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A novel energetic nickel coordination compound based on carbohydrazide and dinitramide

Sergey G. Il'yasov, Vera S. Glukhacheva, Dmitri S. Il'yasov, Egor E. Zhukov, Ilia V. Eltsov and Yuri V. Gatilov

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The decomposition temperature was measured on Mettler Toledo TGA/SDTA 851e and DSC 822e thermal analyzers over temperature ranges of 25-300 °C and 25-500 °C in nitrogen at a heating rate of 10 K min^{-1}. The results were digitized and processed in STARe 11.0 thermal analysis software. Ten density measurements were done using a Micromeritics AccuRus 1340 gas picknometer (Micromeritics, USA). For each measurement, a sample cup (1.0 ml) was filled to about 75% of the volume, weighed, capped, and placed into the picnometer. For each sample, ten successive measurements by helium purging were performed. Arithmetic mean and standard deviations were calculated.

The content of Ni^{2+} was determined by UV VIS spectroscopy (theor. 10.85% on a gross formula basis of $C_3H_{18}O_{11}Ni$).

The sensitivity was tested on a K-44-III tester (Samara city, Russia): friction sensitivity was tested by GOST R no. 50835-95 (Russian State Standard), and impact sensitivity was tested by GOST R no. 4545-88 (Russian State Standard) in a tester no. 2.

Test of synthesized compound **6** as burning-rate modifier of pyrotechnic composites was performed with the use of the following formulations:

1. Sound and flash pyrotechnic composition (Refs. 31,32 of the main text): 70% potassium perchlorate (technical specifications no. 6-09-3801-76, particle size of 63−160 μm) and 30% aluminum (technical specifications no. 48-5-226-87, particle size of 4−10 μm);

2. Igniting pyrotechnic composition (Ref. 31 of the main text): 52% zirconium (technical specifications no. 48-4-234-84, particle size of 1−15 μm) and 48% potassium nitrate (GOST R 4217-77, particle size of 63−160 μm).

The structures of all the resultant compounds were validated using equipment provided by the Biysk Regional Center for Shared Use of Scientific Equipment 'Center for Synthesis and Research of High-Energy Compounds and Specialty Materials' of the SB RAS.

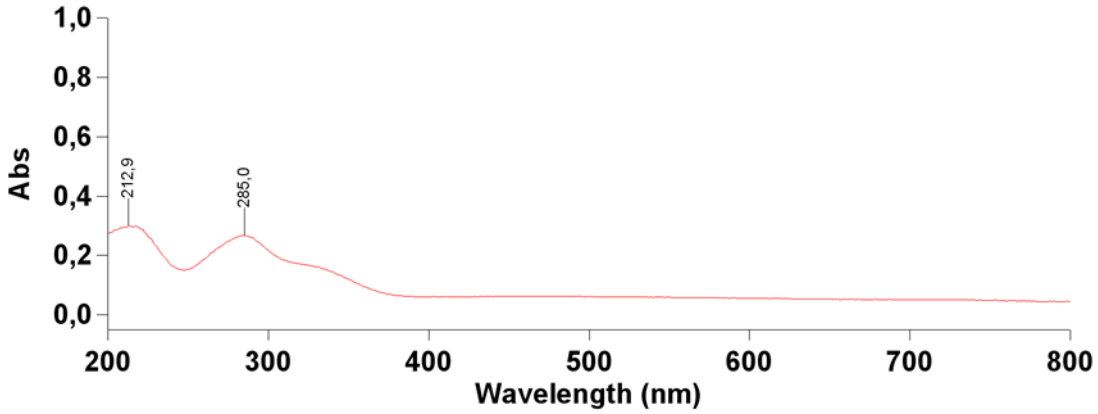


Figure S1. UV spectrum of **3**

Table S1. The optical density of the solution subject to the molar ratio of **6** to **1** by the Ostromyslensky-Zhob method (DNA is dinitramide).

Entry	$Ni(DNA)_2*6H_2O$ 7.58 g in 200 mL 0.0001 mol/mL	DNA 1.8 g in 200 mL 0.0001 mol/mL	Component ratio within 10		Wavelength nm	Density	Molar ratio	
	mL	mL	mL	mL				
	0	25	0	10	0	0	0	5
1	2.5	22.5	1	9	597	0.0905	0.5	4.5
2	5	20	2	8	601	0.1685	1	4
3	5.625	19.375	2.25	7.75	601.5	0.1828	1	3.44
4	6.25	18.75	2.5	7.5	602	0.1913	1	3
5	6.875	18.125	2.75	7.25	605	0.1891	1	2.64
6	7.5	17.5	3	7	610	0.1871	1	2.33
7	8.325	16.675	3.33	6.67	617	0.1803	1	2
8	10	15	4	6	628	0.1708	2	3
9	12.5	12.5	5	5	641	0.1678	1	1
10	15	10	6	4	650	0.1689	3	2
11	16.675	8.325	6.67	3.33	652	0.1727	2	1
12	17.5	7.5	7	3	653.5	0.1737	2.33	1
13	18.75	6.25	7.5	2.5	655	0.1755	3	1
14	20	5	8	2	655	0.1767	4	1
15	22.5	2.5	9	1	656	0.1785	4.5	0.5
16	25	0	10	0	656	0.1883	5	0

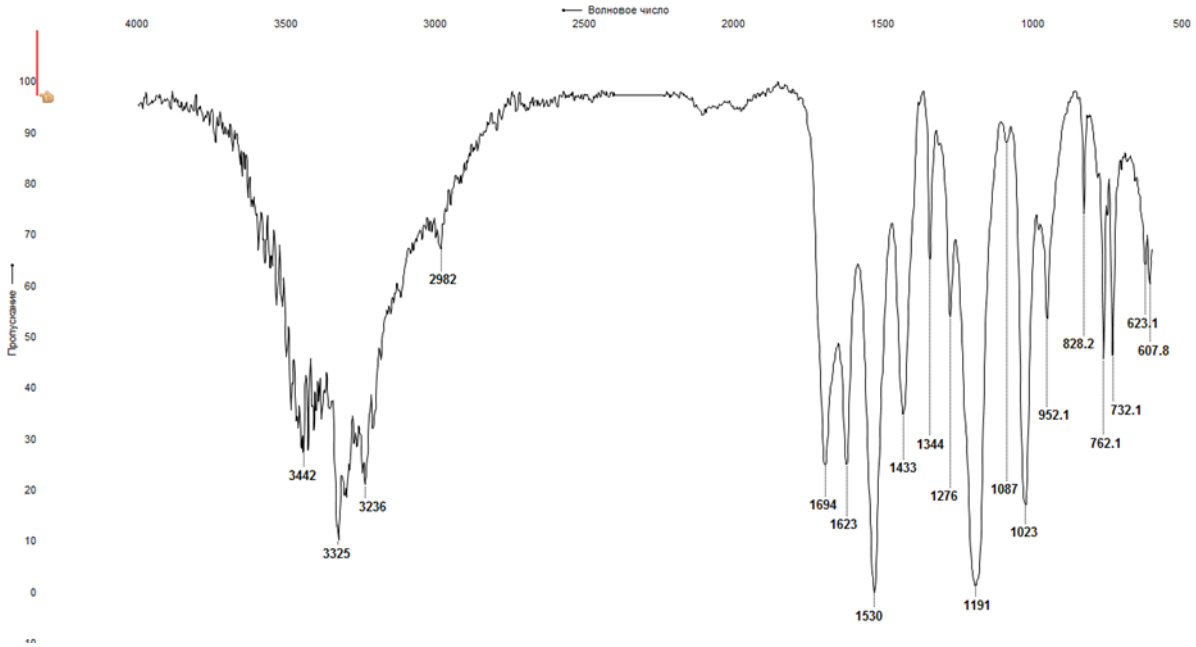


Figure S2. IR spectrum of **3**

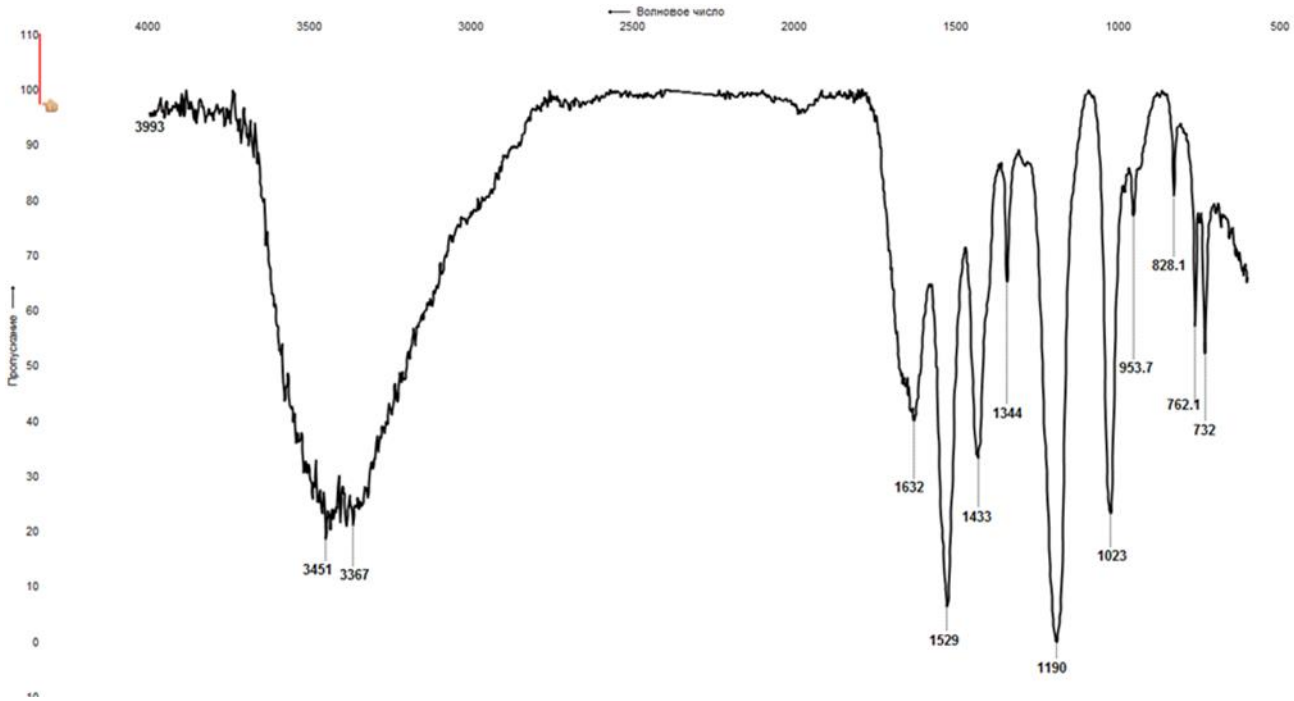


Figure S3. IR spectrum of **4**

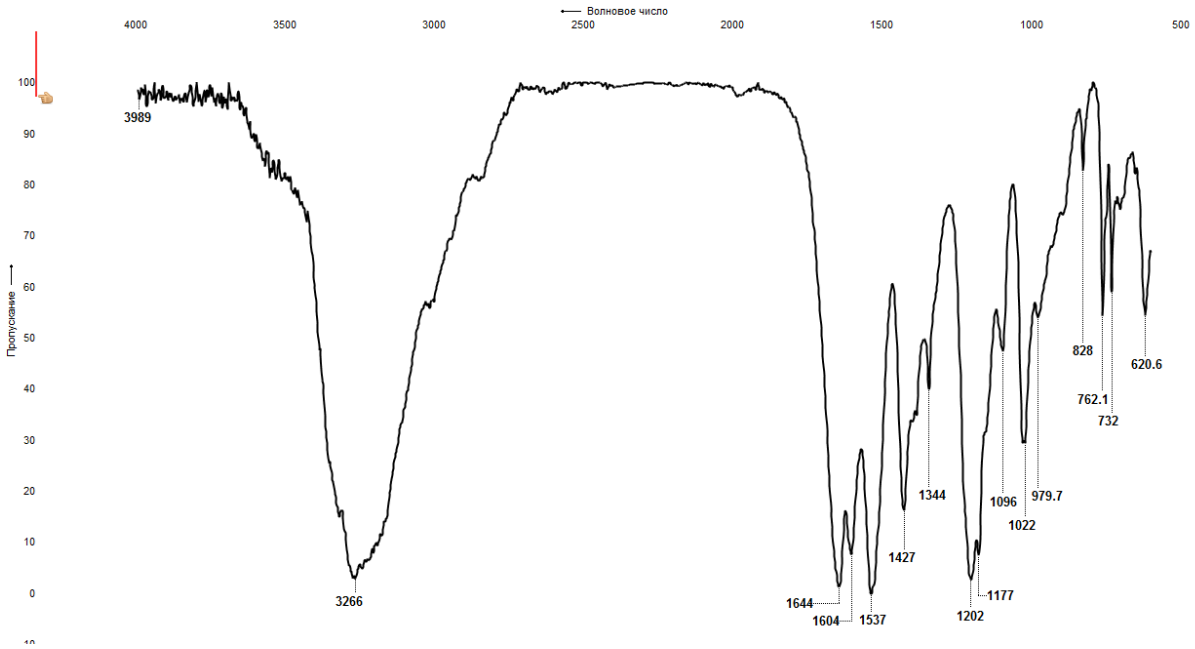
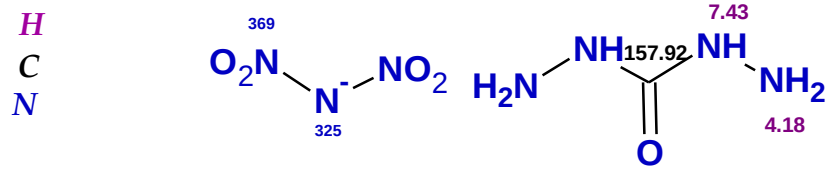


Figure S4. IR spectrum of **6**

Legend:



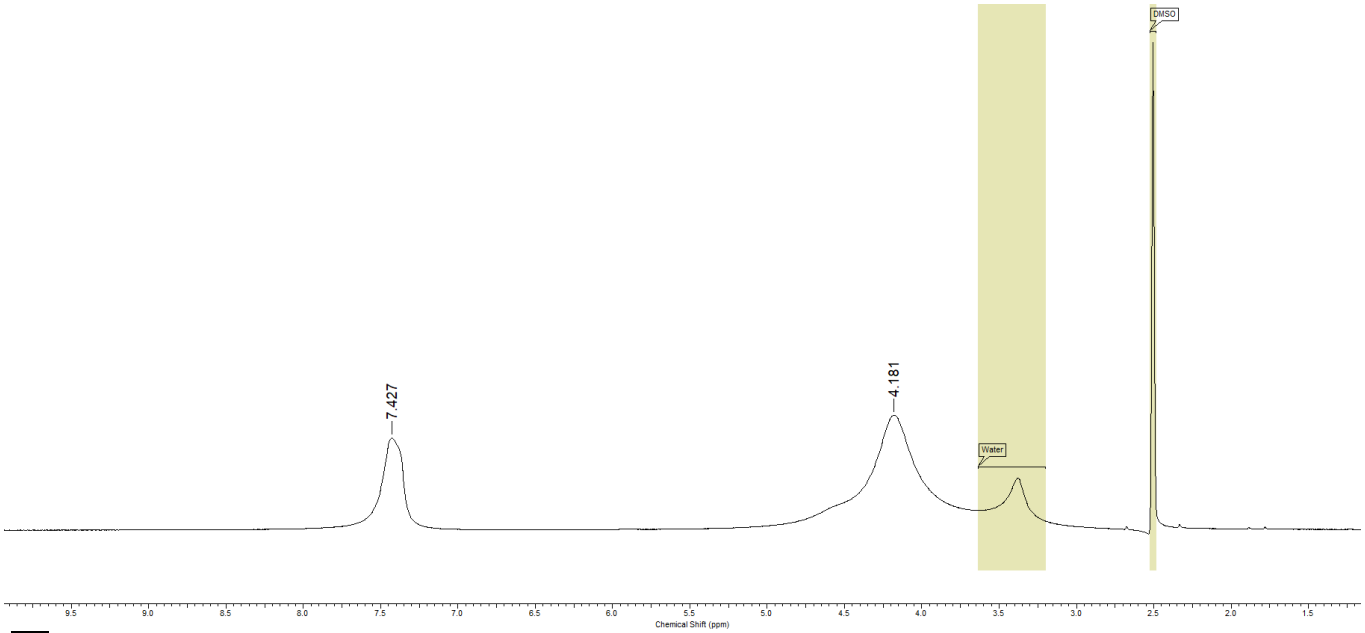


Figure S5. ^{1}H-NMR spectrum of **3** in DMSO-d_6, 400.13 MHz

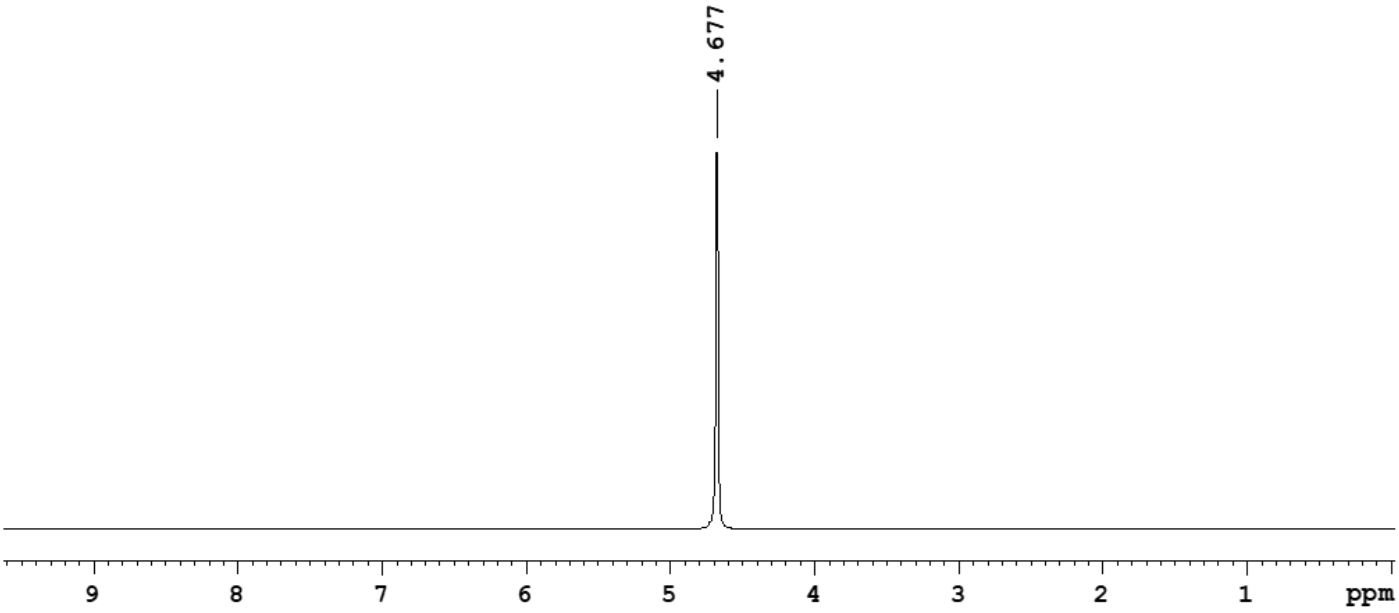


Figure S6. ^{1}H-NMR spectrum of **3** in D_2O, 500.03 MHz

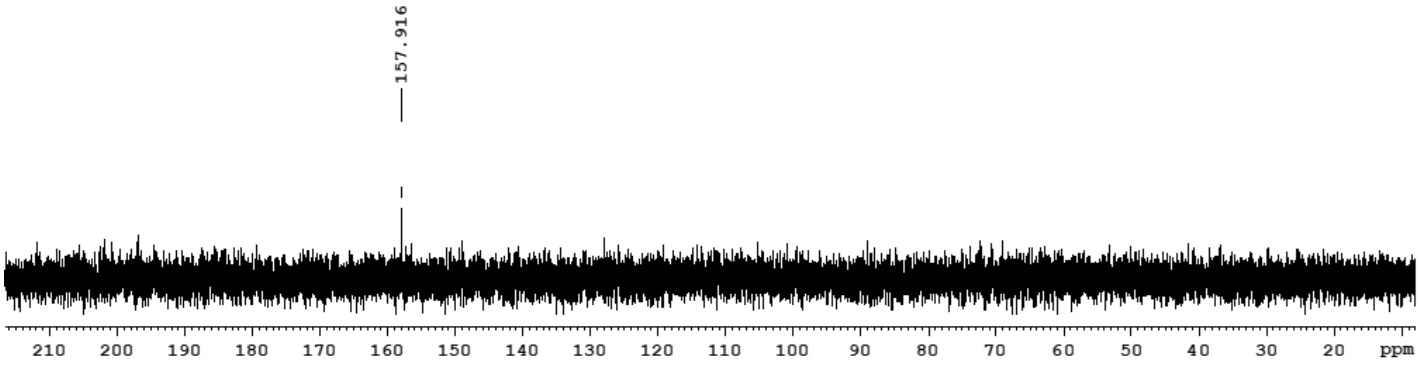


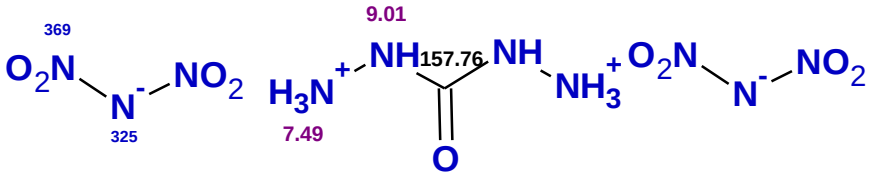
Figure S7. ^{13}C{1H}-NMR spectrum of **3**, D_2O, 125.73 MHz

Legend:

H

C

N



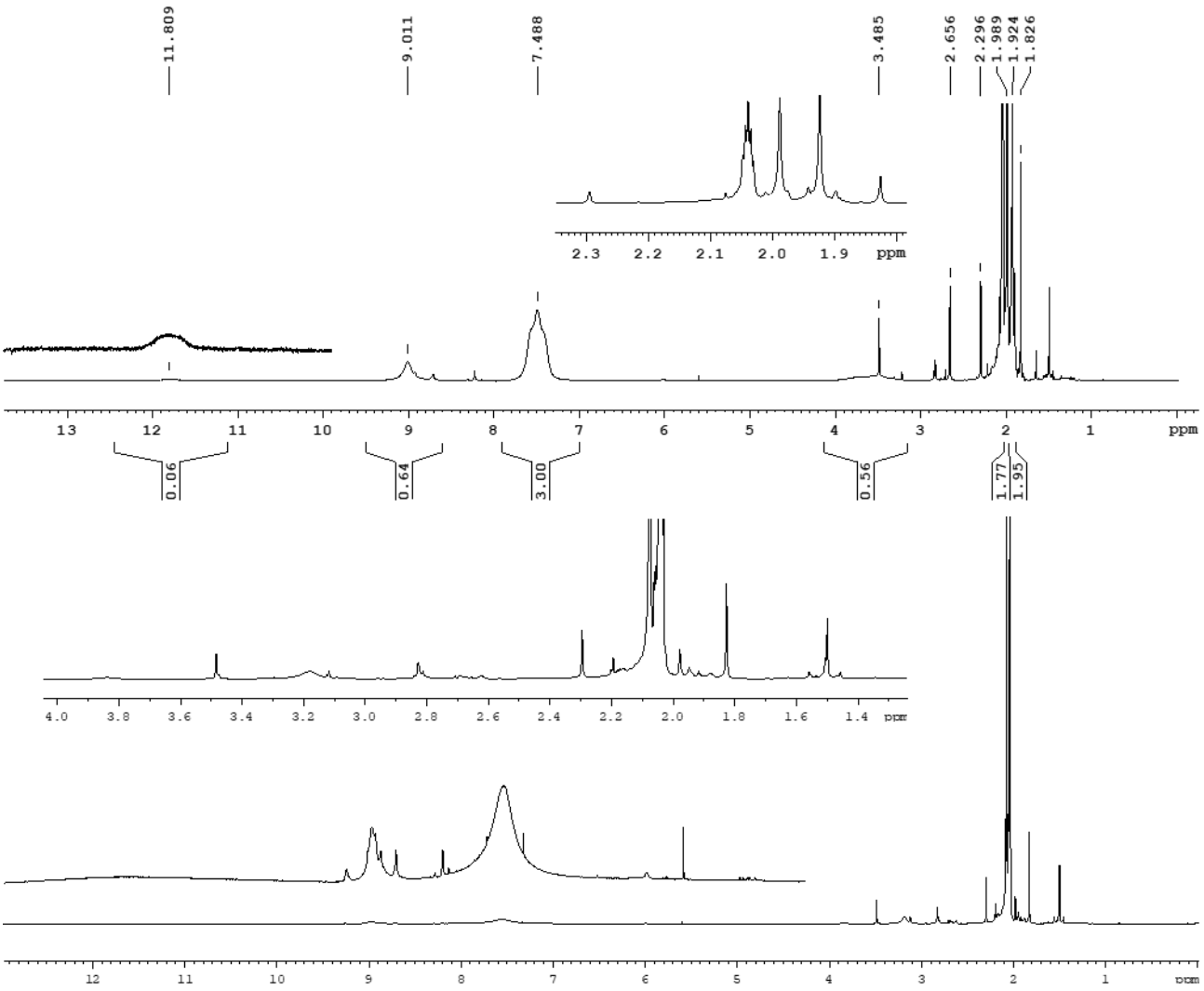


Figure S8. ^{1}H-NMR spectrum of **4** in $(CD_3)_2CO$, 500.03 MHz in the beginning of the experiment (top) and in the end in 24 h (bottom)

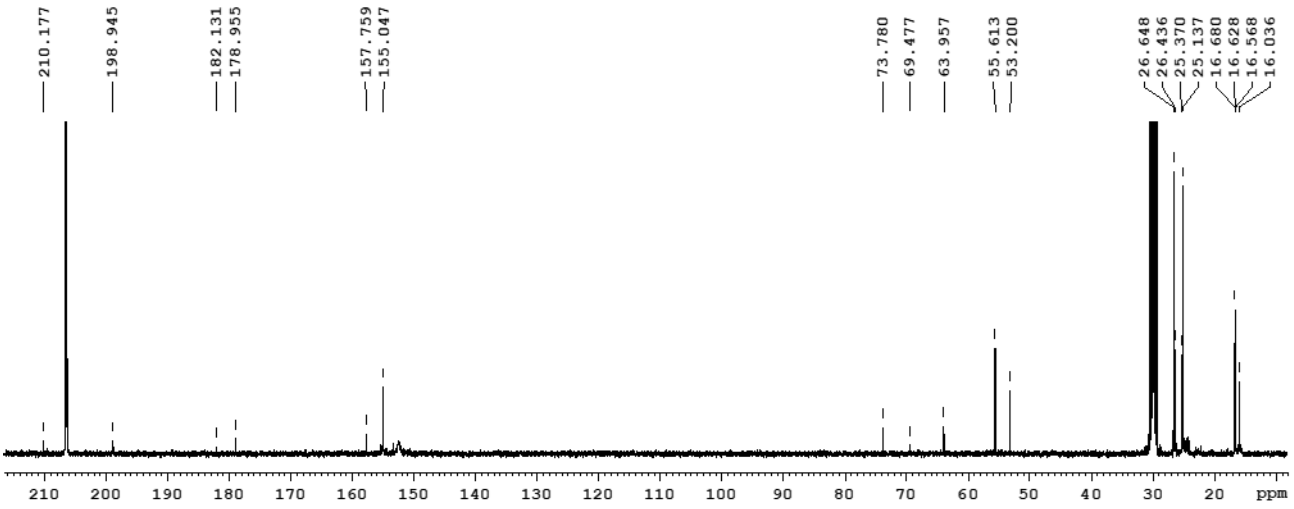


Figure S9. ^{13}C-NMR spectrum of **4**, $(CD_3)_2CO$

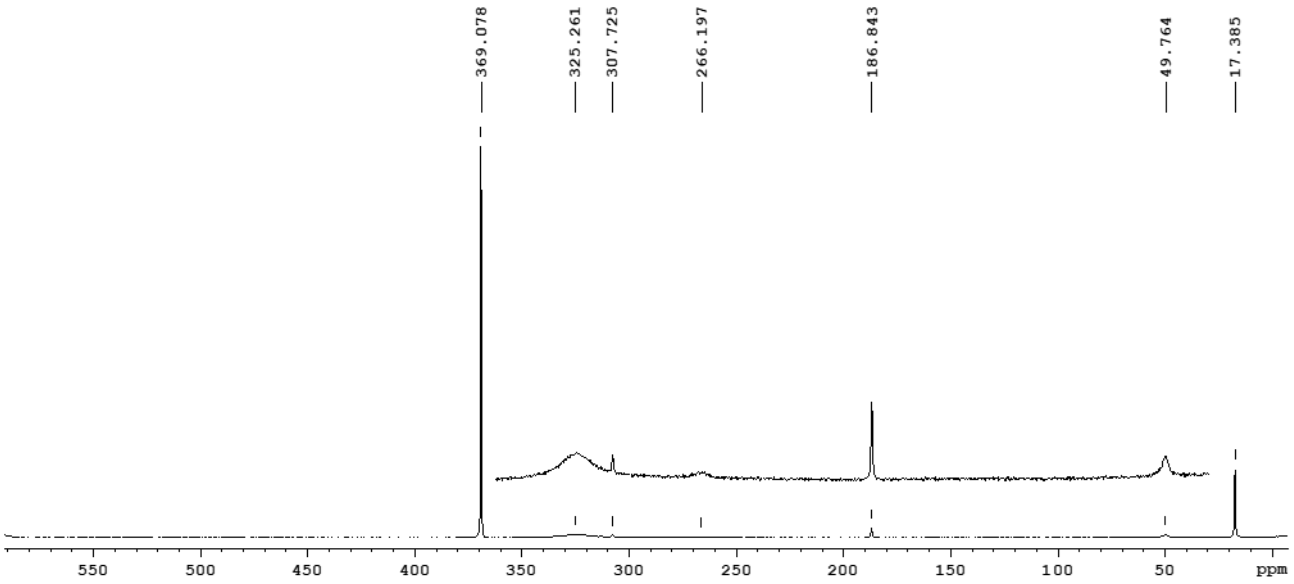


Figure S10. ^{14}N-NMR spectrum of **4**, $(CD_3)_2CO$ recorded relative to formamide as reference standard (δ) = 112.5 ppm

Crystallography. The measurements were carried out at the Collective Chemical Service Center of the SB RAS. The X-ray diffraction of compound **6** was carried out on a Bruker KAPPA APEX II CCD diffractometer with graphite monochromated MoKα (0.71073 Å) radiation at room temperature. Absorption corrections were applied using SADABS [S1]. The structure was resolved by the direct method. Positions and temperature factors for the non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method [S2]. The hydrogen atoms were refined in the riding and isotropic models. Anion molecules located around centers of symmetry are disordered with a 0.5:0.5 ratio. All computations were done using SHELX-2018 programs. The atomic coordinates and the temperature parameters were deposited with the Cambridge Structural Database.

[S1] Sheldrick, G. M. SADABS, Program for Area Detector Adsorption Correction, Institute for Inorganic Chemistry, University of Goettingen, Germany: 1996.

[S2] Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3.

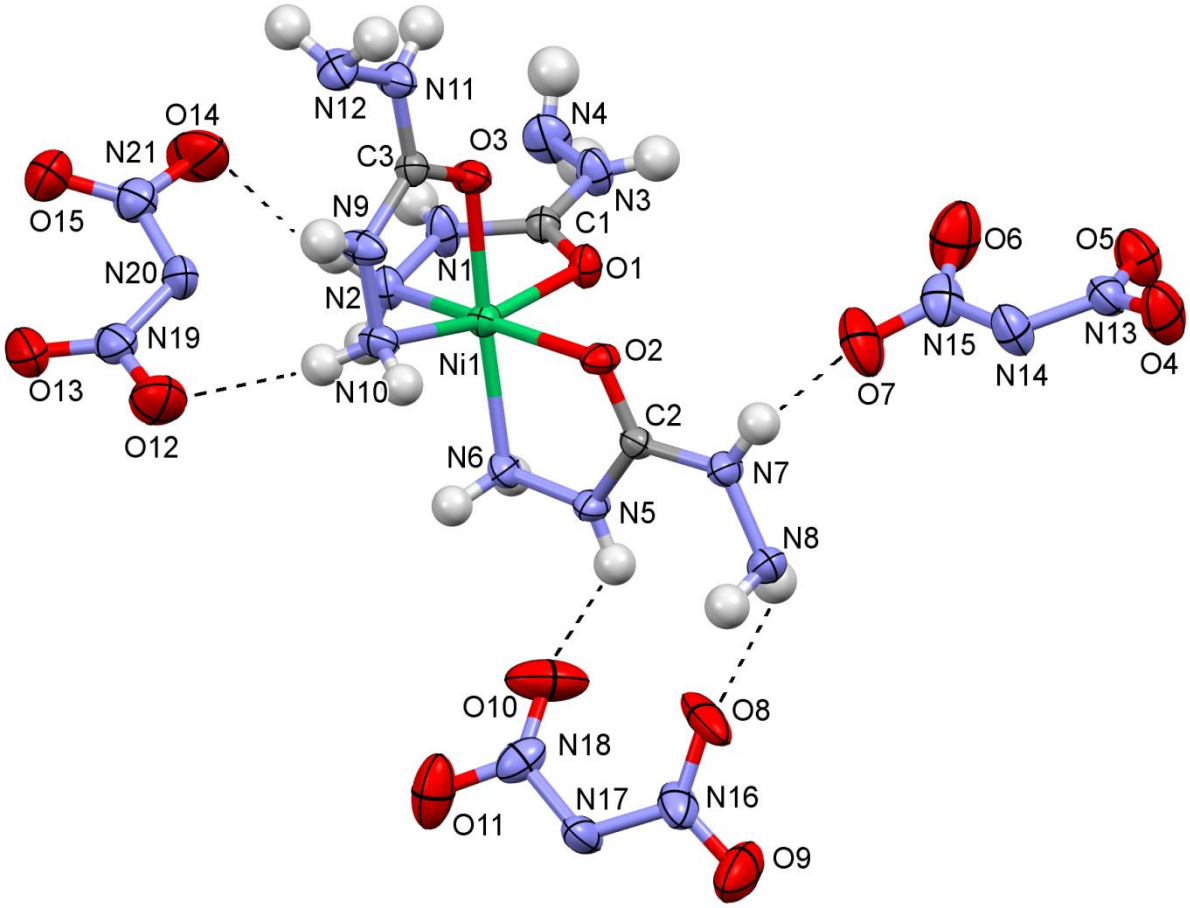


Figure S11. X-ray structure of **6**. Thermal ellipsoids are shown at 50% probability. For the disordered anions: O8 – O11 and O12 – O15 (Fig. S12) only one part of two is shown.

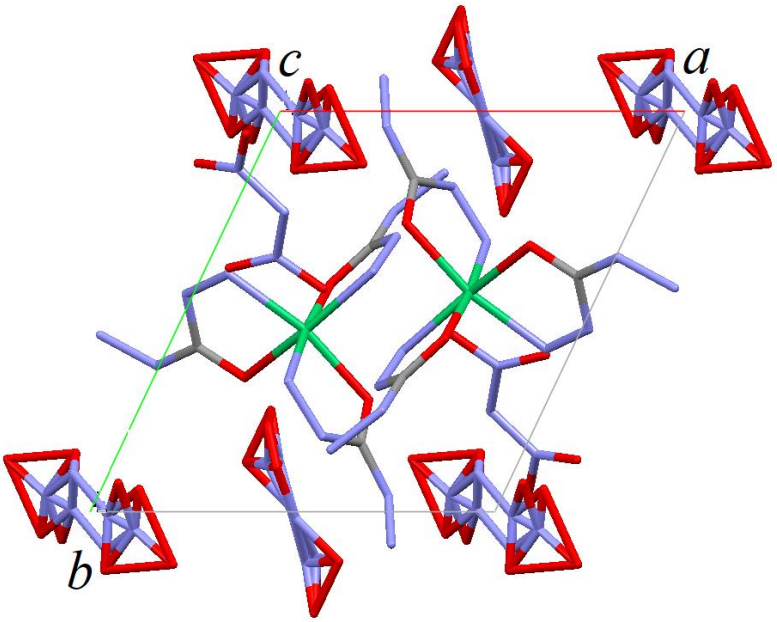


Figure S12. The molecular packing of crystal **6** (view along c axis).

Table S2. Crystal data and structure refinement for **6**

Empirical formula	$C_3H_{18}N_{12}NiO_3$, $2(N_3O_4)$
Formula weight	541.04
Temperature	296(2)
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.9847(14) Å α = 107.144(6)°
	b = 10.1466(19) Å β = 110.703(5)°
	c = 12.477(2) Å γ = 110.703(5)°
Volume	967.5(3) Å^3
Z	2
Density (calculated)	1.857 g/cm^3
Absorption coefficient	1.101 mm^{-1}
F(000)	556
Crystal size	0.12 x 0.39 x 0.46 mm^3
Theta range for data collection	2.33 to 30.70°
Index ranges	-12<= h <=12, -14<= k <=14, -17<= l <=17
Reflections collected	37908
Reflections independent, R_{int}	5983, 0.0448
Observed Data [I>2σ(I)]	5500
Completeness to theta = 25.03°	0.999
Absorption correction	Semi empirical from equivalents
Max. and min. transmission	0.7461 and 0.6549
Refinement method	Full matrix least squares on F^2
Data / restrains / parameters	5983 / 28 / 367
Goodness-of-fit on F^2	1.075
Final R indices [I>2σ(I)]	R_1 = 0.0280, wR_2 = 0.0725
R indices (all data)	R_1 = 0.0315, wR_2 = 0.054
Extinction coefficient	n/a
Largest diff. peak and hole	0.499 and -0.337 e/Å^3
CCDC deposition number	2113879

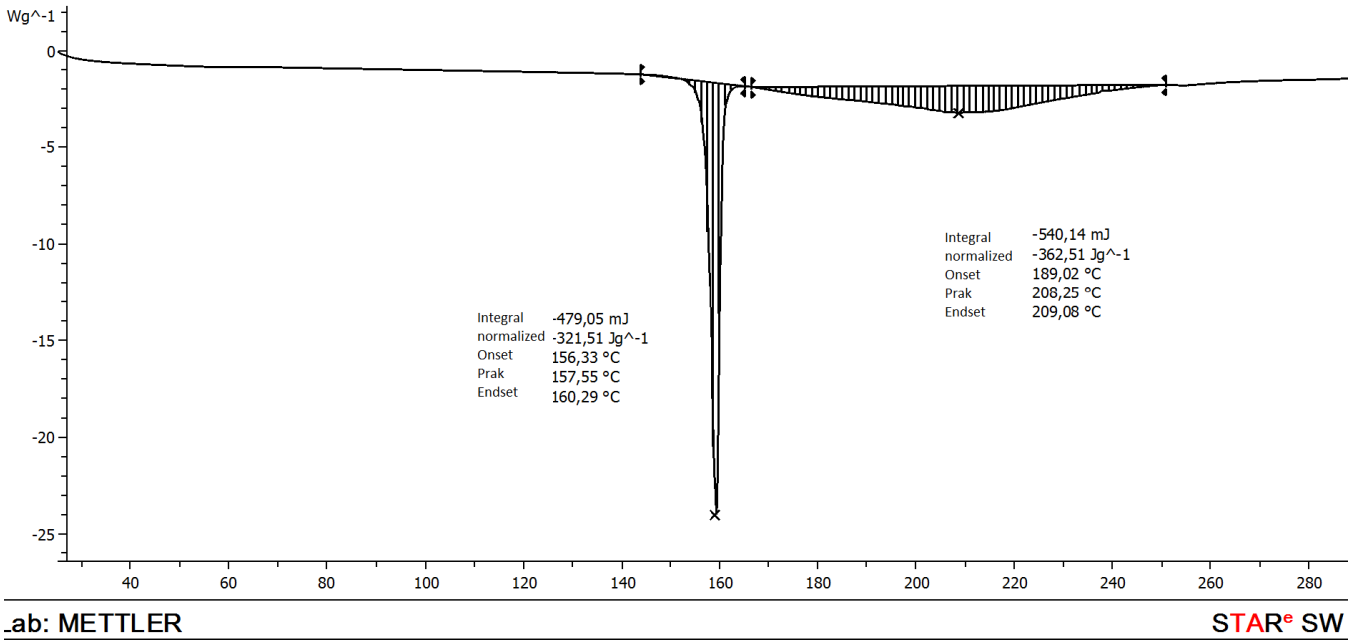


Figure S13. DSC of **1**

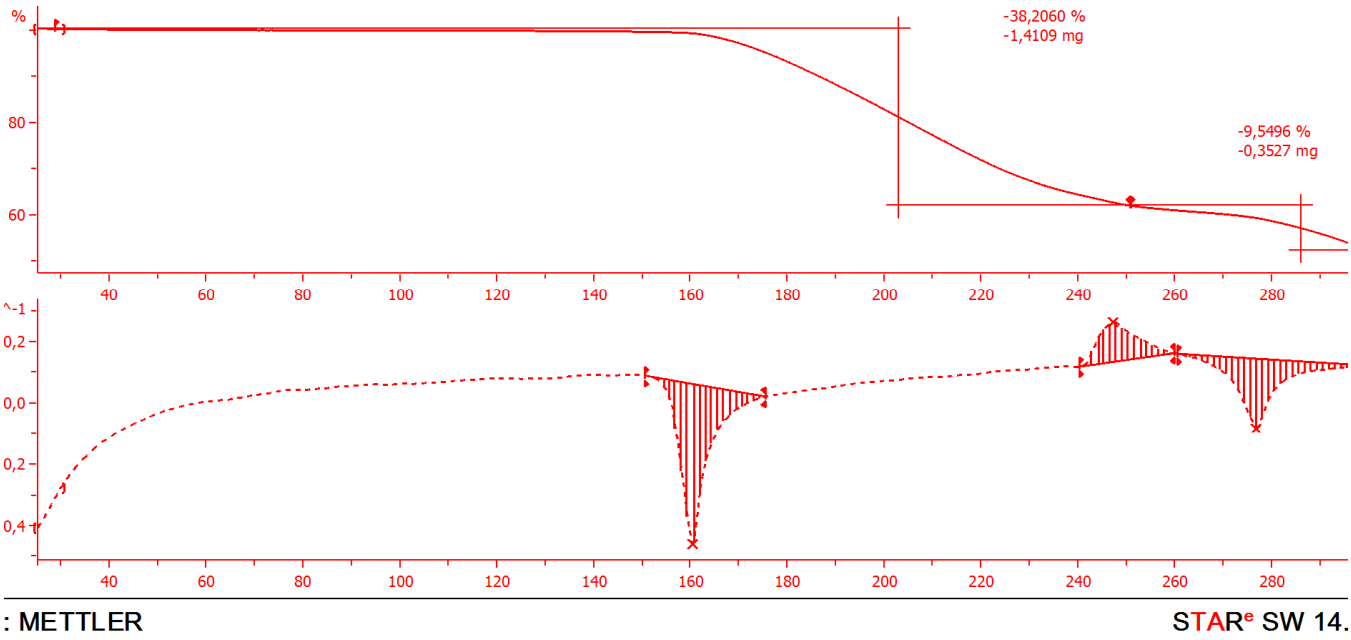


Figure S14. TGA of **1**

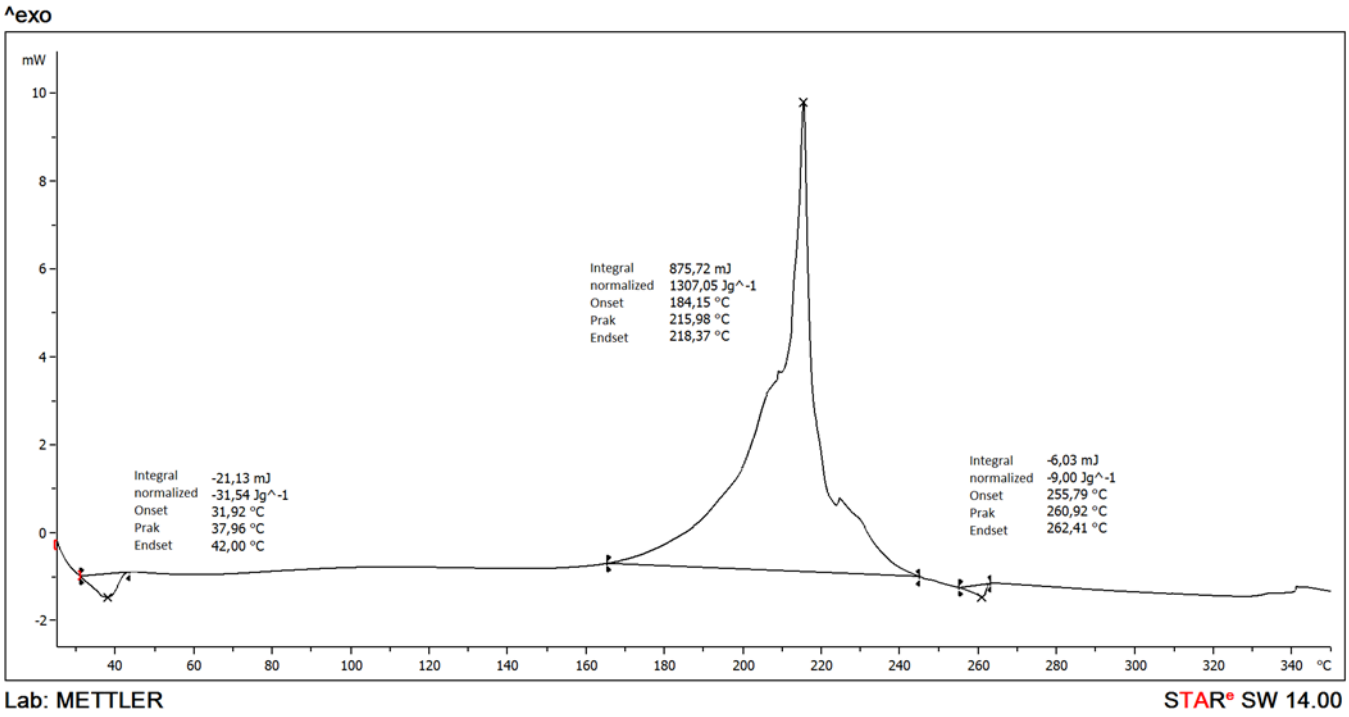


Figure S15. DSC of **3** before drying

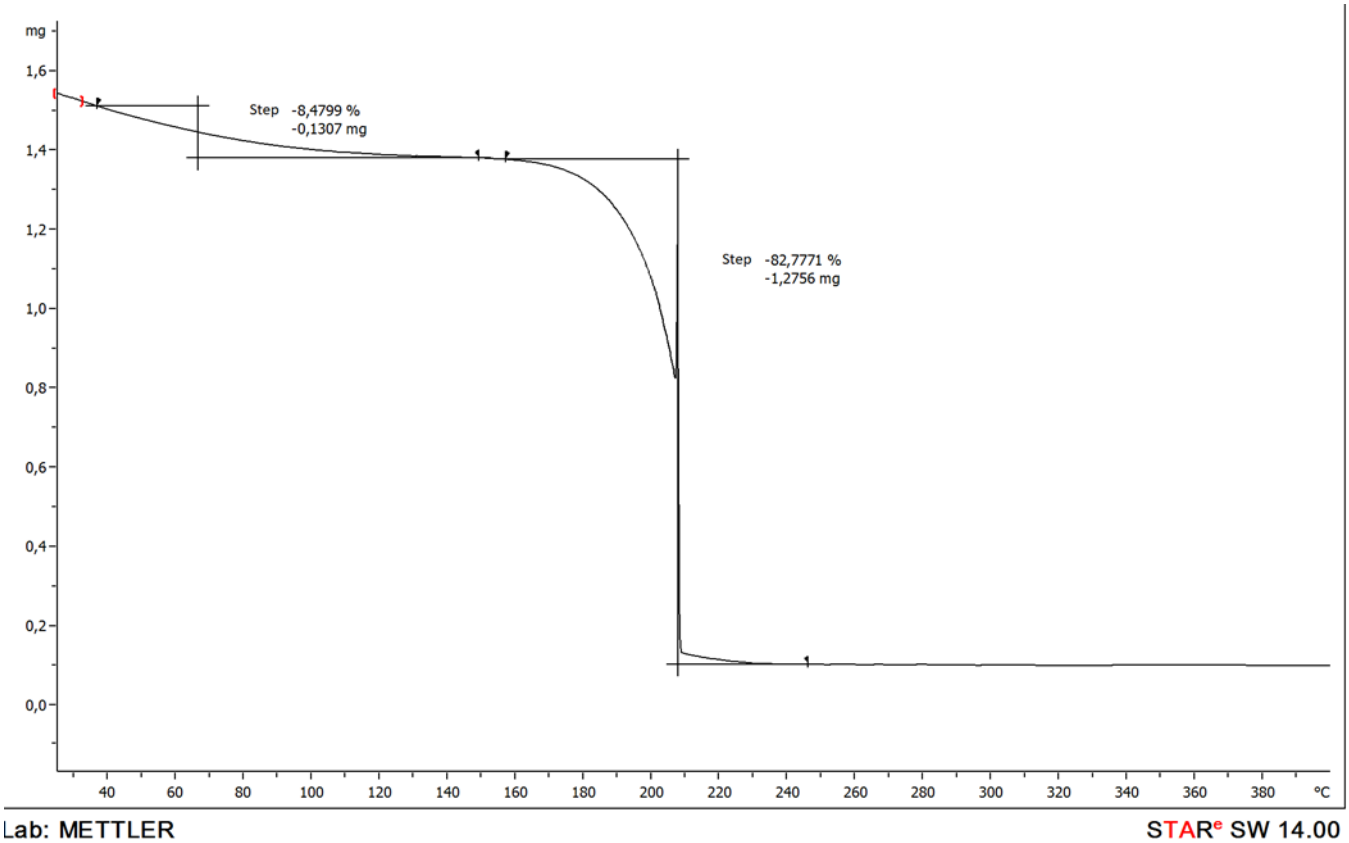


Figure S16. TGA of **3**

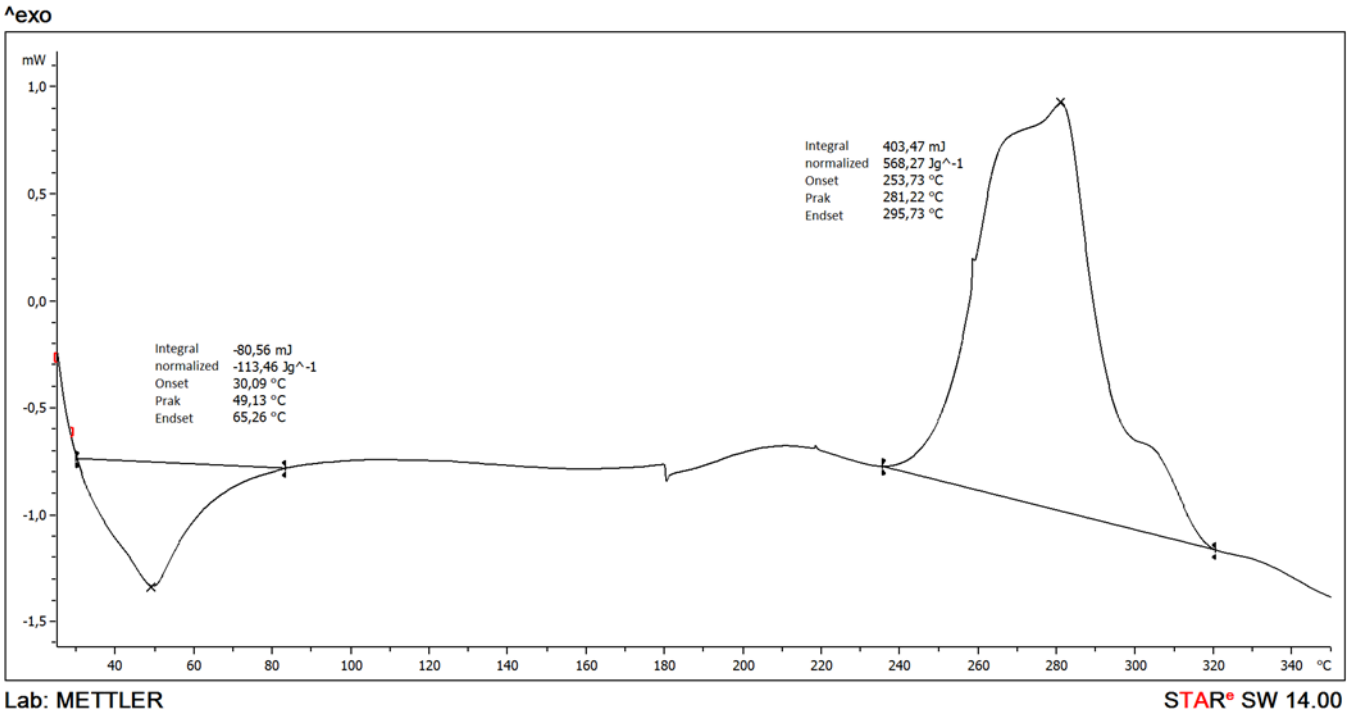


Figure S17. DSC of **4**

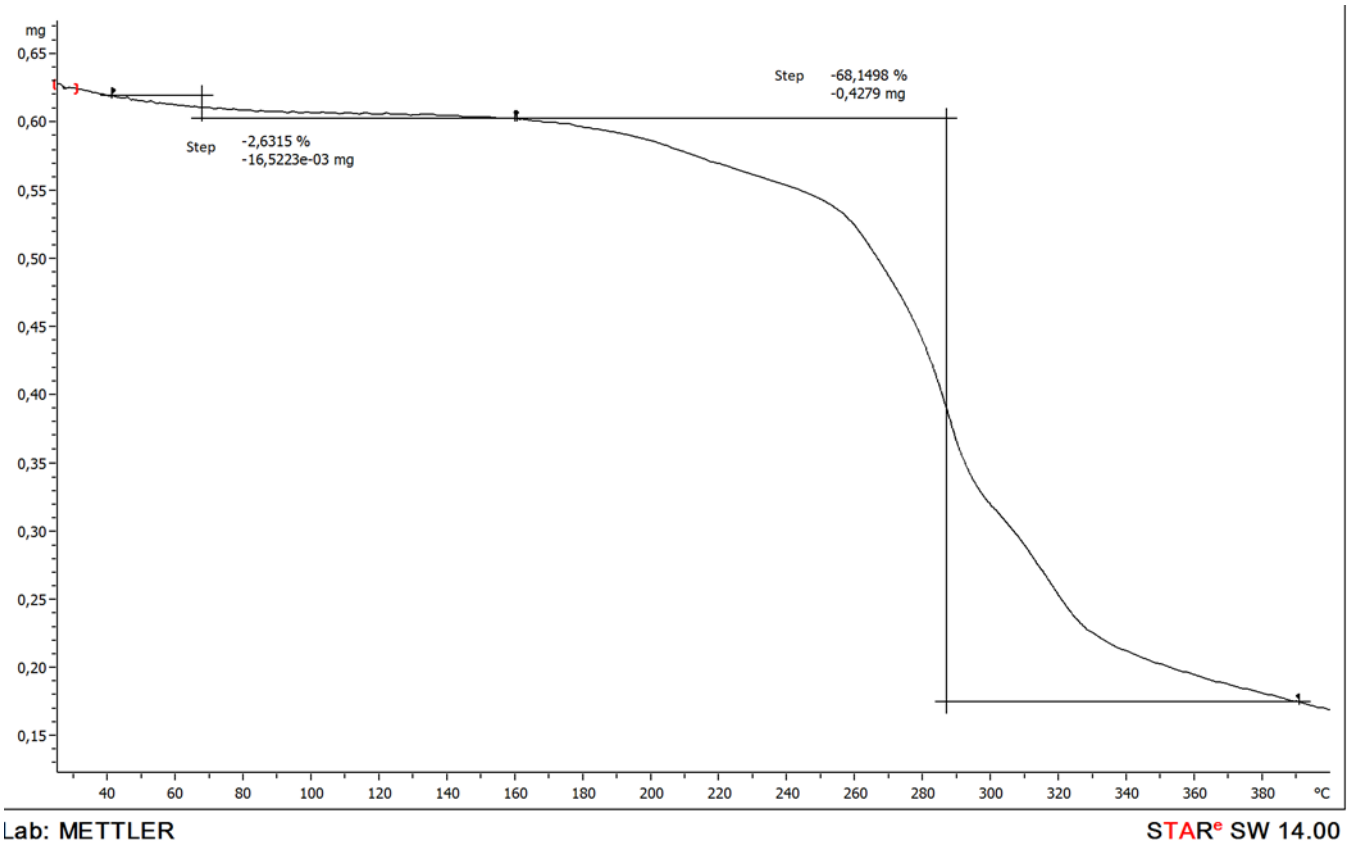


Figure S18. TGA of **4**

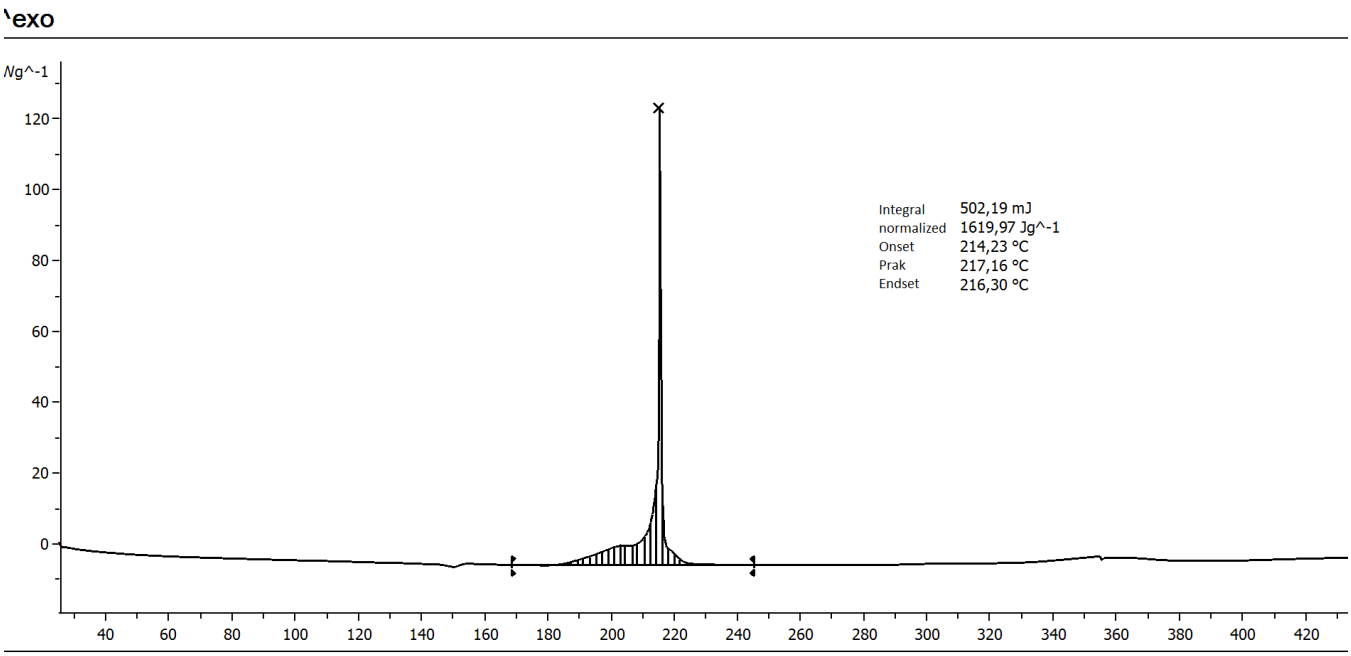


Figure S19. DSC of **6**

All the ingredients were dried at 100 °C to constant weight. The oxidizers were ground in a ball mill and screened through a 63−160-μm sieve. The quantities of tris(carbohydrazide-N,O)nickel(II) dinitramide incorporated into the pyrotechnic formulations were 0.5%, 1.0% and 1.5%, exceeding 100%. The weighed portions of the pyrotechnic ingredients were taken to an accuracy of 0.0001 g. The ingredients were mixed in an agate mortar. The burning-rate measurements were performed by the procedure reported using extruded cylindrical specimens of 10 mm in diameter.

The extrusion force was 20 kg mm^{-2}. The burning rate was recorded by ionization detectors. The burning front passage time between the detectors was documented on an AKTAKOM ASK-3107 oscillograph. The specimens were ignited by a spiral coil made of nichrome wire of 0.5 mm wide.

Synthesis

Dinitramide carbohydrazide **3** and *bis-dinitramide carbohydrazide* **4**: The corresponding weighed portion of ammonium dinitramide was dissolved in water (10 mL) and allowed to pass through a column containing a Dowex-50 ion-exchange resin (H^+ form), and washed with water (40 mL) to pH = 6. The resultant aqueous solution of dinitramide was cooled, and carbohydrazide (0.9 g, 0.01 mol) was added portionwise. This was kept at a temperature of at most 10 °C for 1 h. The aqueous solution was concentrated in vacuo to ca. one-third of the initial volume and then evaporated in a crystallizer until precipitation. The resultant precipitate **3** or **4** (94−99%) was oven-dried at 70−80 °C.

For **3**, mp 216°C. UV (H_2O λ_{max}): 285; 213 nm. ε_{285} = 5992. IR (v/cm^{-1}): 3443, 3326, 3236, 3237, 1694, 1623, 1531, 1433, 1344, 1276, 1192, 1023, 952, 828, 762, 732. ^{1}H NMR (400,13 MHz, DMSO-d_6) δ: 4.18 (s, 2H, NH_2), 7.43 (s, 1H, NH). ^{13}C NMR (125,73 MHz, D_2O-d_6) δ: 157.92.

For **4**, mp 281°C. UV (H_2O λ_{max}): 284; 212 nm. IR (v/cm^{-1}): 3451, 3367, 1632, 1529, 1433, 1344, 1190, 1023, 954, 828, 762, 732. ^{1}H NMR (500.03MHz, $(CD_3)_2CO$-d_6) δ: 7.49 (s, 3H, NH). ^{15}NNMR (51 MHz, $(CD_3)_2CO$-d_6, standard $HCONH_2$) δ: 369.1, 325.

Tris(carbohydrazide-N,O)nickel(II) dinitramide **6**: $Ni[N(NO_2)_2]_2 \bullet 6H_2O$ (1.895 g, 0.005 mol) was dissolved in water (5 mL), and carbohydrazide (1.35 g, 0.005 mol) in water (10 mL) was added with constant stirring at 20−23 °C. This was kept for 15 min. The solution was concentrated to 10 mL and put into a Petri dish. After 72 h, the resultant crystals of **6** (2.5 g, 93.6 %) were combined by filtration, washed with alcohol and ether, and recrystallized from 50% aqueous ethanol. Mp 217°C. IR (v/cm^{-1}): 3266, 1644, 1604, 1537, 1427, 1344, 1202, 1177, 1096, 1022, 980, 828, 762, 732, 621. Found (%): C, 6.59; H, 3.28; N, 46.49. Ni, 10,83. Calculated (%): C, 6.65; H, 3.33; N, 46.58, Ni 10,85. Calcd. for $C_3H_{21}N_{19}NiO_{11}$.