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Crystal Structure of a Novel Nitrogen-rich Energetic Compound $Zn(5\text{-}NATZ)_2(H_2O)_4$

WU Jin-ting, ZHANG Jian-guo, LI Jing-yu, ZHANG Tong-lai, ZHOU Zun-ning, YANG Li

(*State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing*, 100081, *China*)

Tetrazole-based nitrogen-rich compounds are energetic materials due to their high enthalpy of formation, high density and easy to achieve balance of oxygen[1-4]. 5-nitraminotetrazolate (5-NATZ) has been proved to possess excellent energetic properties among the simple tetrazole compounds[5-6] and its metal complexes were thought to be promising energetic materials[7-8]. In this paper, a novel nitrogen-rich energetic compound of $Zn(5\text{-}NATZ)_2(H_2O)_4$ was synthesized and determined by X-ray single crystal diffraction technology.

$Zn(5\text{-}NATZ)_2(H_2O)_4$ was synthesized by reacting 5-NATZ with $Zn(NO_3)_2 \cdot 6H_2O$ at 30 ℃ for 3 h and crystallized by slow evaporation method. The X-ray single crystal data collection for $Zn(5\text{-}NATZ)_2(H_2O)_4$ were performed on a Rigaku AFC-10/Saturn 724 + CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.071073 nm). The datas were collected at 103(2) K in the range of $3.0° \leqslant \theta \leqslant 27.5°$. A semi-empirical absorption correction was made using SADABS software. The structure was solved using the direct methods using SHELXS-97[9], refined using full-matrix least-squares on F^2 with SHELXL-97[10]. Detailed information concerning crystallographic data collection and structure refinement are summarized in Table 1.

Fig. 1 shows the molecular unit of $Zn(5\text{-}NATZ)_2(H_2O)_4$. The Zn^{II} ion with sp^3d^2 hybridization, contributes six empty orbits to accommodate the lone pair electrons from ligands and to coordinate with two nitrogen atoms from two 5-NATZ ions and four oxygen atoms from four water molecules. The bond angle of the nitrogen atoms N(1), N(1A) from two 5-NATZ ligands and the Zn^{II} ion is 180.00° (N(1)—Zn(1)—N(1A) = 180.00°); the bond angle of four water groups and the Zn^{II} ion are 180.0°, 87.53° and 92.47°, respectively (O(3)—Zn(1)—O(3A) = 180.0°, O(3)—Zn(1)—O(4) = 87.53°, O(3)—Zn(1)—O(4A) = 92.47°), the bond angles of nitrogen atoms N(1)、N(1A) from two 5-NAZT groups, O(3) from four water groups, and the Zn^{II} ion are 90.07° and 89.93°, respectively (O(3)—Zn(1)—N(1) = 90.07°, O(3)—Zn(1)—N(1A) = 89.93°). At the same time, the Zn-O(terminal water) distances (range from 2.0431 to 2.2409 Å) are similar to the bond lengths (both are 2.1033 Å) of Zn-N (terminal 5-NATZ). These results indicate that the Zn^{II} ion exhibits a slightly distorted octahedral configuration.

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Biography: WU Jin-ting(1990-), female, Master Candidate.
e-mail: wjt1234@163.com
Corresponding Author: ZHANG Jian-guo(1974-), male, professor.
e-mail: zhangjianguobit@yahoo.com.cn

Table 1 Crystal data and structure refinement for the title compound

items	value
empirical formula	$C_2H_{10}N_{12}O_8Zn$
crystal size/mm	0.37 ×0.37 ×0.40
formula mass	395.61
crystal group	P-1
cystal system	triclinic
a/Å	6.628(3)
b/Å	7.624(3)
c/Å	7.632(3)
α/(°)	105.104(3)
β/(°)	113.537(1)
γ/(°)	104.690(4)
cell volume/Å^3	312.3(2)
λ/Å	0.71073
μ	2.044
reflection collected	3018
observed reflection [$I>2\sigma(I)$]	1341
R_1, wR_2(all data)	0.0220, 0.0501[1)]
$h/k/I$	−6 ~8/−9 ~9/−9 ~9
density/g·cm^{-3}	2.103
F(000)	200
θ/(°)	3.0 ~27.5
independent reflection(Rint)	1412 (0.017)
R_1, wR_2 [$I>2\sigma(I)$]	0.0207, 0.0497[1)]
data/restraints/parameters	1412/0/127

Note: 1) $w=1/[\sigma^2(F_o^2)+(0.0256P)^2+0.1600P]$, where $P=(F_o^2+2F_c^2)/3$

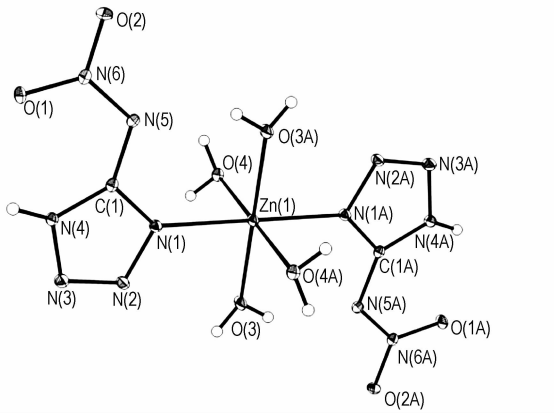

Fig. 1 Molecular unit of 5-$Zn(NATZ)_2(H_2O)_4$

In the $Zn(5\text{-NATZ})_2(H_2O)_4$ molecular structure, the 5-NATZ form the plane *A*, $-2.917x+5.984y+2.977z=2.9493$, and the deviation is 0.0240. Since the torsion angles of Zn(1)—N(1)—C(1)—N(4) and Zn(1)—N(1)—N(2)—N(3) are −178.31° and 178.40°, respectively. Zn(1) and NATZ almost in the same plane . The plane *B* formed from O(3), Zn(1), N(1), C(1), N(4), N(3) and N(2) is $-2.534x+5.962y+2.935z=3.1051$, and the deviation is 0.0513. The angle between *A* and B is 3.7°. O(4), Zn(1) and N(1) formed the plane *C*, $6.083x-0.820y-0.770z=2.2467$, and the deviation is 0. The angles of the plane *C* from *A* and *B* are 95.8° and 92.1°, respectively, which indicates that the plane *A* and *B* are perpendicular to the plane *C*. The whole molecule is central symmetrical.

The O—H···N weak hydrogen bonds between 5-NATZ groups and water ligands were observed in $[Zn(5\text{-NATZ})_2(H_2O)_4]_n$ molecules. It can be seen from the packing diagram (Fig. 2) that all intermolecular hydrogen bonds extend the structure into a 3D supramolecular structure and make an important contribution to enhance the thermal stability of the complex.

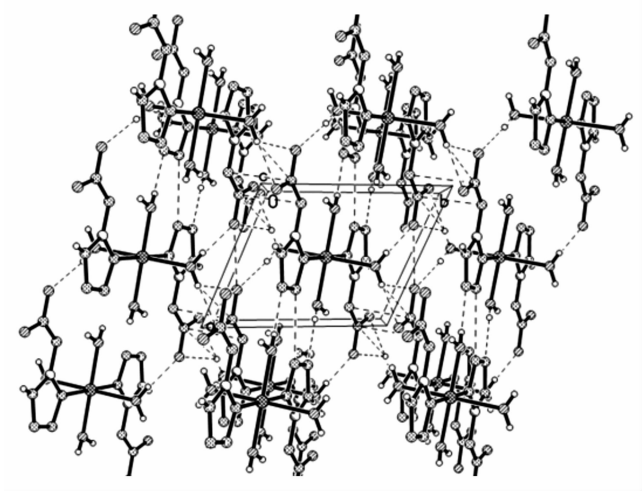

Fig. 2 Packing diagram of $Zn(5\text{-NATZ})_2(H_2O)_4$

Above all, the novel nitrogen-rich energetic compound $Zn(5\text{-NATZ})_2(H_2O)_4$ was synthesized from the corresponding 5-NATZ and $Zn(NO_3)_2\cdot 6H_2O$, which was characterized using X-ray single crystal diffraction. The crystal data indicate that the compound belongs to triclinic, space group P-1. Its crystal structure show that the Zn^{II} ion exhibits a slightly distorted octahedral configuration and the whole molecule is central symmetrical. Its intermolecular hydrogen bonds make a vital contribution to the stable 3D architecture.

References:

[1] Huynh M H V, Hiskey M A, Chavez D E, et al. Synthesis, characterization, and energetic properties of diazido heteroaromatic high-nitrogen C-N compound[J]. *J Am Chem Soc*, 2005, 127(36): 12537−12543.

[2] Neutz J G O, Schaufele S, et al. Synthesis, characterization and thermal behaviour of guanidinium-5-aminotetrazolate (GA)-a new nitrogen-rich compound[J]. *Propellants Expls Pyrotech*, 2003, 28(4): 181−188.

[3] Lesnikovich a I I O A, Levchik S V, et al Thermal decomposition of aminotetrazoles[J]. *Thermochim Acta*, 2002, 388(1−2): 233−251.

[4] Singh R P, Verma R D, Meshri D T, et al. Energetic nitrogen-rich salts and ionic liquids[J]. *Angew Chem*, 2006, 45: 3584−3601.

[5] Klapotke T M. New nitrogen-rich high explosives[J]. *Structure and Bonding*, 2007, 125: 85−121.

[6] Klapoetke T M, Stierstorfer J, Weber B. New energetic materials: Synthesis and characterization of copper 5-nitriminotetrazolates[J]. *Inorganica Chimica Acta*, 2009, 362(7): 2311−2320.

[7] Fischer N, Klapoetke T M, Stierstorfer J. Calcium 5-Nitriminotetrazolate-A green replacement for lead azide in priming charges [J]. *Journal of Energetic Materials*, 2011, 29(1): 61−74.

[8] Semenov S N, Rogachev A Y, Eliseeva S V, et al. 5-Nitroaminotetrazole as a building block for extended network structures: Syntheses and crystal structures of a number of heavy metal derivatives[J]. *Polyhedron*, 2007, 26(17): 4899−4907.

[9] Sheldrick G M. SHELXS-97, program for the refining of crystal structure[CP]. Göttingen: University of Göttingen, 1997.

[10] Sheldrick G M. SHELXL-97, program for the solution of crystal structure[CP]. Göttingen: University of Göttingen, 1997.

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