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Research paper

Two new complexes based on 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ): Synthesis, crystal structure and properties

Tianhong Zhou [a], Xiaohui Wang [a], Kangzhen Xu [a,*], Jirong Song [a], Fengqi Zhao [b]

[a] School of Chemical Engineering, Northwest University, Xi'an 710069, China
[b] Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

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ABSTRACT

Two new energetic complexes, $Zn(NH_3)_2(DNDZ)_2$ and $Cu(NH_3)_2(DNDZ)_2$ [DNDZ = 2-(dinitromethylene)-1,3-diazacyclopentane], were first synthesized and structurally characterized. $Zn(NH_3)_2(DNDZ)_2$ crystallizes in tetragonal crystal system with space group $P_{4(1)2(1)2}$, but the crystal of $Cu(NH_3)_2(DNDZ)_2$ is monoclinic with space group of $C2/c$. Zn^{2+} ion is coordinated by four N atoms from two NH_3 molecules and two $DNDZ^-$ anions to form a distorted tetrahedron structure in $Zn(NH_3)_2(DNDZ)_2$, while central Cu^{2+} ion coordinates with two O atoms and two N atoms from two $DNDZ^-$ anions and two N atoms of two NH_3 molecules to form a six-coordinated octahedral structure in $Cu(NH_3)_2(DNDZ)_2$. The thermal decomposition behaviors of the two complexes were studied with DSC and TG/DTG methods. Self-accelerating decomposition temperatures and critical temperatures are 164.7 and 166.4 °C for $Zn(NH_3)_2(DNDZ)_2$, and 149.6 and 150.8 °C for $Cu(NH_3)_2(DNDZ)_2$, respectively. The impact and friction sensitivities are >17.0 J and 36% for $Zn(NH_3)_2(DNDZ)_2$, and >10.0 J and 56% for $Cu(NH_3)_2(DNDZ)_2$, respectively. The two complexes exhibit lower sensitivity than analogous FOX-7 complexes.

1. Introduction

The design and synthesis of new high-energy compounds are the significant direction of energetic materials. As a new high-energy insensitive material, 1,1-diamino-2,2-dinitroethylene (FOX-7) received much attention for its good application properties since first synthesized in 1998 [1]. It has a density of 1.885 g cm^{-3}, a heat of formation of 133.7 kJ mol^{-1}, a same insensitive to TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and a similar energy density with RDX (1,3,5-trinitroperhydro-1,3,5-triazine) and HMX (cyclotetramethylene tetranitramine) [1,2]. FOX-7 has been considered as the main component of insensitive ammunitions and solid propellants in future [3–11].

FOX-7 is a nitro-enamine compound [12]. Though molecular composition and structure of FOX-7 are every simple, its chemical reactivity is abundant and surprising [13–17]. 2-(Dinitromethylene)-1,3-diazacyclopentane (DNDZ) as a derivative of FOX-7 was prepared by the reaction of FOX-7 and ethanediamine in *N*-methylpyrrolidone (NMP) at 110 °C for 8 h [18]. A glance of the molecular structure tells that DNDZ also belongs to a typical "push-pull" nitro-enamine compound [12], has some tautomers and resonances and exhibits special acidity (Scheme 1). Specifically, after two adjacent amino groups are converted into a five-number heterocycle, the conjugative effect of C–C double bond and the five-number ring is enhanced. Therefore, the stability and sensitivity of DNDZ are better than those of FOX-7 [18].

Some energetic metals (potassium salt, cesium salt and guanidine salt) of DNDZ have been reported recently by our group [19–21]. So we want to prepare some DNDZ complexes like many FOX-7 complexes [22–27], and explore their structure-property relationship. In this paper, we will first report two new DNDZ complexes and compare their properties with that of similar FOX-7 complexes.

2. Experimental

2.1. Synthesis

All chemicals were analytical-grade commercial products. K(DNDZ) was prepared according to Ref. [28].

$Zn(NH_3)_2(DNDZ)_2$ was synthesized as follows: K(DNDZ) (0.212 g, 1 mmol) was put into aqueous ammonia solution (10 mL) and stirred until clear, followed by adding zinc nitrate (0.169 g, 1 mmol). After reacting for 2 h at ambient temperature, the resulting mixture was filtered and allowed to evaporate in an

* Corresponding author.
E-mail address: xukz@nwu.edu.cn (K. Xu).

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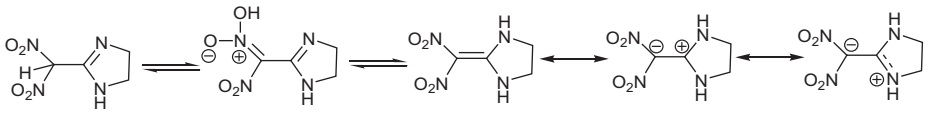

Scheme 1. Tautomers and resonances of DNDZ.

undisturbed condition at ambient temperature. After about 14 days, many yellow crystals of $Zn(NH_3)_2(DNDZ)_2$ formed, which were filtered, washed with water, and dried under vacuum, yielding 0.251 g (56%). IR (KBr): 3327, 2866, 2474, 1583, 1495, 1388, 1188, 1005, 808, 739, 667 cm^{-1}; Anal. Calcd. (%) for $C_8H_{16}N_{10}O_8Zn$: C 21.56, H 3.62, N 31.43; found: C 21.51, H 3.66, N 31.40.

$Cu(NH_3)_2(DNDZ)_2$ was synthesized as follows: K(DNDZ) (0.212 g, 1 mmol) was put into aqueous ammonia solution (5 mL) and stirred until clear, followed by adding copper nitrate (0.121 g, 0.5 mmol). After reacting for 2 h at ambient temperature, the resulting mixture was filtered and allowed to evaporate in an undisturbed condition at ambient temperature. After about 14 days, many dark purple crystals of $Cu(NH_3)_2(DNDZ)_2$ formed, which were filtered, washed with water, and dried under vacuum, yielding 0.275 g (62%). IR (KBr): 3425, 3363, 3332, 3271, 3192, 2974, 2882, 2457, 1841, 1743, 1626, 1572, 1488, 1393, 1283, 1200, 1138, 1044, 1019, 956, 813, 773, 746 cm^{-1}; Anal. Calcd. (%) for $C_8H_{16}N_{10}O_8Cu$: C 23.56, H 4.17, N 30.53; found: C 23.39, H 4.37, N 30.41.

2.2. Experimental equipments and conditions

Elemental analyses were performed on a VarioEL III elemental analyzer (Elementar, Germany). IR spectra were determined on EQUINX55 with KBr pellets. The DSC experiments were performed using a DSC200 F3 apparatus (NETZSCH, Germany). The TG/DTG experiment was determined using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min^{-1}. The impact and friction sensitivities were determined by using a ZBL-B impact sensitivity instrument and a MGY-2 friction sensitivity instrument (Nachen Co., China), respectively. The mass of fall-weight is 2.0 kg. The swing angle and gauge pressure are 50° and 0.6 MPa. The sample used for each test is 30 mg.

2.3. Determination of single-crystal structure

Single crystals for the two complexes were obtained by solvent evaporation method at ambient temperature. X-ray diffraction data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.071073 nm). The structures were solved by the direct methods (*SHELXTL-97*) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [29,30]. The hydrogen atoms were added according to the theoretical models. Crystal data and refinement results are summarized in Table 1. Selected bond lengths and bond angles of $Zn(NH_3)_2(DNDZ)_2$ and $Cu(NH_3)_2(DNDZ)_2$ are listed in Table 2 [18].

3. Results and discussion

3.1. Structural characterizations

$Zn(NH_3)_2(DNDZ)_2$ crystallized in the tetragonal crystal system with space group $P_{4(1)2(1)2}$. The crystal cell has same *a* (length) and *b* (width) as 8.5839 Å. But the crystal of $Cu(NH_3)_2(DNDZ)_2$ is monoclinic with space group of *C*2/*c*. To the two complexes, each crystal cell includes four molecules.

Table 1
Crystal data and structures refinement details of $Zn(NH_3)_2(DNDZ)_2$ and $Cu(NH_3)_2(DNDZ)_2$.

Compound	$Zn(NH_3)_2(DNDZ)_2$	$Cu(NH_3)_2(DNDZ)_2$
Chemical formula	$C_8H_{16}N_{10}O_8Zn$	$C_8H_{16}N_{10}O_8Cu$
Formula weight ($g \cdot mol^{-1}$)	445.68	443.86
Temperature (K)	296(2)	296(2)
Crystal system	Tetragonal	Monoclinic
Space group	$P_{4(1)2(1)2}$	*C*2/*c*
a (Å)	8.5839(8)	13.313(4)
b (Å)	8.5839(8)	8.558(2)
c (Å)	22.244(3)	14.320(4)
β (°)	90	98.473(4)
Volume ($Å^3$)	1639.0(3)	1613.7(8)
Z	4	4
D_{calc} ($g\ cm^{-3}$)	1.806	1.827
Absorption coefficient (mm^{-1})	1.566	1.422
F(0 0 0)	912	908
θ range (°)	2.54–25.09	2.84–25.09
Index ranges	$-4 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 10$, $-26 \leqslant l \leqslant 26$	$-14 \leqslant h \leqslant 15$, $-10 \leqslant k \leqslant 9$, $-17 \leqslant l \leqslant 13$
Reflections collected	8179	3800
Reflections unique	1463	1438
Goodness-of-fit on F^2	1.049	1.109
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1126$	$R_1 = 0.0349$, $wR_2 = 0.0965$
R indices (all data)	$R_1 = 0.0448$, $wR_2 = 0.1140$	$R_1 = 0.0377$, $wR_2 = 0.0991$
Largest diff. peak and hole (e $Å^{-3}$)	0.21 and −0.23	0.916 and −0.538

Table 2
Selected bond lengths (Å) and angles (°) of $Zn(NH_3)_2(DNDZ)_2$ and $Cu(NH_3)_2(DNDZ)_2$.

$Zn(NH_3)_2(DNDZ)_2$		$Cu(NH_3)_2(DNDZ)_2$	
Zn1–N3	1.989(4)	Cu1–N3A#2	1.987(2)
Zn1–N3A#1	1.989(4)	Cu1–N3	1.987(2)
Zn1–N5A #1	2.035(4)	Cu1–N5A#2	2.020(2)
Zn1–N5	2.035(4)	Cu1–N5	2.020(2)
		Cu1–O2A#2	2.424(2)
		Cu1–O2	2.424(2)
N3A#1–Zn1–N3	105.9(2)	N3A#2–Cu1–N3	92.0(1)
N3A#1–Zn1–N5	106.8(2)	N3A#2–Cu1–N5A#2	166.5(1)
N3A#1–Zn1–N5A#1	112.9(2)	N3–Cu1–N5A#2	90.3(1)
N3–Zn1–N5	112.9(2)	N3A#2–Cu1–N5	90.3(1)
N3–Zn1–N5A#1	106.8(2)	N3–Cu1–N5	166.5(1)
N5–Zn1–N5A#1	111.6(2)	N5A#2–Cu1–N5	90.6(1)
		N3A#2–Cu1–O2A#2	75.1(1)
		N3–Cu1–O2A#2	91.6(1)
		N5A#2–Cu1–O2A#2	91.5(1)
		N5–Cu1–O2A#2	101.8(1)
		N3A#2–Cu1–O2	91.6(1)
		N3–Cu1–O2	75.1(8)
		N5A#2–Cu1–O2	101.8(1)
		N5–Cu1–O2	91.5(1)
		O2A#2–Cu1–O2	161.1(1)

Symmetry transformation: #1 y, x, −z; #2 −x + 1, y, −z + 1/2.

As shown in Fig. 1, complex $Zn(NH_3)_2(DNDZ)_2$ consisted of one Zn^{2+} ion, two $DNDZ^-$ anions and two ammonia molecules. The whole molecule exhibits a chiral structure. Zn^{2+} ion was coordinated by four N atoms from two NH_3 molecules and two $DNDZ^-$