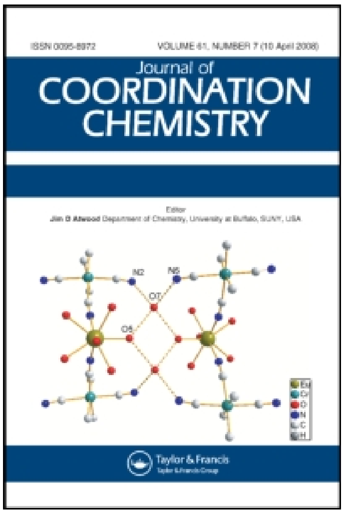

## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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# Syntheses, crystal structures and thermodecomposition behaviors of three energetic compounds

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**To cite this Article** Zhou, Qiu-Ping , Zhang, Guo-Fang , Zhao, Feng-Qi , Li, Ji-Zhen and Fan, Xue-Zhong(2008) 'Syntheses, crystal structures and thermodecomposition behaviors of three energetic compounds', Journal of Coordination Chemistry, 61: 19, 3180 — 3188

**To link to this Article: DOI:** 10.1080/00958970802029807

**URL:** http://dx.doi.org/10.1080/00958970802029807

*Journal of Coordination Chemistry*
Vol. 61, No. 19, 10 October 2008, 3180–3188

# Syntheses, crystal structures and thermodecomposition behaviors of three energetic compounds

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(*Received 29 October 2007; in final form 18 December 2007*)

Three new energetic compounds, nickel(II) 3,5-dinitro-2-pyridonate ($Ni(2DNPO)_2(H_2O)_4$, **1**), copper(II) 3,5-dinitro-4-pyridonate ($Cu(4DNPO)_2(H_2O)_4$, **2**) and cobalt(II) 3,5-dinitro-4-pyridone-*N*-hydroxylate ($[Co(4DNPOH)_2(H_2O)_4]\cdot 2DMF$, **3**·2DMF), were characterized by elemental analysis, FT–IR, TG-DSC and X-ray single crystal diffraction analysis. Complexes **1** and **2** are similar in structure with the metal ion coordinated by oxygen donors of four water molecules on the equatorial position and two nitrogen donors of the pyridone rings of two ligands in the axial positions. The cobalt(II) complex **3**·2DMF is a heavily distorted octahedral geometry. The Co(II) has equatorial positions defined by oxygens of four water molecules. Its axial positions are filled with two oxygen atoms of the pyridone-*N*-hydroxylate of two ligands. The TG-DSC results reveal that **1** is the most stable, with higher initial thermal decomposition temperature and enthalpy. Based on the thermoanalyses, the nickel compound is a promising candidate as a component in catalyzed RDX-CMDB propellants in comparison with our earlier lead(II) analogs.

*Keywords*: Energetic compound; Dinitropyridone; Transition-metal compound; Crystal structure; Thermodecomposition behavior

## 1. Introduction

Energetic catalysts, which usually contain nitro groups are of interest for solid propellants. Energetic catalysts in two-base propellants containing metal salts, particularly copper and lead salts, of polynitrophenols [1], picric acids [2] and NTO [3], have been extensively studied. In contrast, few metal salts of polynitropyridone derivatives, as energetic catalysts, are investigated and no crystal structures have been reported to the best of our knowledge [4]. From 2002, we began to investigate effects of transition metal salts of polynitropyridones on the combustion properties of RDX-composite modified double-base (RDX-CMDB) propellants, and the results showed that 3,5-dinitro-2-pyridonate of lead(II) ($Pb(2DNP)_2$ has the highest catalytic

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*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802029807

efficiency in all six energetic catalyst candidates examined [5]. Additionally, crystal structures of two Pb(II) and Cu(II) salts and a number of alkali and alkaline-earth metal salts derived from three kinds of dinitropyridone ligands, i.e. 2(4)-hydroxyl-3, 5-dinitropyridine(-*N*-oxide) (2HDNP, 4HDNP and 4HDNPO), have been determined and their thermodecomposition behaviors investigated [6]. As an extension of our work, herein we report the syntheses, crystal structures and thermal behaviors of the 3,5-dinitro-2-pyridonate of nickel(II) ($Ni(2DNP)_2(H_2O)_4$, **1**), the 3,5-dinitro-4-pyridonate of copper(II) ($Cu(4DNP)_2(H_2O)$, **2**) and the 3,5-dinitro-4-pyridone-*N*-hydroxylate of cobalt(II) ($[Co(4DNPO)_2(H_2O)_4]\cdot 2DMF$, **3** · 2DMF).

## 2. Experimental

### 2.1. *Syntheses*

All reagents used in the syntheses were of analytical grade and used directly without further purification. The ligands, 2-hydroxyl-3,5-dinitropyridine (2HDNP), 4-hydroxyl-3,5-dinitro-pyridine (4HDNP) and 4-hydroxyl-3,5-dinitropyridine-*N*-oxide (4HDNPO) were synthesized following methods previously described with slight modification [4]. For **1**: to a solution of 2-hydroxyl-3,5-dinitropyridine (1.85 g, 10 mmol) in 60 mL distilled water at 60°C was added nickel carbonate (0.530 g, 5 mmol) under stirring until the precipitate disappeared. The reaction was maintained for at least 30 min for completion and the pH of this solution was approx. 7.0. The water was evaporated completely after filtration and the residue was recrystallized in ethanol to afford green powder 1.65 g (Yield: 77.3%). Complex **2** was prepared by the procedure described in our earlier work [5a] and the cobalt complex **3** · 2DMF was prepared by a procedure similar to that of **1** (Yield: 81.3%). Single crystals of three complexes suitable for single crystal X-ray diffraction were grown from aqueous solution (**1** and **2**) or DMF solution (**3** · 2DMF) by solvent evolution method.

IR spectra of the complexes were recorded on a Perkin–Elmer FT–IR spectrophotometer in the 4000–400 $cm^{-1}$ region using KBr pellets. Carbon, hydrogen and nitrogen were determined by a German Vario EL III analyzer. $Ni(2DNP)_2(H_2O)_4$, **1**, $Cu(4DNP)_2(H_2O)_4$, **2**, and $[Co(4DNPO)_2(H_2O)_4]\cdot 2DMF$, **3** · 2DMF, are consistent with the results of single crystal X-ray diffraction analyses. Anal. Calcd for $C_{10}H_{12}N_6NiO_{14}$, **1**, (%): C, 24.07; H, 2.42; N, 16.84. Found: C, 23.80; H, 2.36; N, 16.41. Anal. Calcd for $C_{10}H_{12}CuN_6O_{14}$, **2**, (%): C, 23.84; H, 2.40; N, 16.68. Found: C, 23.50; H, 2.36; N, 16.41. Anal. Calcd for $C_{16}H_{26}CoN_8O_{18}$, **3** · 2DMF, (%): C, 28.37; H, 3.87; N, 16.54. Found: C, 27.71; H, 3.63; N, 17.07. The TG-DTG curves and DSC curves were obtained with a Model TGA 2950 thermobalance and a Model DSC 190S differential scanning calorimeter made by American TA Company, respectively, using sample less than 1.00 mg with a heating rate of 10°C $min^{-1}$ under flowing $N_2$ gas.

### 2.2. *X-ray diffraction analysis*

Determination of the unit cell and the data collection for **1**, **2** and **3** · 2DMF were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$-$2\theta$ scan technique. The structures were solved by direct methods and refined on $F^2$ by full matrix least-squares with SHELXL-97 [7]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. Data collection detail and structure determination results are summarized in table 1. Selected bond lengths and angles are presented in table 2.

Table 1. Crystal data and structure refinements for **1**, **2** and **3** · 2DMF.

| | **1** | **2** | **3** · 2DMF |
|---|---|---|---|
| Empirical formula | $C_{10}H_{12}N_6NiO_{14}$ | $C_{10}H_{12}CuN_6O_{14}$ | $C_{16}H_{26}CoN_8O_{18}$ |
| Crystal size (mm$^3$) | 0.40 × 0.28 × 0.13 | 0.39 × 0.22 × 0.15 | 0.38 × 0.26 × 0.21 |
| Molecular mass | 498.97 | 503.80 | 677.38 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2(1)/c$ | $P2(1)/n$ | $P2(1)/c$ |
| Unit cell dimensions (Å, °) | | | |
| $a$ | 9.8344(12) | 9.4921(11) | 11.6964(11) |
| $b$ | 6.6582(8) | 8.7001(10) | 9.9132(10) |
| $c$ | 13.4397(17) | 10.2303(11) | 12.1000(12) |
| $\beta$ | 96.8340 | 98.8390(10) | 92.1330(10) |
| $V$ (Å$^3$) | 873.77(19) | 834.81(16) | 1402.0(2) |
| $Z$ | 2 | 2 | 2 |
| Temperature (K) | 291(2) | 291(2) | 291(2) |
| $D_{\mathrm{Calcd}}$ (g cm$^{-3}$) | 1.896 | 2.004 | 1.605 |
| $F(000)$ | 508 | 510 | 698 |
| Reflections collected | 5495 | 6009 | 10394 |
| Independent reflections | 1620 | 1559 | 2603 |
| Data/restraints/parameters | 1620/6/142 | 1559/0/142 | 2603/375/216 |
| Goodness-of-fit on $F^2$ | 1.105 | 1.109 | 1.047 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0237$,<br>$wR_2 = 0.0604$ | $R_1 = 0.0228$,<br>$wR_2 = 0.0626$ | $R_1 = 0.0391$,<br>$wR_2 = 0.0997$ |
| $R$ indices (all data) | $R_1 = 0.0265$,<br>$wR_2 = 0.0624$ | $R_1 = 0.0256$,<br>$wR_2 = 0.0649$ | $R_1 = 0.0460$,<br>$wR_2 = 0.1055$ |

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2** and **3** · 2DMF.

| **1** | | **2** | | **3** · 2DMF | |
|---|---|---|---|---|---|
| Ni(1)–O(7)A | 2.0614(12) | Cu(1)–N(1) | 2.0133(14) | Co(1)–O(1)A | 2.0307(19) |
| Ni(1)–O(7) | 2.0615(12) | Cu(1)–N(1)A | 2.0134(14) | Co(1)–O(1) | 2.0308(19) |
| Ni(1)–O(6)A | 2.0847(13) | Cu(1)–O(6)A | 2.0735(13) | Co(1)–O(8) | 2.118(2) |
| Ni(1)–O(6) | 2.0848(13) | Cu(1)–O(6) | 2.0735(13) | Co(1)–O(8)A | 2.118(2) |
| Ni(1)–N(1)A | 2.1622(15) | Cu(1)–O(7)A | 2.2714(14) | Co(1)–O(7) | 2.1226(19) |
| Ni(1)–N(1) | 2.1622(15) | Cu(1)–O(7) | 2.2715(14) | Co(1)–O(7)A | 2.1226(19) |
| | | | | O(1)–N(1) | 1.352(3) |
| O(7)–Ni(1)–O(6)A | 90.72(5) | N(1)–Cu(1)–O(6) | 90.33(5) | O(1)–Co(1)–O(8)A | 88.25(8) |
| O(7)–Ni(1)–O(6) | 89.28(5) | N(1)–Cu(1)–O(6)A | 89.67(5) | N(1)–O(1)–Co(1) | 119.77(15) |
| O(7)–Ni(1)–N(1) | 91.09(5) | N(1)–Cu(1)–O(7)A | 90.85(6) | O(1)–Co(1)–O(7)A | 88.12(8) |
| O(6)–Ni(1)–N(1) | 88.27(5) | O(6)–Cu(1)–O(7)A | 93.00(5) | O(1)–Co(1)–O(8) | 91.75(8) |
| O(7)–Ni(1)–N(1)A | 88.91(5) | N(1)–Cu(1)–O(7) | 89.15(6) | O(8)–Co(1)–O(7)A | 89.08(8) |
| O(6)–Ni(1)–N(1)A | 91.73(5) | O(6)–Cu(1)–O(7) | 87.00(5) | O(8)–Co(1)–O(7) | 90.92(8) |
| O(7)A–Ni(1)–O(6)A | 89.28(5) | N(1)A–Cu(1)–O(7) | 90.85(6) | O(1)–Co(1)–O(7) | 91.88(8) |
| | | | | O(7)–Co(1)–O(7)A | 180.00 |

Symmetry transformations (A) in **1** and **2**: $-x$, $-y+1$, $-z$; (A) in **3** · 2DMF: $-x$, $-y$, $-z$.

## 3. Results and discussion

### 3.1. *Crystal structures*

The molecular structure of **1** is shown in figure 1. Selected bond distances and angles are listed in table 2. The nickel(II) has slightly distorted octahedral coordination, equatorially by four waters and axially by two nitrogens from two ligands, with an inversion center located on Ni. Each pyridone is monodentate. The bond distances of Ni–$O_{water}$ are slightly different at adjacent positions with the average distance 2.0731(13) Å. The two Ni–$N_{py}$ bond distances are equal (2.1622(15) Å) and considerably longer than those of Ni–$O_{water}$ bonds. Thus, the coordination geometry around nickel is an elongated octahedron.

There exist a number of intra- and inter-molecular hydrogen bonds in 2DNP itself and between carboxyl and nitro groups of 2DNP ligand and water molecules as well as between water molecules. They are intramolecular O(7)–H(4W)$\cdots$N(1) 3.0157(19) Å, 112.8°; O(7)–H(4W)$\cdots$O(1) 2.616(2) Å, 171.0° and intermolecular O(6)–H(2W)$\cdots$O(5)#2 3.081(2) Å, 117.2°; O(6)–H(2W)$\cdots$O(1)#2 2.730(2) Å, 157.2°; O(7)–H(3W)$\cdots$O(4)#3 2.866(2) Å, 161.9°; O(6)–H(1W)$\cdots$O(3)#4 2.973(2) Å, 151.7° (#2: $x$, $y-1$, $z$; #3: $-x+1/2$, $y-1/2$, $-z+1/2$; #4: $x+1/2$, $-y+1/2$, $z-1/2$). These hydrogen bond interactions contribute to stabilization of the crystal structure.

The molecular structure of **2** is illustrated in figure 2. Selected bond distances and angles are listed in table 2. The structure of **2** is similar to that of **1**, although being coordinated by different ligands. The main difference between both compounds

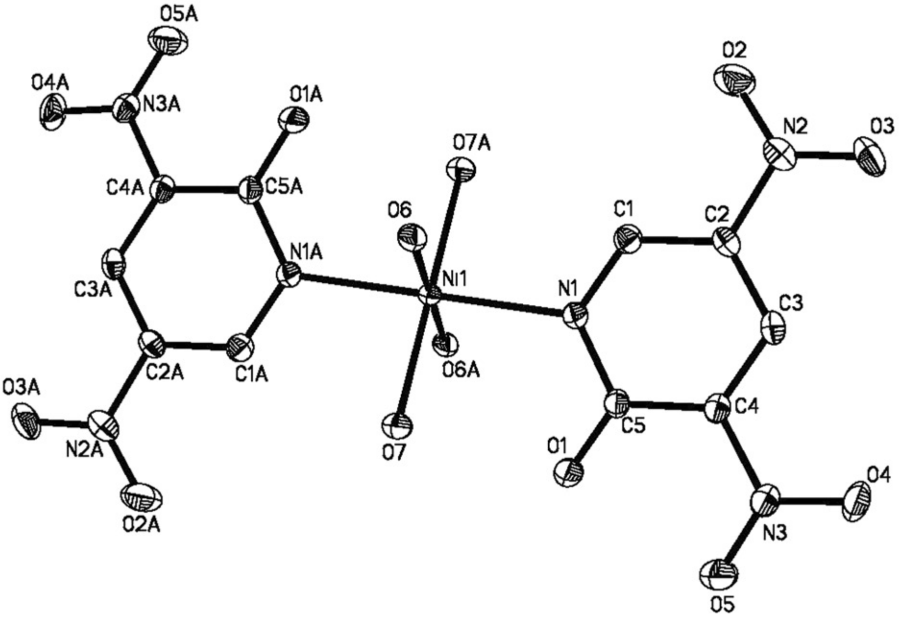

Figure 1. The structure of $Ni(2DNP)_2(H_2O)_4$ showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

is in **2**, the two longer Cu–$O_{water}$ bonds are considerably longer (by ~0.2 Å) than the two shorter Cu–$O_{water}$ bonds and the Cu–$N_{py}$ bond distances are shorter than those of Cu–$O_{water}$. Therefore, **2** displays a compressed octahedral geometry. There exist abundant intermolecular hydrogen bonds between O atom of the carboxyl and nitro groups of 4DNP ligand and O atoms of water: O(6)–H(1W)···O(1)#2 2.917(2) Å, 167.9°; O(6)–H(2W)···O(3)#3 2.7516(17) Å, 147.7°; O(7)–H(3W)···O(3)#3 2.7843(19) Å, 147.8°; O(7)–H(4W)···O(5)#4 2.960(2) Å, 149.8° (#2: $-x+2$, $-y$, $-z+2$; #3: $-x+3/2$, $y-1/2$, $-z+5/2$; #4: $-x+5/2$, $y-1/2$, $-z+3/2$), etc.

The molecular structure and perspective view of **3**·2DMF are illustrated in figures 3 and 4. Selected bond distances and angles are listed in table 2. As with **1** and **2**,

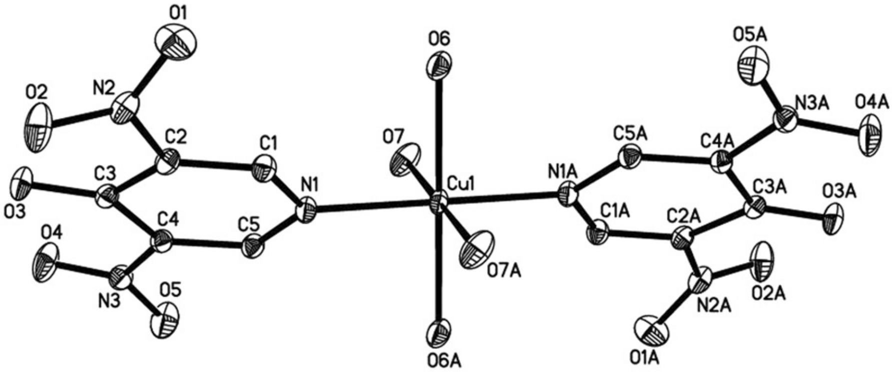

Figure 2. The structure of $Cu(4DNP)_2(H_2O)_4$ showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

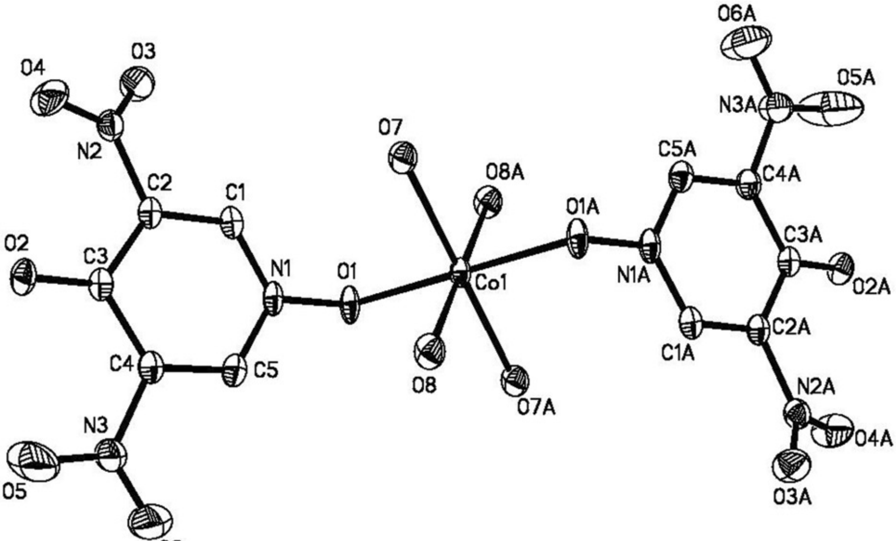

Figure 3. The structure of $[Co(4DNPO)_2(H_2O)_4]\cdot 2DMF$ showing 30% probability displacement ellipsoids. Hydrogen atoms and solvent molecules (DMF) are omitted for clarity.

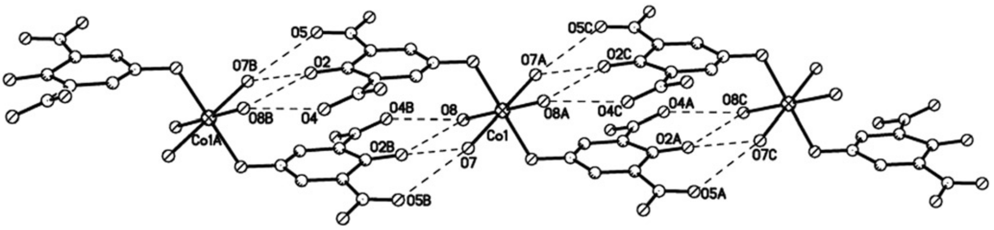

Figure 4. One-dimensional chain of **3** · 2DMF emphasizing the tri-centered hydrogen bonds with respect to the middle molecule.

the Co(II) center in compound **3** · 2DMF is six-coordinate with six oxygen donors from four water molecules and two 3,5-dinitro-4-pyridone-*N*-hydroxyl anions to furnish centro-symmetric octahedral geometry with heavy distortions. The equatorial positions are occupied by four oxygen atoms (O7, O7A, O8, O8A) with bond angles of 90.92(8), 89.08(8) and 180.00 (°) of O(7)–Co(1)–O(8), O(7)A–Co(1)–O(8), O(7)–Co(1)–O(7)A (table 2), indicating that the metal center locates on the equatorial plane defined by the four waters. The axial positions of the octahedral geometry are occupied by oxygen atoms O1, O1A with O1–Co1–O1A bond angle of 180.0°, and the angle of O1–Co1–O7(O7A) is 91.88(8) (88.12(8)°). The Co1–O1 bond distance (2.0308(19) Å) is significantly shorter by ~0.1 Å than those of average Co1–O(W) bond distance (2.1203(11) Å), indicating that the Co(II) complex displays compressed octahedral geometry as for **2** and $Cu(4DNPO)_2(H_2O)_4$ [5a]. DMF exhibits twofold disorder in the crystal lattice.

There are several inter- and intramolecular hydrogen bonds within the structure of **3** · 2DMF. Each $[Co(4DNPO)_2(H_2O)_4]$ unit connects two other units through its four coordinated water molecules to form tri-centered hydrogen bonds, which link the molecules into an infinite one-dimensional chain (figure 4). The tri-centered hydrogen bonds are one donor with two proton acceptors. They are O7–H(1W)–O2i 2.767(3) Å, 156.7°; O7–H(1W)–O5i 2.955(4) Å, 120.4°; O8–H(3W)–O2i 2.756(3) Å, 157.0°; O8–H(3W)–O4i 2.906(3) Å, 122.3°; the chain is further extended into a two-dimensional network with the adjacent molecule by weak O1 ··· O2ii interactions with the length of 3.007(3) Å (i: $-x$, $1-y$, $-z$; ii: $-x$, $-1/2+y$, $1/2-z$).

### 3.2. *IR spectra*

The strong and wide adsorption peaks between 3600 and 3200 $cm^{-1}$ for the complexes are characteristic of OH in coordinated water. The peaks at 1668, 1656 and 1666 $cm^{-1}$ for **1**, **2** and **3** · 2DMF, respectively, could be comparable to the stretching mode of CO groups of the corresponding ligands (1666, 1660 and 1664 $cm^{-1}$, respectively, in the free ligands), indicating no coordination of the metal ions with the CO groups. The N–O stretching of the pyridine-*N*-oxide ring in **3** · 2DMF (1263 $cm^{-1}$) shifts to low wave-number compared with that in the free ligand (1288 $cm^{-1}$), showing coordination of the Co(II) ion with the O of the pyridine *N*-oxide moiety of the ligand leading to decrease of intensity of the N–O bond. The IR spectra are consistent with the single crystal structural analysis.

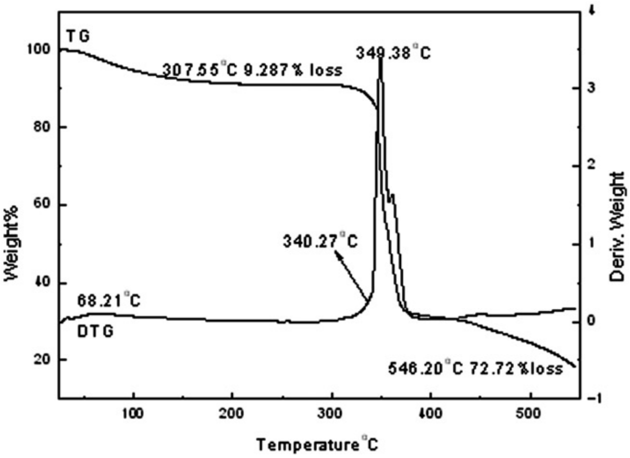

Figure 5. The TG-DTG curves of **1**.

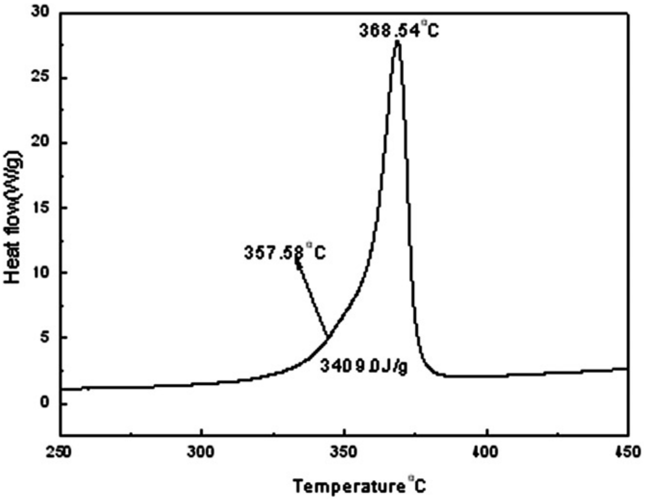

Figure 6. The DSC curve of **1**.

### 3.3. *Thermal analysis of 1 and 3*

There are two peaks (68 and 349°C) on the DTG curve of **1** (figure 5) indicating two stages of decomposition. The first stage from ca 30 to 307°C has 9.29% mass loss, in agreement with the theoretical mass loss of 10.8%, corresponding to the dehydration of three waters. After the second stage, the mass of the residue is 17.99% indicating NiO+C (18.52%). The corresponding DSC curve, as shown in figure 6, shows one exothermic peak (368°C) with the heat release of 3409 J.g$^{-1}$ and the initial decomposition temperature of 358°C. These results showed that the decomposition temperature and heat release of **1** is higher than the corresponding lead(II) salts [5b] and that the nickel(II) compound could be a promising energetic catalyst in propellants.

The TG-DTG curves of **3** · 2DMF showed two main weight-loss stages. The first mass loss of 12.88% is in agreement with the theoretical value of 13.56%, corresponding to dehydration of all four waters. Correspondingly, the DSC curve shows an endothermic peak at 184°C. After the second stage the mass of the residue (29.46%) is consistent with $Co_2O_3$ (31.25%). Correspondingly, its DSC curve shows an exothermic peak at 342°C with the heat release of 3225 $J.g^{-1}$ and the initial decomposition temperature of 244°C. On comparison with the thermal decomposition behavior of nickel compound **1**, the cobalt compound **3** · 2DMF is relatively unstable.

## 4. Conclusions

We have synthesized and determined the molecular structures of $Ni(2DNP)_2(H_2O)_4$ (**1**), $Cu(4DNP)_2(H_2O)_4$ (**2**) and $[Co(4DNPO)_2(H_2O)_4] \cdot 2DMF$ (**3** · 2DMF). The crystal structures showed that each metal center is octahedral, with the equatorial positions occupied by water molecules and the axial positions by two ligand molecules. The thermoanalyses of these three complexes showed that the nickel compound (**1**) is the most stable with larger heat release during decomposition. The nickel compound will be a promising candidate of energetic catalysts for double-base propellants.

## Supplementary materials

CCDC-650335 (**1**), CCDC-650336 (**2**) and CCDC-650337 (**3** · 2DMF) contain 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 Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

## Acknowledgements

The authors thank the National Defense Key Laboratory of Propellant and Explosive Combustion of China for financial support.

## References

[1] A. Patchornik. *Polym. Adv. Technol.*, **13**, 1078 (2002).

[2] (a) S.M. Kaye. *Encyclopedia of Explosives and Related Items*, U.S. Army ARDEC, Dover, NJ, **8**, 274 (1978); (b) T.B. Brill, P.J. Brush, K.J. James, J.E. Shepherd, K.J. Pfeiffer. *Appl. Spectrosc.*, **46**, 900 (1991); (c) Z. Meng, R. Hu. *Therm. Anal.*, **45**, 79 (1995); (d) Brill, T. Zhang, B.C. Tappan. *Combust Flame*, **121**, 662 (2000); (e) Y. Wang, C. Chen, S. Lin. *J. Mol. Struc.* (*Theochem*), **460**, 79 (1999).

[3] (a) M.D. Coburn, K.Y. Lee. *J. Heterocycl. Chem.*, **27**, 575 (1990); (b) J. Song, R. Hu, B. Kang, F. Li. *Thermochim. Acta*, **331**, 49 (1999); (c) J. Song, Z. Chen, H. Xiao, R. Hu, F. Li. *Chin. Sci. Bull.*, **44**, 214 (1999); (d) Y. Yang, T. Zhang, J. Zhang, B. Shao, K. Yu. *Chin. J. Struct. Chem.*, **21**, 321 (2002);

(e) G. Fang, L. Xu, H. Xiao, X. Ju. *Acta Chim. Sinica*, **63**, 1055 (2005); (f) T. Zhang, S. Wang, L. Yang, Y. Sun, J. Zhang, X. Qiao. *Chin. J. Inorg. Chem.*, **22**, 1819 (2006); (g) S.S. Yun, J.K. Kim, C.H. Kim. *J. Alloys Comp.*, **408–412**, 945 (2006).

[4] (a) Smolenski, W. Czuba. *Zeszyty Nauk. Politech. Wroclaw. Chem.*, **2**, 3 (1955); (b) B. Glowiak. *Zeszyty Nauk. Politech. Wroclaw. Chem.*, **7**, 49 (1961).

[5] (a) Y. Zhen, M. Deng, F. Zhao, C. Yuan. *Chin. J. Explos. Propellants*, **4**, 51 (2002); (b) F. Zhao, P. Chen, Y. Luo, R. Zhang, S. Li, M. Deng, Y. Zhen. *Chin. J. Explos. Propellants*, **3**, 1 (2003); (c) P. Chen, F. Zhao, Y. Luo, R. Hu, Y. Zheng, M. Deng, Y. Gao. *Acta Chim. Sinica*, **13**, 1197 (2004); (d) F. Zhao, H. Gao, Y. Luo, R. Hu, P. Chen, S. Gao, X.Y.Q. Shi. *J. Therm. Anal. Calorim.*, **85**, 791 **(**2006).

[6] (a) G. Zhang, J. She, Y. Dou, Q. Zhou, M. Yin. *J. Coord. Chem.* **61**, 865 (2008); (b) J. She, G. Zhang, F. Zhao, Z. Lei, X. Fan. *Struct. Chem.*, **18**, 373 (2007); (c) Q. Zhou, G. Zhang, J. She. *J. Coord. Chem*; (accepted).

[7] (a) G.M. Sheldrick. *SHELXL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997); (b) *SHELXTL-5.03 (PC-version)*, *Program Library for Structure Solution and Molecular Graphics*, Siemens Analytical Instrument Division, Madison, WI (1995).