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Three unexpected cadmium(II)-based energetic metal–organic frameworks derived from 2-(dinitromethylene)-1,3-diazacyclopentane

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ABSTRACT

One cadmium–DNDZ [DNDZ = 2-(dinitromethylene)-1,3-diazacyclopentane] complex $[Cd(NH_3)_4(DNDZ)_2$ (**1**)] and three unexpected cadmium–ADNA [ADNA = N-(2-aminoethyl)-2,2-dinitroacetamide] metal–organic frameworks (MOFs) $\{[Cd(NH_3)_2(ADNA)_2]_n$ (**2**), $[Cd(CH_3NH_2)_2(ADNA)_2]_n$ (**3**) and $[Cd(CH_3CH_2NH_2)_2(ADNA)_2]_n$ (**4**)} were first synthesized by reactions of cadmium nitrate and DNDZ potassium salt in different aqueous amines. DNDZ molecules underwent a ring-opening reaction resulting in the formation of a new chain-like molecule ADNA, which is found for the first time and only in the cadmium(II) coordination environment compared with the previous other metal–DNDZ complexes, so the cadmium(II) ions should have special catalysis to the ring-opening reaction. The single crystal structures of complexes **1**, **3** and **4** were obtained. The central cadmium(II) ion can form a distorted octahedral structure with six coordination atoms. Thermal behaviors and impact sensitivities of the four complexes were studied. Complex **1** presents one exothermic decomposition process (248.17 °C) after two consecutive endothermic processes, but the three MOFs present only one exothermic decomposition process and their peak temperatures are close to one another (about 168 °C). The impact sensitivities of the four complexes are tested to be >20 J for **1**, >16 J for **2**, >17 J for **3** and >11 J for **4**, respectively.

1. Introduction

Energetic metal–organic frameworks (MOFs), as a novel class of energetic materials, have attracted a lot of interest because of their intriguing structures, high densities and good properties of detonation [1–8]. In general, energetic MOFs usually consist of metal cations and energetic nitrogen-rich ligands [9–11]. For example, Wang *et al.* [12] recently reported a three-dimensional (3D) energetic MOFs (CEMOF-1), with high detonation velocity (10.07 km s^{-1}), high detonation pressure (49.36 GPa), and good thermal stability with a decomposition temperature of 445 °C, synthesized by using cadmium(II) and 4-amino-4H-1,2,4-triazole-3,5-diol as the metal cation and the ligand respectively. The study of structure and properties of energetic MOFs is of great significance to energetic materials.

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a famous high-energetic material with high thermal stability and low sensitivity [13–28]. FOX-7 has been considered as the main component of insensitive ammunition and solid propellants and has been continually reported since it was first reported in 1998 [29–34]. FOX-7 presents certain acidic properties and can react with some nucleophiles to form many new energetic derivatives [35–42]. 2-(Dinitromethylene)-1,3-diazacyclopentane (DNDZ) is a closed-loop derivative of FOX-7, possesses similar characteristics with FOX-7 and presents many tautomers and resonances (Scheme 1) [43,44]. DNDZ exhibits better application performance than FOX-7 [45,46]. After two amino groups become a symmetrical five-number ring, the conjugative effect is further improved, which makes DNDZ more stable than FOX-7 [37,47]. Zinc, copper, nickel and silver complexes of DNDZ have been reported recently by our research group [48–50].

In order to further explore the structure–property relationship of metal–DNDZ complexes, we tried to prepare cadmium–DNDZ complexes in aqueous ammonia and different aqueous amines. However, a new molecule [N-(2-aminoethyl)-2,2-dinitroacetamide (ADNA)] was found due to the ring-opening reaction of the DNDZ molecule. Thus, we obtained one cadmium–DNDZ complex and three new one-dimensional (1D) cadmium–ADNA energetic MOFs surprisingly through in-situ reactions. In addition, although we tried to change reaction conditions, all the attempts to prepare cadmium–DNDZ complexes and MOFs with ethylenediamine failed. In this paper, we mainly report the syntheses, crystal structures and thermal behaviors of the one cadmium–DNDZ complex

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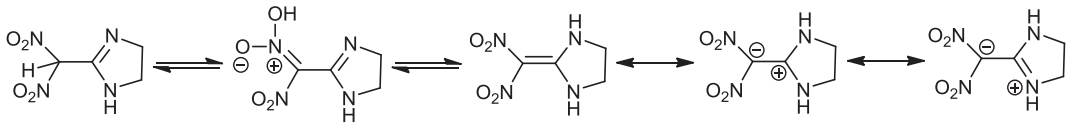

Scheme 1. Tautomers and resonances of DNDZ.

and three new 1D energetic MOFs. This work further enriches research on DNDZ.

2. Experimental

2.1. General methods

IR spectra were measured with EQUINX55 spectrometer via KBr pellets for solids. Elemental analyses (C, H and N) were performed on VarioEL III elemental analyzer. Thermogravimetry/differential thermogravimetry (TG/DTG) experiments were determined by SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min^{-1}, and the heating rate was 10.0 °C min^{-1} from ambient temperature to 400 °C. The differential scanning calorimetry (DSC) curves under the condition of flowing nitrogen gas were obtained by NETZSCH 200 *F3* instrument over the range of 50–300 °C at heating rates of 5.0, 7.5, 10.0 and 12.5 °C min^{-1} respectively. The impact sensitivity experiments were determined by using a ZBL-B impact sensitivity instrument, and the mass of fall-weight is 2.0 kg.

2.2. Synthesis

All chemicals used for the synthesis were of analytical grade and commercially available, except that K(DNDZ) was prepared according to Ref. [46].

$Cd(NH_3)_4(DNDZ)_2$ (**1**): K(DNDZ) (0.424 g, 2 mmol) and Cd $(NO_3)_2{\cdot}4H_2O$ (0.37012 g, 1.2 mmol in 1 mL of water) were stirred slowly in aqueous ammonia (15 mL, 37% in mass) for 4 h. Gradually buff crystals appeared from the solution and were identified as **1** (yield 65%, 0.345 g). IR (KBr): 409, 430, 474, 590, 665, 754, 773, 806, 920, 951, 989, 1022, 1124, 1190, 1256, 1306, 1344, 1360, 1445, 1481, 1506, 1572, 1614, 2995, 3358 cm^{-1}. *Anal.* Calc. for $C_8H_{22}N_{12}O_8Cd$ (526.79): C, 18.24; H, 4.21; N 31.91. Found: C, 18.15; H, 4.38; N, 31.84%.

$[Cd(NH_3)_2(ADNA)_2]_n$ (**2**): K(DNDZ) (0.424 g, 2 mmol) and Cd $(NO_3)_2{\cdot}4H_2O$ (0.37012 g, 1.2 mmol) were stirred in aqueous ammonia (15 mL, 37% in mass) till yellow precipitates appeared (about 4 h). Then the solution was filtered, and the resulting filtrate stood for 2 weeks to evaporate. Gradually yellow solids appeared from the filtrate and were identified as **2** (yield 32%, 0.169 g). IR (KBr): 722, 748, 792, 821, 873, 1035, 1057, 1104, 1162, 1236, 1329, 1366, 1462, 1512, 1629, 2958, 3321, 3348 cm^{-1}. *Anal.* Calc. for $C_8H_{18}N_{10}O_{10}Cd$ (526.70): C, 18.24; H, 3.44; N, 26.59. Found: C, 18.10; H, 3.51; N, 26.39%.

$[Cd(CH_3NH_2)_2(ADNA)_2]_n$ (**3**): K(DNDZ) (0.424 g, 2 mmol) and Cd $(NO_3)_2{\cdot}4H_2O$ (0.37012 g, 1.2 mmol) were stirred in aqueous methylamine (15 mL, 67% in mass) for 4 h, and a clear solution was obtained. Then let the solution stand for 2 weeks to evaporate. Gradually primrose yellow crystals occurred from the solution and were identified as **3** (yield 76%, 0.4210 g). IR: 615, 638, 752, 762, 910, 991, 1034, 1065, 1123, 1155, 1177, 1258, 1310, 1346, 1385, 1487, 1553, 1587, 1668, 3076, 3260, 3470 cm^{-1}. *Anal.* Calc. for $C_{10}H_{24}N_{10}O_{10}Cd$ (556.77): C, 21.57; H, 4.34; N, 25.16. Found: C, 21.52; H, 4.11; N, 25.13%.

$[Cd(CH_3CH_2NH_2)_2(ADNA)_2]_n$ (**4**): Procedure was the same as that for **3** except replacing aqueous methylamine with aqueous ethylamine (15 mL, 67% in mass). Gradually yellow crystals occurred from the solution and were identified as **4** (yield 67%, 0.3897 g). IR: 571, 619, 750, 771, 822, 889, 1022, 1047, 1103, 1126, 1176, 1248, 1333, 1356, 1466, 1525, 1628, 2937, 3311, 3346, 3348 cm^{-1}. *Anal.* Calc. for $C_{12}H_{28}N_{10}O_{10}Cd$ (584.85): C, 24.64; H, 4.83; N, 23.95. Found: C, 24.59; H, 4.62; N, 23.88%.

Table 1
Crystal data and structure refinement details for **1**, **3** and **4**.

Complexes	**1**	**3**	**4**
Chemical formula	$C_8H_{22}N_{12}O_8Cd$	$C_{10}H_{24}N_{10}O_{10}Cd$	$C_{12}H_{28}N_{10}O_{10}Cd$
Formula weight (g mol^{-1})	526.79	556.77	584.85
T (K)	296(2)	296(2)	296(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	*P*-1	*P*-1
Unit cell dimensions			
a (Å)	8.5306(8)	7.2016(13)	7.1727(10)
b (Å)	15.2063(15)	8.904(3)	8.8214(12)
c (Å)	8.2261(8)	9.3207(16)	9.3114(13)
α (°)	90.00	108.001(3)	72.631(2)
β (°)	118.341(1)	112.637(2)	84.304(2)
γ (°)	90.00	98.858(3)	73.412(2)
V ($Å^3$)	939.18(16)	498.6(2)	538.83(13)
Z	2	1	1
D_{Calc} (g cm^{-3})	1.863	1.848	1.796
Absorption coefficient (mm^{-1})	1.231	1.169	1.087
F(000)	532	282	298
θ range (°)	2.71–26.82	2.53–28.24	2.29–25.99
Index ranges	$-10 \le h \le 9$, $-19 \le k \le 18$, $-10 \le l \le 9$	$-4 \le h \le 9$, $-10 \le k \le 11$, $-12 \le l \le 11$	$-8 \le h \le 8$, $-7 \le k \le 10$, $-11 \le l \le 11$
Reflections collected	5117	2923	2838
Reflections unique	1975 [R_{int} = 0.0203]	2170 [R_{int} = 0.0149]	2037 [R_{int} = 0.0121]
Goodness-of-fit (GOF) on F^2	1.063	1.118	1.062
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0226, wR_2 = 0.0552	R_1 = 0.0240, wR_2 = 0.0679	R_1 = 0.0259, wR_2 = 0.0680
R indices (all data)	R_1 = 0.0262, wR_2 = 0.0573	R_1 = 0.0240, wR_2 = 0.0680	R_1 = 0.0262, wR_2 = 0.0684
Largest difference peak and hole (e $Å^{-3}$)	0.27 and −0.55	0.62 and −0.83	0.68 and −0.76

2.3. Crystal structure determinations

Single-crystal X-ray diffraction data were collected on 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 (SHELXS-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [51,52]. All H atoms could be generated from a difference Fourier map, but those attached to carbon atoms were repositioned geometrically. Crystal data and refinement results are summarized in Table 1.

3. Results and discussion

3.1. Synthetic reactions

We have synthesized zinc, copper, nickel and silver complexes of DNDZ in the previous experiments [48–50], so we continue to