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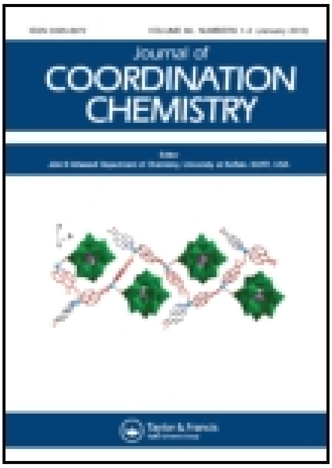

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Synthesis and characterization of a new cadmium complex based on 1,1-diamino-2,2-dinitroethylene

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Synthesis and characterization of a new cadmium complex based on 1,1-diamino-2,2-dinitroethylene

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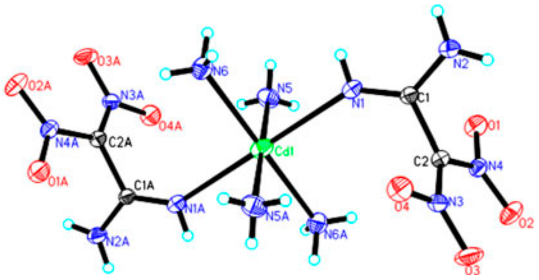

A new cadmium complex of 1,1-diamino-2,2-dinitroethylene (FOX-7) was synthesized and structurally determined. Central Cd^{2+} is coordinated by six nitrogens from four NH_3 molecules and two $FOX\text{-}7^{-}$ anions to form an octahedral structure. The thermal decomposition of $Cd(NH_3)_4(FOX\text{-}7)_2$ was studied with differential scanning calorimeter and TG–DTG methods. The apparent activation energy and pre-exponential constant of the exothermic process are 220.6 kJ M^{-1} and $10^{17.86}$ s^{-1}, respectively. $Cd(NH_3)_4(FOX\text{-}7)_2$ is sensitive.

Keywords: 1,1-Diamino-2,2-dinitroethylene (FOX-7); Cadmium complex; Crystal structure; Thermal behavior

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a high-energy material with good thermal stability and low sensitivity, with a density of 1.885 g cm^{-3}, a heat of formation of 133.7 kJ M^{-1}, a similar insensitivity to TATB (1,3,5-triamino-2,4,6-trinitrobenzene), and a close energy density with RDX (1,3,5-trinitroperhydro-1,3,5-triazine) [1, 2]. Since first synthesized in 1998 [1], FOX-7 received much attention and was considered as the main component of insensitive ammunitions and solid propellants [3–11]. FOX-7 is a nitro-enamine compound and exhibits certain acidic properties [12–14]. So, FOX-7 can react

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*Corresponding author. Email: xukz@nwu.edu.cn with strong alkalis to prepare some energetic salts, such as potassium salt, cesium salt, and guanidine salt [15–20]. Other salts and metal complexes of FOX-7 also could be synthesized through replacement reaction. Garg and He *et al.* reported Ag(amine)(FOX-7), Cu(amine)$_2$(FOX-7)$_2$, and other FOX-7 complexes recently [21–24]. In this article, we report a cadmium-FOX-7 complex [Cd(NH$_3$)$_4$(FOX-7)$_2$].

The light-yellow blocky crystals of Cd(NH$_3$)$_4$(FOX-7)$_2$ were synthesized by reacting K (FOX-7)·H$_2$O and Cd(NO$_3$)$_2$·6H$_2$O in excess 28% ammonia water solution at room temperature for seven days with the evaporation of solvent. The crystals of Cd(NH$_3$)$_4$(FOX-7)$_2$ are not stable in air for a long time, so we put them in vaseline before X-ray diffraction. Yield 48%. Anal. Calcd (%) for $C_4H_{18}N_{12}O_8Cd$: C, 10.12; H, 3.822; N, 35.41. Found (%): C, 10.10; H, 3.16; N, 35.39. IR (KBr): 3408, 3329, 1642, 1529, 1471, 1392, 1241, 1125, 1022, 839, 748 cm^{-1}.

Single crystals suitable for X-ray measurement were obtained by slow evaporation of solution. A bright-yellow crystal with dimensions of 0.28 mm × 0.22 mm × 0.18 mm was chosen for X-ray determination. The data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.071073 nm). The structure was solved by direct methods (SHELXTL-97) and refined by full-matrix-block least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [25, 26]. The hydrogens were added according to theoretical models. Crystal data and refinement results are summarized in table 1.

Cd(NH$_3$)$_4$(FOX-7)$_2$ crystallized in the monoclinic crystal system with space group $P2_1/n$ containing two molecules per unit cell. As shown in figure 1, Cd(NH$_3$)$_4$(FOX-7)$_2$ has a Cd^{2+}, two FOX-7$^-$ anions, and four ammonia molecules. The whole complex exhibits a centrosymmetric structure around Cd^{2+} (symmetry transformation: #1 = $-x + 1$, $-y$, $-z + 1$). Central Cd^{2+} is connected with six nitrogens from four ammonia molecules and

Table 1. Crystal data and structure refinement details.

Chemical formula	$C_4H_{18}N_{12}O_8Cd$
Formula weight (g M^{-1})	474.70
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.4112(8)
b (Å)	7.4767(6)
c (Å)	11.7862(9)
β (°)	101.7180(10)
Volume (Å^3)	812.05(11)
Z	2
D_{Calcd} (g cm^{-3})	1.941
Absorption coefficient (mm^{-1})	0.1412
F (0 0 0)	476
θ Range (°)	2.53–25.09
Index ranges	$-10 \le h \le 11$, $-8 \le k \le 8$, $-14 \le l \le 11$
Reflections collected	1433
Reflections unique	1345
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.164
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0177$, $wR_2 = 0.0478$
R indices (all data)	$R_1 = 0.0189$, $wR_2 = 0.0486$
Largest diff. peak and hole (e Å^{-3})	0.292 and −0.204

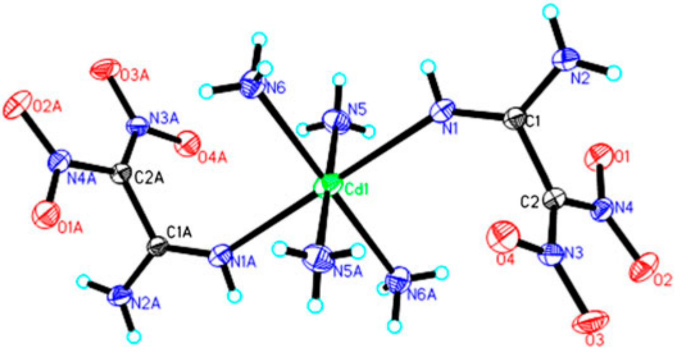

Figure 1. Molecular structure of $Cd(NH_3)_4(FOX\text{-}7)_2$.

two FOX-7^- anions (Cd–N1 = 2.4707 Å; Cd–N5 = 2.3303 Å; Cd–N6 = 2.3379 Å) in an octahedral structure, two nitrogens from two FOX-7^- anions (N1 and N1A) are two apexes. Comparing with the structures of analogous $Cu(NH_3)_2(FOX\text{-}7)_2$ and $Zn(NH_3)_2(FOX\text{-}7)_2$ [21, 24], the two compounds are centrosymmetric on metal ion and two FOX-7^- anions are coordinated, but the central metal ion in the above two complexes have a planar and a tetrahedral structure, respectively. So the central metal ion decides the structural result.

In addition, nine kinds of weak N–H···O hydrogen-bond interactions exist in crystal packing of $Cd(NH_3)_4(FOX\text{-}7)_2$. Four hydrogen-bond interactions (two kinds) (N2···O2#2 = 3.186 Å, N2···O3#2 = 3.252 Å, symmetry transformations: #2 = $-x$, $-y + 1$, $-z + 1$) between two adjacent FOX-7^- anions make $Cd(NH_3)_4(FOX\text{-}7)_2$ molecule form a 1-D chain. There are four weak N–H···O hydrogen-bond interactions (two kinds) between two adjacent 1-D chains (N5···O4#3 = 3.135 Å, N5···O3#4 = 3.245 Å, symmetry transformations: #3 = $-x + 1$, $-y$, $-z + 1$; #4 = $x + 1/2$, $-y + 1/2$, $z + 1/2$), which connect them to form a 2-D layer infinite network (figure 2). Five other kinds of N–H···O interactions (N6···O1#5 = 3.066 Å, N1···O3#4 = 3.055 Å, N2···O1#6 = 3.066 Å, N2···O2#4 = 3.188 Å, N6···O4#7 = 3.140 Å, symmetry transformations: #5 = $x + 1$, y, z; #6 = $-x + 1/2$, $-y + 1/2$, $-z + 3/2$; #7 = $-x + 1$, $-y + 1$, $-z + 1$) exist in two adjacent 2-D layers and lead to the formation of a 3-D network as shown in figure 3, in which various channels are formed and

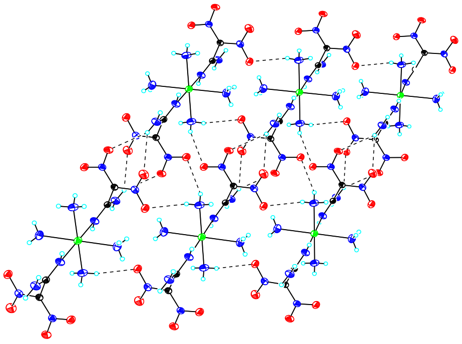

Figure 2. 2-D layer structure of $Cd(NH_3)_4(FOX\text{-}7)_2$.

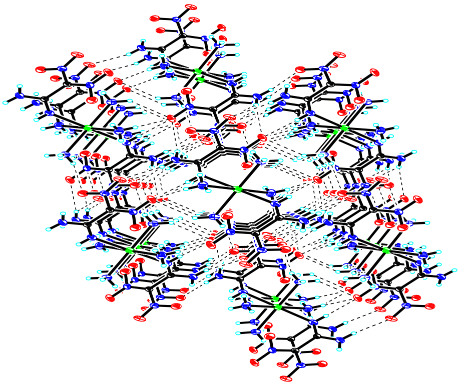

Figure 3. Crystal packing of $Cd(NH_3)_4(FOX\text{-}7)_2$.

sustained by covalent bonds, coordination bonds, and hydrogen bonds. The packing is highly ordered.

The space configuration of $FOX\text{-}7^{-}$ changes from one plane to two approximate orthogonal planes (non-hydrogen atoms) [27], supporting with torsion angles of N1–C1–C2–N3 (−88.3°), N2–C1–C2–N3 (92.05°), N1–C1–C2–N4 (101.9°), and N2–C1–C2–N4 (−77.8°), and the intersection of two approximate orthogonal planes is C1–C2 bond. This structural change also can be found in other salts of FOX-7 [17, 24]. The bond lengths and bond angles change greatly from molecular state to ionic state. Theoretical C1–C2 double bond (1.493 Å) in $FOX\text{-}7^{-}$ anion is much closer to C–C single bond (1.53 Å) than that in FOX-7 molecule (1.456) [27]. Two equal-length C1–N1 and C1–N2 bonds (1.32 Å) present big deviations (1.280 and 1.346 Å). C1–N1 in $FOX\text{-}7^{-}$ is a typical C–N double bond. FOX-7 has changed into its one tautomer format.

Differential scanning calorimeter (DSC) experiments were performed using a DSC200 F3 apparatus (NETZSCH, Germany) under a nitrogen atmosphere at a flow rate of 80 mL min^{-1}. The heating rates were 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 °C min^{-1} from ambient temperature to 450 °C, respectively. The thermogravimetry/differential thermogravimetry (TG/DTG) experiment was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min^{-1}. The heating rate was 10.0 °C min^{-1} from ambient temperature to 350 °C. Typical DSC and TG–DTG curves (figure 4) indicate that the

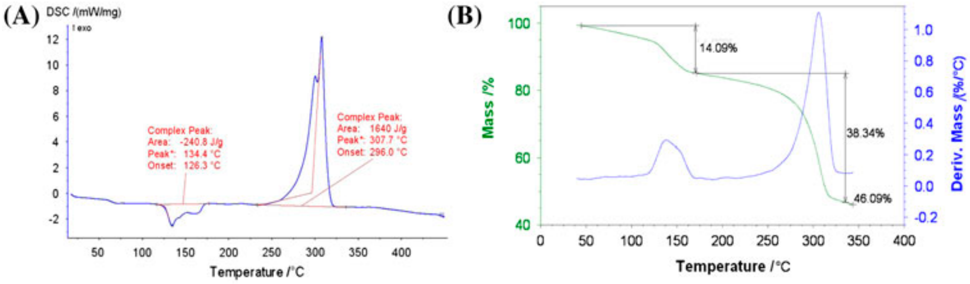

Figure 4. DSC (A) and TG/DTG (B) curves of $Cd(NH_3)_4(FOX\text{-}7)_2$.

thermal decomposition behavior of $Cd(NH_3)_4(FOX\text{-}7)_2$ can be divided into two obvious decomposition stages. The first stage is an endothermic decomposition process, occurring at 120–180 °C with a mass loss of about 14.09%, which is consistent with the theoretical value (14.3%) of losing four ammonia molecules. The extrapolated onset temperature, peak temperature, and decomposition enthalpy of the process are 126.3 °C, 134.4 °C, and 240.8 J g^{-1} at a heating rate of 10.0 °C min^{-1}, respectively. The second is an intense exothermic decomposition process with a mass loss of about 38.34% from 180 to 330 °C, and the extrapolated onset temperature, peak temperature, and decomposition enthalpy of the process are 296.0 °C, 307.7 °C, and −1660 J g^{-1} at a heating rate of 10.0 °C min^{-1}, respectively. The final residue at 350 °C is about 46.09%, which should be CdO (27.05%) and some organic matter. The thermal behavior of $Cd(NH_3)_4(FOX\text{-}7)_2$ is vastly different from those of $Cu(NH_3)_2(FOX\text{-}7)_2$ and $Zn(NH_3)_2(FOX\text{-}7)_2$, which have no endothermic decomposition process of losing ammonia [28, 29]. Maybe weak coordination between Cd^{2+} and ammonia leads to the special result.

A multiple heating method was employed to obtain the kinetic parameters [the apparent activation energy (E) and pre-exponential constant (A)] of the exothermic decomposition process (table 2) [30, 31]. The calculated results indicate that E obtained by Kissinger method is consistent with that by Ozawa method and the linear correlation coefficients (r) are all close to 1, so the result is credible.

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two important parameters required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability [32, 33]. T_{SADT} and T_b for $Cd(NH_3)_4(FOX\text{-}7)_2$ are 275.3 °C and 287.2 °C, respectively. The impact sensitivity for $Cd(NH_3)_4(FOX\text{-}7)_2$ was tested to be >8.0 J, which is lower than that of $Cu(NH_3)_2(FOX\text{-}7)_2$ (>5 J) [21], much higher than that of FOX-7 (>24.7 J) [2], but close to that of $Zn(NH_3)_2(FOX\text{-}7)_2$ (>9 J) and RDX (>7.4 J) [24, 2]. The result should be supported by their crystal structures and the effects of metal ion to energetic components. Cu^{2+} has good catalytic action to energetic components, so the sensitivity of compound will descend with the introduction of Cu^{2+} to the insensitive FOX-7. However, Zn^{2+} and Cd $^{2+}$ ions have no catalytic action, so $Zn(NH_3)_2(FOX\text{-}7)_2$ and $Cd(NH_3)_4(FOX\text{-}7)_2$ exhibit lower sensitivity than $Cu(NH_3)_2(FOX\text{-}7)_2$. Sensitivity rises greatly with the introduction of metal ion and ammonia molecules, which is consistent with the change of thermal stability. The introduction of metal ion and ammonia molecules can result in increased instability.

In conclusion, $Cd(NH_3)_4(FOX\text{-}7)_2$ was synthesized and structurally determined. $Cd(NH_3)_4(FOX\text{-}7)_2$ crystallized in the monoclinic crystal system with space group $P2_1/n$. Central Cd^{2+} forms a centrosymmetric octahedral structure. The thermal decomposition of $Cd(NH_3)_4(FOX\text{-}7)_2$ exhibits an endothermic process of losing four ammonia molecules and an

Table 2. The values of T_e, T_p, and kinetic parameters of the exothermic decomposition process determined from the DSC curves at various heating rates (β).

β (K min^{-1})	T_e (°C)	T_p (°C)	E_k (kJ M^{-1})	log (A/s^{-1})	r_k	E_O (kJ M^{-1})	r_O
2.5	282.4	294.1	220.6	17.86	0.9714	218.9	0.9737
5.0	286.7	303.2					
7.5	293.3	305.5					
10.0	296.4	307.7					
12.5	299.1	314.6					

Notes: β, the heating rate; T_e, extrapolated onset temperature; T_p, peak temperature; subscript k, data obtained by Kissinger method; subscript o, data obtained by Ozawa method.

intense exothermic process. The sensitivity of $Cd(NH_3)_4(FOX\text{-}7)_2$ is lower than that of $Cu(NH_3)_2(FOX\text{-}7)_2$, much higher than that of FOX-7, but close to that of $Zn(NH_3)_2(FOX\text{-}7)_2$ and RDX.

Supplementary material

CCDC-946932 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2, 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

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