2282 | O(5)—Zn(1)—N(2) | 89.69(13) | 90.01 |
| Zn(1)—N(2A) | 0.2278(3) | 0.2282 | O(5A)—Zn(1)—N(2) | 90.31(13) | 89.99 |
| N(1A)—Zn(1)—N(2) | 99.02(12) | 98.39 | O(5)—Zn(1)—O(5A) | 180.0 | 180 |
| N(1)—Zn(1)—N(2) | 80.98(12) | 81.61 | N(1)—Zn(1)—N(2A) | 99.02(12) | 98.38 |
| O(5)—Zn(1)—N(2A) | 90.31(13) | 90.01 | O(5)—Zn(1)—N(1A) | 89.32(13) | 89.98 |
| O(5A)—Zn(1)—N(2A) | 89.69(13) | 89.99 | N(2)—Zn(1)—N(2A) | 180.0 | 180 |
| N(1A)—Zn(1)—N(2A) | 80.98(12) | 81.61 |  |  |  |

**Figure 1**   Crystal structure of [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$.



**Figure 2**   Cell packing of [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$.



**Figure 3**   Two-dimensional chain structure of [Zn(dafo)$_2$-(H$_2$O)$_2$](NO$_3$)$_2$.

of the existing of hydrogen bonds, the one-dimensional chain supramolecular complex, showed in Figure 3, is formed. Figure 4 indicates that the two-dimensional sandwich structure is formed by the compactly packing of the one-dimensional chain supramolecular complex. It is significant to make further research on this type of structure for multidimensional assembly molecular engineering.[1]

**IR photoemission spectroscopy**

The IR spectra of the title complex and the ligand



**Figure 4**   Two-dimensional sandwich structure of [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$.

dafo were obtained as KBr discs in the rang of 4000—400 cm$^{-1}$. The IR spectra were determined in comparison with the literature[8] and the standard spectra. The IR spectra of the complex show $v_{C=O}$ at about 1724 cm$^{-1}$, which is red-shifted compared with the corresponding value of $v_{C=O}$ at about 1715 cm$^{-1}$ in the ligand dafo. The absorbed peaks of the complex are 1566, 1385, 915, 760 cm$^{-1}$ and those of the ligand are 1553, 1397, 907, 755 cm$^{-1}$. These data indicate that the absorbed peaks of the complex shift correspondingly. The shifting of absorbed peaks is due to the intramolecular coordinate bonds and hydrogen bonds of the complex.

**Thermal analysis**

Typical TG-DSC curve of the title complex was measured by the heating speed of 10 ℃/min in the temperature range of 0—600 ℃. The operation progress is in the N$_2$ atmosphere. During the heating time, the complex [Zn(dafo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ had two weight-losses. One weight-loss is for two water molecules in the temperature range of 140—205 ℃ and the peak temperature in DSC curve is at 181.9 ℃, the weight-loss value is 6.07% (theoretical 6.10%). The other weight-loss is for two dafo molecules in the temperature range of 210—368 ℃ and the peak temperature in DSC curve is at 252.3 and 292.2 ℃, the weight-loss value is 61.79% (theoretical 61.72%). The temperature of losing water is between 140 ℃ and 205 ℃. It is higher than that of the dissociated water. The fact of the experiment indicates that the water in the title complex is coordinated water. The result is in accord with the measurement result for crystal structure. The losing course of the ligand dafo shows exothermic effect, which indicates that the endotherm of the coordinated bond breakage is smaller than the heat release of new bond configuration (the decomposition of the organic ligand).

**Theoretical calculation**

On the basis of the experimentation, the complex was calculated by DFT-B3LYP/ LANL2DZ in Gaus-

sian-98w. The data of the main bond length and bond angle in the optimization structure are showed in Table 1. The average deviation of the calculation value from the experimental value is in the rang of 1%—2%. The reason of the deviation is maybe as follows: the approximation of calculation methods and setup groups, the neglecting anionic effect in the course of calculation, and the chemical environmental difference of the complex (calculation was based on gas geometry configuration). The deviation can be accepted in theoretical calculation for big system.

The IR spectral frequencies in experimentation are 1724, 915, 760, 1566, and 1385 cm$^{-1}$, and those in computation are 1724, 910, 739, 1612 and 1341 cm$^{-1}$. These data are fairly fit together.

The charge layout of Zn and its coordination atoms are showed in Table 2 by Mulliken layout analysis and natural population analysis. The two modes of the analyses indicate the same tendency: the positive charge of Zn ion is less than its chemical valence ($+2$), that is, in the title complex, the positive charge of the center is brought down; similarly, the negative charge absolute value of the coordination atoms is brought down also. This situation corresponds to Pauling's electric neuter principle,[9] and proves the existence of the coordination bonds, which makes the charge transfer between the metal ion and the coordination atoms.

The front molecular orbital energy (a.u.) of the complex obtained from the calculation is HOMO, $-0.4788$; LUMO, $-0.3255$. The energy D-value [$\Delta\varepsilon$(L—H)] of $E_{HOMO}$ and $E_{LUMO}$ is 0.1533. The value of $\Delta\varepsilon$(L—H) is higher, which proves that the complex can not be excited easily in the illumination. It is comparatively stable.

**Table 2** Atomic net charge populations (%)

| Zn(1) | O(5) | O(5A) | N(1) | N(2) | N(1A) | N(2A) |
|---|---|---|---|---|---|---|
| Mulliken layout analysis | | | | | | |
| 1.0593 | $-0.7557$ | $-0.7557$ | $-0.2231$ | $-0.2232$ | $-0.2231$ | $-0.2232$ |
| Natural population analysis | | | | | | |
| 1.7186 | $-1.0473$ | $-1.0474$ | $-0.6398$ | $-0.6399$ | $-0.6398$ | $-0.63985$ |

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