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A novel energetic nickel coordination compound based on carbohydrazide and dinitramide

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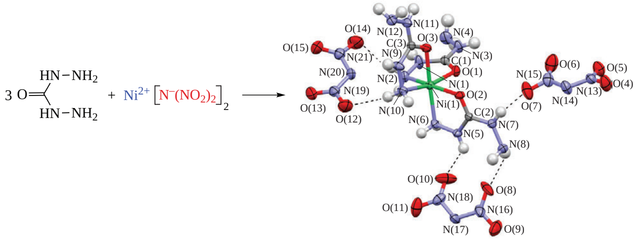
Dinitramide was reacted with carbohydrazide to furnish the corresponding mono- and bis-susbtituted salts. The nickel salt of dinitramide when reacted with carbohydrazide produced the coordination compound, tris(carbohydrazide-*N*,*O*)nickel(II) bis-dinitramide, whose crystal structure was characterized by X-ray diffraction.



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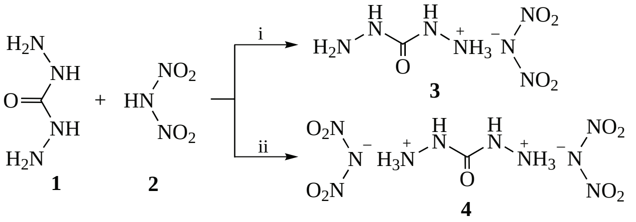
Even though dinitramide[1–5] salts are commonly known and well-studied, the first reports in public sources emerged in the 70-ies of the last century.[5–7] The need for the synthesis of novel salts arises today as well primarily due to the high oxygen content per unit mass and environmental safety of the very product, combustion products and production technology.[8–12] Ammonium dinitramide is the most interesting among dinitramide salts in the context of 'green' energy use.[13–20]

The literature overview shows that compounds based on dinitramide and carbohydrazide **1** have not been described. Although carbohydrazide whose structure is rich in nitrogen and hydrogen is of interest in terms of producing light gases in gas generators, it has already proved to be an energetic material used in the development of salt-like energy-rich compounds.[21–24] Dinitramide and carbohydrazide are also considered as ligands in the synthesis of coordination compounds.[25–29]

In this context, a composition based on carbohydrazide **1** and dinitramide combined with a complexing metal cation has success to be promising for the synthesis of new units in chemistry of high-energy materials. The present study was aimed to synthesize new energy-rich compounds starting from dinitramide salts. Carbohydrazide **1** being the base reacts with an aqueous solution of dinitramide **2** to yield the corresponding mono- and bis-substituted salts **3** and **4** (Scheme 1, for experimental details see Online Supplementary Materials). Dinitramide **2** was prepared from its potassium salt[30] by the reported procedure.[3]



Scheme 1 *Reagents and conditions*: i, **1**/**2** = 1 : 1–2 (mol/mol), 10 °C, H_2O, 1 h; ii, **1**/**2** = 1 : 3 (mol/mol), 10 °C, H_2O, 1 h.

The use of aqueous solutions is associated with the process safety and good solubility of the starting reactants. An optimal temperature is 10 °C. When the reaction is carried out at 20 °C, gas formation would occur indicating the decomposition process and, hence, the product yield becomes 10−15% lower. Further raising the reaction temperature is even more undesirable from the viewpoint of safety.

At a 1 : 1−2 molar ratio of the starting reactants **1** and **2**, dinitramide carbohydrazide **3** was the major reaction product representing a paste-like hygroscopic substance with a maximum decomposition temperature of 215 °C. Drying in a vacuum oven at 70–80 °C for 6 h furnished a material with a melting point of 92 °C and a decomposition point of 215 °C. When a weighed portion (0.67 mg) was heated, compound **3** exploded; the TGA data showed a sharp weight loss of –83% at near 184–218 °C, which corresponded to a sharp heat release. The DSC data corresponded to an explosive nature of the decomposition process. The UV spectrum of compound **3** has two absorption maxima at 213 and 285 nm, which is compatible with absorption of dinitramide anion.[2] The quantitative determination of the dinitramide content in salt **3** from the UV spectrum (ε = 5992) showed that one anion related to one carbohydrazide cation.

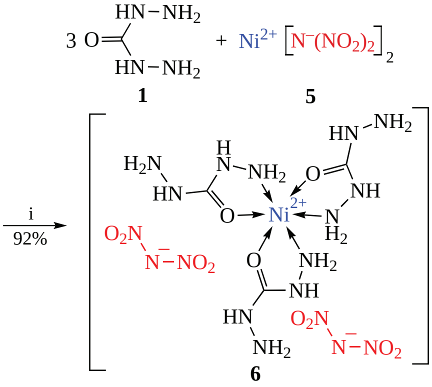
The IR spectrum of isolated crystalline precipitate **3** showed the presence of the most characteristically intense absorption bands for the dinitramide group at 1530, 1192 and 1023 cm^{-1}. The absorption bands at 3325–3236, 1694 and 3442 cm^{-1} refer to the NH_2 group, C=O and OH group of water, respectively. Its ^1H NMR spectrum in DMSO-d_6 revealed the downfield shift of signals compared to the starting carbohydrazide **1**. In fact, the signal for the N*H*-C(O) group shifted from 7.16 to 7.43 ppm, while that for the NH_2 amino group appeared at 4.18 ppm rather than at 3.94 ppm. It is worth noting that small amount of water present in the sample was engaged in the proton exchange to generate a broad signal at 3.8 ppm.

The use of dinitramide **2** in a excess over 3 mol resulted in a product **4** having a melting point of 45 °C. The UV spectrum of compound **4** has two absorption maxima at 212 and 284 nm, which is compatible with the absorption of dinitramide anion. The quantification of dinitramide content in salt **4** form the UV spectrum ($\varepsilon = 5992$) showed the presence of its two anions per one carbohydrazide cation. The IR spectrum of sample **4** showed representative absorption bands of the dinitramide group at 1529, 1190 and 1023 cm^{-1} as well as an absorption band of C=O at 1632 cm^{-1} whereas no representative absorption bands for the NH_2 and NH groups were present. The ^1H NMR spectrum of compound **4** in acetone-d_6 revealed a significant shift of the N*H*–C(O) signal to 7.49 ppm. Thus, the reaction between carboxyhydrazide **1** and dinitramide **2** proceeds to yield dinitramide carbohydrazide **3** when the **1**/**2** ratio is 1 : 1−2 and to yield bis-dinitramide carbohydrazide **4** when this ratio is 1 : 3.

Mixing aqueous solutions of nickel(II) dinitramide **5** and carbohydrazide **1** at room temperature resulted in a clear dark-blue solution which upon concentrating would release dark-blue crystals of tris(carbohydrazide-*N*,*O*)nickel(II) bis-dinitramide **6** (Scheme 2). The yield of product **6** was 92% (for details, see Online Supplementary Materials).

The solubility of sample **6** in DMSO turned out to be high enough, however the paramagnetic nature of the central Ni^{2+} ion did not allow us to record its NMR spectrum. The IR spectrum of complex **6** had representative absorption bands of dinitramide anion, namely, $\nu_{as}(NO_2) = 1537$ cm^{-1}, $\nu_s(NO_2) = 1202$, 1177 cm^{-1}, and $\nu_{as}(N_3) = 1022$ cm^{-1}, as well as an absorption band of C=O at 1644 cm^{-1}. In addition, it contained characteristic bands for the NH_2 and NH groups at 3266 and 1604 cm^{-1}. Salt **6** was well-soluble in water, DMF and DMSO and was air-stable. When heated above 180 °C, the decomposition of **6** exhibited an explosive effect. The composition of complex **6** determined by the Ostromyslensky–Zhob method with UV spectroscopy showed that the maximum concentration of the resulting complex **6** occurred when the ratio of the starting components **5** and **1** was 1 : 3.

The X-ray diffraction study of single crystal **6** (Figure 1)[†] established that the site of complexation was Ni^{2+} cation coordinated *via* the O (C=O) and N (NH_2) linked to three carbohydrazide molecules forming three five-membered rings, while dinitramide anions were located in the second sphere.



Scheme 2 *Reagents and conditions*: i, **1/5** = 1 : 1 (mol/mol), H_2O, room temperature, 15 min.

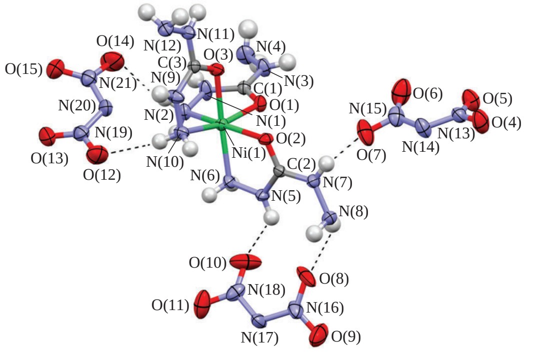


Figure 1 Molecular structure of compound **6**. Thermal ellipsoids are shown at 50% probability.

The comparison of IR spectra of complex **6** and starting carbohydrazide **1** and dinitramide **2** showed that absorption bands of the functional groups of **1** and **2** underwent a shift to 50 cm^{-1} upon complexation. The absorption band shift is due to the formation of associated forms of the functional groups. The representative bands correlate well to vibrations of the NO_2 groups, namely, 1528 cm^{-1} along with 828, 761, 733, 727 (for dinitramide) and 1542 cm^{-1} along with 816, 759, 750, 731 (for complex **6**). For individual compound **1**, these regions are transparent. In contrast, the absorption bands near 1539–1604, 1455–1425 and 1344 cm^{-1} inherent in compound **1** are present in the spectrum of complex **6** and are absent in the spectrum of dinitramide. A tendency of absorption band displacement for the groups engaged in the coordination with the metal was observed, *i.e.*, for ν(C=O) at 1639 cm^{-1} (**1**), 1651 cm^{-1} (**6**), and for $\delta(NH_2)$ at 1539 cm^{-1} (**1**), 1604 cm^{-1} (**6**).

Crystalline complex **6** is well soluble in water and insoluble in alcohol. It explodes when heated, and is very sensitive to impact and friction. The physicochemical characteristics are listed in Table 1.

Table 1 Physicochemical characteristics of compounds **3**,**4**,**6**.[a]

Compound	$T_{dec.}$/°C	d^{22}/g cm^{-3}	Ni content[b] (%)	Colour	Sensitivity (lower limit) to	
					impact/mm	friction/kgf cm^{-2}
3	216	1.771	–	white	<50	2500
4	281	1.747	–	white	<50	2400
6	217	1.8945	10.8	dark-brown	<50	2200

[a] The experimental details and methods are outlined in the Online Supplementary Materials. [b] Determined by UV-VIS spectroscopy; calc.: 10.85% for $C_3H_{18}NiO_{11}$.

[†] *Crystal data for* **6**. $C_3H_{18}N_{12}NiO_3$, $2(N_3O_4)$ ($M = 541.04$), triclinic system, space group $P\bar{1}$ at 296 K: $a = 8.9847(14)$, $b = 10.1466(19)$ and $c = 12.477(2)$ Å, $\alpha = 107.144(6)°$, $\beta = 99.812(5)°$, $\gamma = 110.703(5)°$, $V = 967.5(3)$ Å^3, $Z = 2$, $d_{calc} = 1.857$ g cm^{-3}, μ(MoKα) = 1.101 mm^{-1}, $F(000) = 556$. Total of 37908 reflections were collected (5983 independent reflections, $R_{int} = 0.0448$) and used in the refinement, which converged to wR_2 0.0754, GOOF 1.075 for all independent reflections [$R_1 = 0.0280$ was calculated for 5983 reflections with $I \geqslant 2\sigma(I)$].

The X-ray diffraction analysis was carried out on a Bruker KAPPA APEX II CCD diffractometer (MoKα radiation $\lambda = 0.71073$ Å, graphite monochromator). Absorption corrections were applied using SADABS.[33] 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. The hydrogen atoms were refined in the riding and isotropic models. Anion molecules located around centers of symmetry are disordered with 0.5 : 0.5 ratio. All computations were done using SHELX-2018 programs.[34]

CCDC 2113879 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

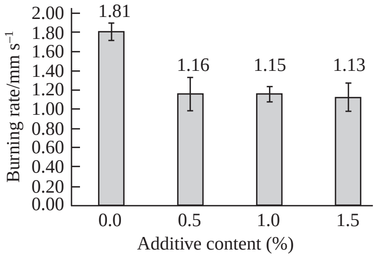


Figure 2 Efficiency of tris(carbohydrazide-*N*,*O*)nickel(II) dinitramide **6** as the burning-rate modifier of Al/$KClO_4$ pyrotechnic composition.

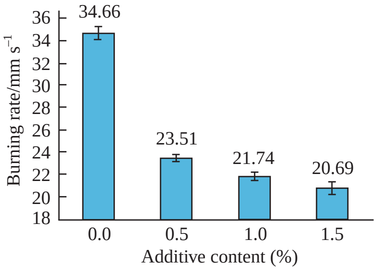


Figure 3 Efficiency of tris(carbohydrazide-*N*,*O*)nickel(II) dinitramide **6** as the burning-rate modifier of Zr/KNO_3 pyrotechnic composition.

Compound **6** was also tested as the burning-rate modifier of pyrotechnic composites in order to increase the sensitivity of the compositions from the sources of the initial pulse (from the sources of primary initiation) and to increase the light-noise effect for the composites (Figures 2 and 3). The formulations used for testing were as follows. (1) Sound and flash pyrotechnic composition[31,32] (70% potassium perchlorate and 30% aluminum) and (2) igniting pyrotechnic composition[31] (52% zirconium and 48% potassium nitrate). For more details, see Online Supplementary Materials.

The studies demonstrated that addition of up to 1.5% of compound **6** reduced the burning rate; for example, the burning rate of the high-rate Zr/KNO_3 composite declined from 34.66 to 20.68 mm s^{-1}, while that of the low-rate Al/$KClO_4$ composite was observed to decrease from 1.80 to 1.12 mm s^{-1}. In this case, the incorporation of the initiating explosive resulted in an increased sound and flash effect while reducing the burning rate.

In summary, mono- and bis-dinitramide salts of carbohydrazide, as well as a nickel(II) coordination compound **6** based on dinitramide and carbohydrazide, have been synthesized for the first time. In complex **6**, nickel(II) and carbohydrazide are coordinated *via* the oxygen and nitrogen of the amino hydrazide group, while dinitramide anion is located in the second sphere. Despite high sensitivity, compound **6** can successfully act as a burning-rate modifier of high- or low-rate pyrotechnic compositions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.017.

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