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3D High-Energy-Density Materials and Low Sensitivity: Synthesis, Structure and Physicochemical Property of An Azide-Cu(II) Complex with 3,5-Dinitrobenzoic Acid

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ABSTRACT

A novel 3D energetic coordination polymer of azide-Cu(II), Cu(3,5-DNBA)(N_3), was synthesized and structurally characterized by single crystal X-ray diffraction, where 3,5-DNBA represents 3,5-dinitrobenzoic acid. Structural analysis reveals that the central Cu(II) ion coordinates with two azide anions and three 3,5-dinitrobenzoic acid anions to form a five-coordinated tetragonal pyramid structure. Noteworthily, one oxygen atom in nitro group displays rare coordination to Cu(II) ions in known complexes. The as-prepared compound showed an abrupt thermal decomposition at 268 ^{o}C, representing explosive performance and superior thermostability based on DSC and TG-DTG analyses. Sensitivity tests revealed that the title complex was insensitive to external stimuli. The kinetic parameters of an exothermic process for the complex were studied by the Kissinger's and Ozawa–Doyle's methods. In addition, the constant-volume combustion energy of the complex was determined by a precise rotating-bomb calorimeter, and the standard molar enthalpy of combustion and the standard molar enthalpy of formation were calculated, respectively.

Keywords: Cu(II)-Azide complex Thermal property Non-isothermal kinetics Enthalpy of formation

1. Introduction

Energetic materials include explosives, propellants, and pyrotechnics that are used for a variety of military purposes and civilian applications [1-3]. Explosives may be classified as primary and secondary explosives: the former are very sensitive and low-performing compounds [4, 5], which are commonly used to initiate a more powerful and less sensitive secondary explosive [6]. Unfortunately, high performance and low sensitivity tend to be contradicting aspects [7]. In combination with tailored performance, insensitivity, stability, oxygen balance and environmental safety [2, 8-10], novel energetic materials have been scarcely reported [11].

As known, Cu(II) exhibits a good coordination ability to different kinds of ligands, more importantly, is an environmentally-friendly ion compared with the heavy metal ions such as lead and mercury [12,13]. Until now, uncountable Cu(II)-nitrogen complexes have been synthesized and characterized in literature [14]. Of particular interest, Cu(II) complexes with nitrogen-rich ligands can be used as green energetic materials [15-21]. Azide, as a simple nitrogen-rich ligand with the highest nitrogen content — 100%, is a prominent energetic moiety which can increase the heat of formation by about 355 kJ mol^{-1} and easy to implement oxygen balance, and the combustion product of azide is environment-friendly [2,22,23]. Furthermore, as a member of short bridging ligands, azide is able to connect transition metal ions *via* multiple coordination modes. However, for azide-metal complexes, much attention focuses mostly on the magnetic properties [24-27]. Probably because of the high sensitivity of azide, there are limited literatures about the energetic property of azide-metal complexes so far. Although the literature disclosed that the sensitivity of azide compound depended on the minimum distance between N atoms of adjacent azides [28], how to fine-tune structure to balance energy and sensitivity of azide compounds has still been the hotspot and difficulty in the field of energetic materials.

In present work, we take attention to the high-energy of azide-Cu(II) system. Due to the favorable oxygen balance with which compounds are suitable as energetic fillers in high explosive compositions [29], meanwhile, in order to improve the insensitivity and the stability of complex, 3,5-dinitrobenzoic acid (3,5-DNBA) as a co-ligand is introduced into azide-Cu(II) energy system because of its advantages such as stable rigid framework, variety of coordination modes, high oxygen content and explosive property [30, 31]. In addition, because the sensitivity of an explosive depends on properties such as shear strength and molecular orientations of the crystalline material [32], the research of the structure-directing property for the energetic materials has been an object of permanent interest.

In view of the observations above, we present here the synthesis, crystal structure of a 3D azide-Cu(II) complex Cu(3,5-DNBA)(N_3). Exceptionally, an oxygen atom in nitro from 3,5-dinitrobenzoic acid connected with Cu(II), which is rare example in the Cu-based energetic coordination compounds in spite of the same coordination action occurring in other metal compounds [33-35]. 3D framework of the complex is further benefit for increasing the stability and reducing the sensitivity of energetic complex but no influence on explosive property. In addition, thermogravimetric analysis, sensitivity measurements, the thermokinetics and the standard molar enthalpy of formation were investigated.

2. Experimental

General caution: azide, 3,5-DNBA and the title complex are energetic materials and tend to explode under certain conditions. Although no difficulties were experienced in the synthesis of these materials, proper protective measures should be taken, especially when the complex is prepared on a large scale.

2.1. Materials and instruments

All reagents (analytic grade) were purchased commercially and used without further purification unless otherwise stated.

Elemental analysis was performed on a Vario EL III analyzer fully automated trace element analyzer. The FT-IR spectra were recorded on a Bruker FTIR instrument as KBr pellets. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a Netzsch STA 449C instrument and a CDR-4P thermal analyzer of Shanghai Balance Instrument factory, respectively, using dry oxygen-free nitrogen as the atmosphere, with a flowing rate of 10 mL min^{-1}. About 0.5 mg of the sample was sealed in aluminum pans for DSC and a temperature range of 50-600 ^{o}C was used. The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$) [36]. Friction sensitivity of the complex was determined on a Julius Peter's apparatus by following the BAM method [37]. The phase purity of the bulk sample was verified by X-ray powder diffraction (XRPD) radiation

(λ = 1.5406 Å), with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ. The constant-volume combustion energy of the complex was determined with an RBC-type II rotating-bomb calorimeter.

2.2. X-ray structure determinations

The single crystal X-ray experiment was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073Å) using ω and φ scan mode. The structure was solved by direct methods using SHELXS-97 [38] and refined by means of full-matrix least-squares procedures on F^2 with SHELXL-97 program [39]. All non-H atoms were located using subsequent Fourier-difference methods and refined anisotropically. In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection parameters and refinement statistics are given in Table 1. Selected bond lengths and bond angles of title complex are listed in Table S1. Further information concerning the crystal structure determinations in CIF format is available in the Supporting information.

Table 1

2.3. Synthesis of complex

A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.072 g, 0.3 mmol), 3,5-DNBA (0.085 g, 0.4 mmol) and NaN_3 (0.013 g, 0.2 mmol) in ethanol (20 ml) were kept stirring for 1h at room temperature. Upon being undisturbed for one week, atrovirens flake crystals were obtained and collected from the mixture system above. (Yield 55%, based on Cu). Anal. Calcd. For $CuC_7H_3N_5O_6$ (316.68): C, 26.53; H, 0.95; N, 22.10%. Found: C, 26.81; H, 1.09; N, 22.38%. Main IR (KBr, cm^{-1}): 2048 (s), 1604(m), 1537 (s), 1500(m), 1465 (m), 1409 (s), 1272(w), 1207 (m), 1058 (m), 912 (m), 786 (s).

3. Results and discussion

3.1. Structure description

Single-crystal analysis reveals the complex crystallizes in Orthorhombic and exists as a 3D network structure. As shown in Fig. 1a, the asymmetric unit contains one crystallographic independent Cu(II), in which Cu(II) is occupied by two nitrogen atoms from two μ-1,1-azide anions [Cu1-N1 = 1.990 Å Cu1-N1A = 1.967 Å], two oxygen atoms of carboxylic group from two 3,5-DNBA [Cu1-O1 = 1.939 Å, Cu1-O2 = 1.950 Å] and one oxygen atom on nitro group from another 3,5-DNBA [Cu1-O4 = 2.609 Å] (occupied the apical position). Selected bond lengths and bond angles are shown in Table S1. The carboxylate group in 3,5-DNBA interacts with Cu(II) in a doubly-bridging fashion, while nitro in a monodentate bridging mode (Fig. 1b). Adjacent Cu(II) ions are linked by an azide bridge with μ-1,1 (or end-on, EO) mode and a carboxylate bridge with *syn-syn* mode, yielding a formally 1D chain along the crystallographic *a* direction (Fig. 1c). Finally, nitro groups on intrachain 3,5-DNBA are connected to Cu(II) ions from other chains, forming a three-dimensional network structure (Fig. 1d). It is noteworthy that one oxygen atom in nitro coordinates to Cu(II), which is rare in the complex with nitro groups [33-35].

Fig. 1.

3.2. Thermal decomposition

DSC and TG-DTG curves under the linear heating rate of 10 ^{o}C min^{-1} with nitrogen atmosphere are shown in Figs. 2 and 3 to demonstrate the thermal decomposition processes of powder samples Cu(3,5-DNBA)(N_3). In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiment has been carried out for the powder sample of the complex (Fig. S1). The experimental pattern is in good agreement with the corresponding simulated one, indicating the phase purity of the as-synthesized product.

Fig. 2.

Fig. 3.

In the DSC curve, there is one intense and sharp exothermic process occurs at 268 ^{o}C, ends at 280 ^{o}C with a peak temperature of 275 ^{o}C (Fig. 2). Typical TG/DTG curve is shown in Fig. 3. Sample as small as 0.5 mg detonates at 268 ^{o}C in open crucible made of Al_2O_3. In this case, detonation completely is accompanied by phut and without destroys the crucible maybe due to a little quantity of sample. As noticed in TG curve, there is one mass-loss stage, corresponding to only one peak in DSC curve. A sudden weight loss is observed at 268 ^{o}C and stops at 278 ^{o}C, accompanying about 76.1% mass loss, which is attributed to the fully decomposition process for the main framework of complex. The final residue mass is 23.9% of the initial mass, coincident with the calculation value of CuO (25.3%) determined by XRPD (JPCDS 05-0661). TG analysis shows explosive performance and good thermal stability of the complex. Additionally, the oxygen balance value is calculated as being -48.0%.

The decomposition temperatures [40], oxygen balance and density values of RDX, HMX, TNT [41] and title complex are summarized in Table 2. Obviously, the density of complex is highest compared to other explosives, the thermal stability of complex is more preferable than RDX and TNT, while oxygen balance is better than TNT.

Table 2

3.3. Sensitivity test

Impact sensitivity is determined by Fall Hammer Apparatus. Twenty milligrams of Cu(3,5-DNBA)(N_3) is compacted to a copper cap under the press of 39.2 MPa, and is hit by 2 kg drop hammer, and calculated value of H_{50} represent the drop height of 50% initiation probability. The test shows that the impact sensitivity value of the complex is 120 cm, which corresponds to the impact energy of 23.5 J. Under the same test condition, the impact sensitivity value (H_{50}) of TNT is 76.5 cm (15.0 J) [42]. Consequently, the impact sensitivity of the title complex is lower than that of TNT.

Friction sensitivity of the complex is measured by applying a Julius Peter's machine using 20 mg sample. No friction sensitivity is observed up to 36 kg (360 N). The friction sensitivity of the complex is lower than that of RDX 12 kg [43].

The title compound was roughly tested for ESD sensitivity by spraying sparks across a small (5 crystals) sample of material using a tesla coil. Although not being confirmed by quantitative testing, the compounds are most likely less sensitive to electrostatic discharge than both TNT and RDX.

The results revealed that the title complex is very insensitive to external stimuli due to the structure characteristic of title complex, which is probably assigned that the nitro is bonded to metal ion.

3.4. Non-isothermal kinetics

In this work, Kissinger's method [44] and Ozawa–Doyle's method [45, 46] were applied to determine the apparent activation energy (E) and the pre-exponential factor (A). The Kissinger (Eq. (1)) and Ozawa–Doyle (Eq. (2)) equations are as follows:

$$\ln(\frac{\beta}{T_p^2}) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_p} \qquad (1)$$

$$\log\beta + \frac{0.4567E}{RT_p} = C \qquad (2)$$

where T_p is the peak temperature; R is the gas constant, 8.314 J mol^{-1} $^\mathrm{o}$C^{-1}; A is the pre-exponential factor; E is the apparent activation energy; β is the linear heating rate and C is a constant.

Based on the exothermic peak temperatures measured at four different heating rates of 5, 8, 10, and 15 $^\mathrm{o}$C min^{-1}, the thermokinetic parameters of the complex were obtained. The apparent activation energy E_k and E_O, pre-exponential factor A_k and linear correlation coefficients R_k and R_O are shown in Table 3.

The calculation results using both methods are quite close, which are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials [47]. The E_a value (301.05 kJ mol^{-1}) for the thermal decomposition stage shows that the exothermic process can not readily proceed. Using the obtained E_a (the average of E_k and E_o) and lnA_k value, the Arrhenius equation can be expressed by as $\ln k = 27.4 - 301.05\times 10^3/RT$ for the exothermic process, which can be used to estimate the rate constant of the initial thermal decomposition process of title complex.

Table 3

3.5. *Standard molar enthalpy of formation for the complex*

The methods of determination and calculation of the constant-volume combustion energy for the complex is the same as for the calibration of the calorimeter with benzoic acid (SRM, 39i, NIST). The experimental procedures are described in Supporting Information. The experiment result is (-10971.11 ± 6.56) J g^{-1}, which has an equivalence of (-3474.33 ± 2.08) kJ mol^{-1} for the complex.

The standard molar combustion enthalpy of the complex, $\Delta_c H_m^\theta$, refers to the combustion enthalpy change of the following ideal combustion reaction (Eq. (3)) at 298.15 K and 101.325 kPa.

$$CuC_7H_3N_5O_6(s) + \frac{21}{4} O_2(g) = CuO(s) + 7CO_2(g) + \frac{3}{2} H_2O(l) + \frac{5}{2} N_2(g) \qquad (3)$$

The standard molar combustion enthalpy of the complex is calculated by the following equations.

$$\Delta_c H_m^\theta = \Delta_c U + \Delta nRT \qquad (4)$$

$$\Delta n = n_g \text{ (products) - } n_g \text{ (reactants)} \qquad (5)$$

where n_g is the total amount in mole of gases present as products or as reactants, R = 8.314 J mol^{-1}, T = 298.15 K. The standard molar enthalpy of combustion, $\Delta_c H_m^\theta$, is calculated as being (-3464.45 ± 2.08) kJ mol^{-1}, equivalent to -10.93 MJ kg^{-1}. As reported in literature [48], the enthalpies of combustion of RDX, HMX and TNT were -9.60 MJ kg^{-1}, -9.44 to -9.88 MJ kg^{-1} and -15.22 MJ kg^{-1}, respectively. So the enthalpy of combustion of title complex is higher to those of RDX and HMX, lower to that of TNT.

The standard molar enthalpy of formation of the complex, $\Delta_f H_m^\theta$, is calculated by Hess's law according to the thermochemical Eq. (6).

$$\Delta_f H_m^\theta(CuC_7H_3N_5O_6,s) = [\Delta_f H_m^\theta(CuO,s) + 7\Delta_f H_m^\theta(CO_2,g) + \frac{3}{2}\Delta_f H_m^\theta(H_2O,l)] - \Delta_c H_m^\theta(CuC_7H_3N_5O_6,s) \qquad (6)$$

where $\Delta_f H_m^\theta$(CuO, s) = -157.3 kJ mol^{-1} [49]; $CO_2(g)$, $\Delta_f H_m^\theta$(CO_2, g) = (-393.51 ± 0.13) kJ mol^{-1} [49]; $H_2O(l)$, $\Delta_f H_m^\theta$ (H_2O, l) = (-285.830 ± 0.040) kJ mol^{-1} [49]. According to the Eq. (6), the enthalpy of formation for the complex, $\Delta_f H_m^\theta$, is calculated as being (129.28 ± 2.54) kJ mol^{-1}.

4. Conclusion

A novel three-dimensional azide-bridged Cu(II) coordination polymer, Cu(3,5-DNBA)(N_3), has been synthesized and characterized, noteworthy, one oxygen atom in nitro coordinates to Cu(II). The result of non-isothermal kinetics analysis shows that the apparent activation energy is 301.05 kJ·mol^{-1}. The enthalpy of combustion of complex is higher to RDX and HMX. The complex shows superior thermostability and insensitiveness compared to RDX and TNT. The results above show that the complex would be exampled as green, high energy and insensitivity material.

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Appendix A. Supplementary data

The CIF file gives crystallographic data for complex. Fig. S1 and Table S1 see supporting information..

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Figure captions:

Fig. 1. (a) Coordination environment of the Cu center in complex. (b) Coordinate mode of 3,5-DNBA. (c) Chain with mixed carboxylate and azide bridges. (d) 3D network extended based on chains. Hydrogen atoms are omitted for clarity.

Fig. 2. DSC curve of the complex.

Fig. 3. TG-DTG curve of the complex.

Table 1 Crystal data and structure refinement details for the title complex.

Table 2 Density values (ρ), decomposition temperatures (T_{dec}) and oxygen balance values (Ω) of complex in comparison to RDX, HMX and TNT.

Table 3 Peak temperatures of the exothermic stage at different heating rates and the kinetic parameters.

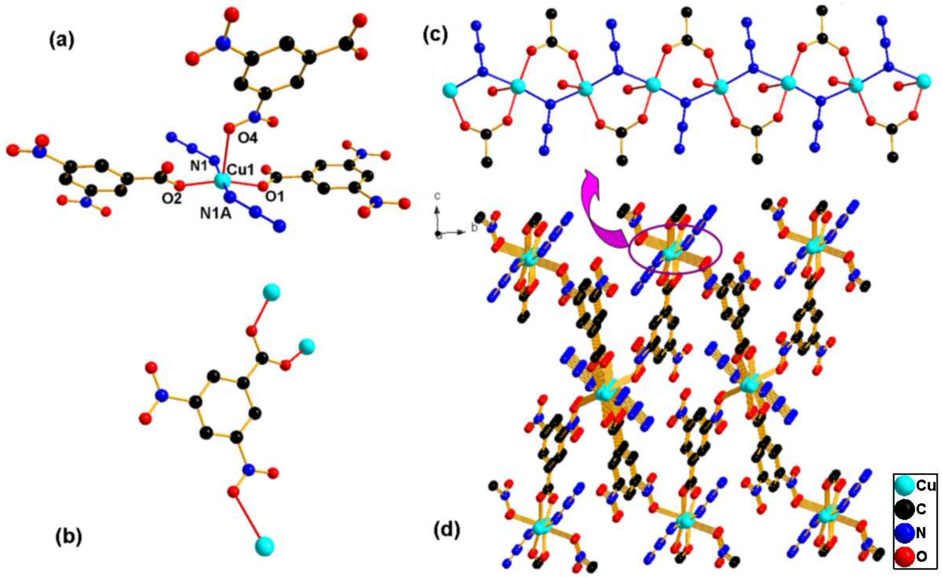


Fig. 1.

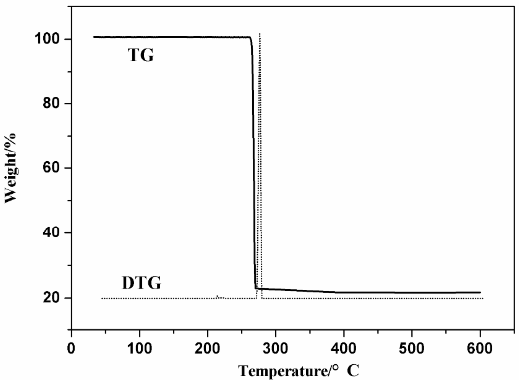


Fig. 2.

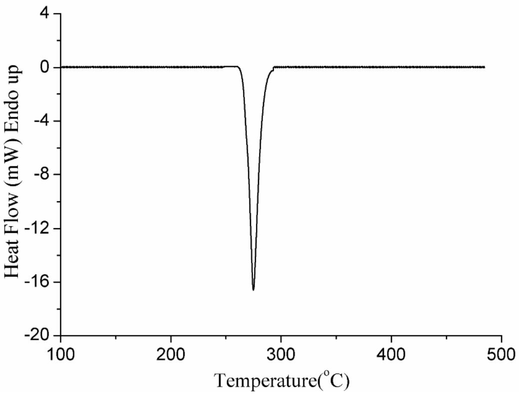


Fig. 3.

Table 1

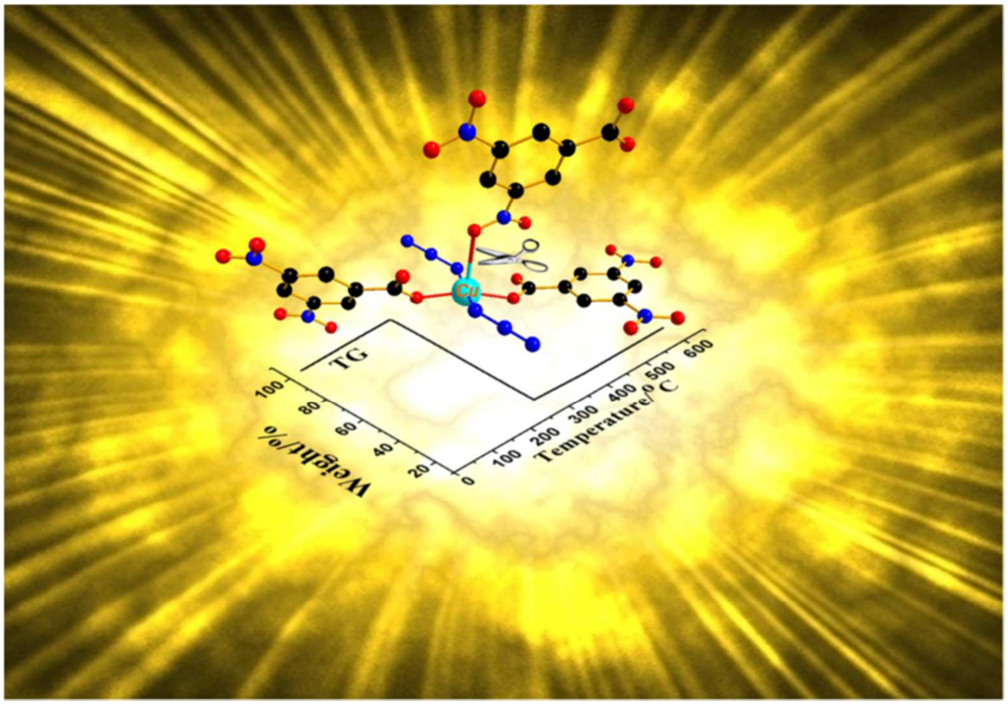
Empirical formula	$C_7H_3CuN_5O_6$
Formula weight	316.68
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
a (Å)	6.747(2)
b (Å)	9.047(3)
c (Å)	16.973(5)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1036.0(5)
Z	4
μ (mm^{-1})	2.145
Unique reflections	2041
Observed reflections	5301
R_{int}	0.0818
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0537$, $wR_2 = 0.1270$
R indices (all data)	$R_1 = 0.0777$, $wR_2 = 0.1408$

Table 2

	RDX	HMX	TNT	Complex
Formula	$C_3H_6N_6O_6$	$C_4H_8O_8N_8$	$C_7H_5N_3O_6$	$C_7H_3CuN_5O_6$
Molecular Mass (g mol^{-1})	222.1	296.2	227.1	316.7
ρ (g cm^{-3})	1.800	1.905	1.654	2.030
T_{dec} (°C)	210	282	244	268
Ω (%)	-21.6	-21.6	-74.0	-48.0

Table 3

Heating rates (^{o}C min^{-1})	Peak temperature (^{o}C)
5	268.2
8	272.3
10	274.8
15	276.3
The calculation results by Kissinger's method	
E_k (kJ mol^{-1})	304.2
Log A_k(s^{-1})	27.4
Linear correlation coefficient (R_k)	0.9976
The calculation results by Ozawa–Doyle's method E_o (kJ mol^{-1})	297.9
Linear correlation coefficient (R_o)	0.9968



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