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Laser Initiation of Tris(carbohydrazide)metal(II) Perchlorates and Bis(carbohydrazide)diperchlorato-copper(II)

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Dedicated to Professor Mikhail A. Ilyushin

Abstract: The literature-known tris(carbohydrazide)metal(II) perchlorates [M(CHZ)$_3$](ClO$_4$)$_2$ (M=Mg^{2+} (**1**), Mn^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), and Zn^{2+} (**5**)) and the bis(carbohydrazide)diperchloratocopper(II) (**6**) were prepared and characterized by elemental analysis, IR and Vis/NIR spectroscopy. The sensitivities toward mechanical, thermal, and electrical stimuli were determined for all complexes **1**–**6**. Following, confined samples of **1**–**6** were irradiated with a monopulsed laser beam at a wavelength of 940 nm. The function times between beginning irradiation and complete decomposition ("breakout" at the end of the device) were measured. Further, the influence of light-absorbing additives was investigated to proof if the laser initiation mechanism might be photothermal or photochemical. Addition of 1% active carbon to the samples decreased the function time and the correlated initiation threshold enormously. This was an indication that the initiation mechanism seems to be thermal.

Keywords: Laser initiation · Diode laser · Initiation mechanism · Vis/NIR · Additives

1 Introduction

The main topics in the recent research of energetic materials are safety, environmental acceptability, and high performance. Thus, the development of new materials, which achieve the desired requirements, is necessary. Promising primary and secondary explosives, oxidizers and pyrotechnics have been presented in the last years [1]. However, there has always been a demand for safe initiation methods to improve and facilitate the handling of explosives, too. While classic primary explosives are stimulated by e.g. impact, friction or heat and consequently susceptible to undesired initiation [2], exploding bridgewire (EBW) and foil initiators (EFI) represent a class of safe non-primary explosive detonators [3]. These type of electric detonators is considerably less susceptible toward unintended initiation by electric impulses than simple hot-wire initiators [3a], however, they are improper for some applications due to several other reasons [4] e.g. large size of the required power sources.

As a consequence, laser initiation was suggested as an alternative. In the late 1960s and early 1970s, the first laser initiation experiments were made by Brish et al. as well as Menichelli and Yang [5]. Common primary (lead azide) as well as secondary explosives (like pentaerythritol tetranitrate, cyclotrimethylentrinitramine, and *N*-methyl-*N*-2,4,6-tetranitroaniline) were irradiated by Q-switched neodymium glass and ruby lasers of high power. In the work of Menichelli and Yang for example, the energy of the Q-switched ruby laser ranged from 0.8 to 4.0 J for a pulse width of 25 ns [5c]. Owing to high costs and large size, the practical use of neodymium or ruby lasers for initiation was very limited. The practical application of laser radiation as initiation source firstly received importance in the 1980s by the introduction of laser diodes, which were smaller and cheaper [4a]. However, the energy output of laser diodes was much lower than that of high-power Nd:YAG or ruby lasers. But for an alternative to fast-functioning detonators like EBWs and EFIs, it is necessary to exhibit a short ignition delay, which can be achieved by direct shock initiation of the explosive with a high laser power. Another possibility for short ignition delay times is the use of energetic materials, which show a high susceptibility to laser radiation and are ignited by low laser power densities. Complex perchlorates with hydrazinoazoles as ligands were presented as a novel class of explosives, which exhibited a high sensitivi-

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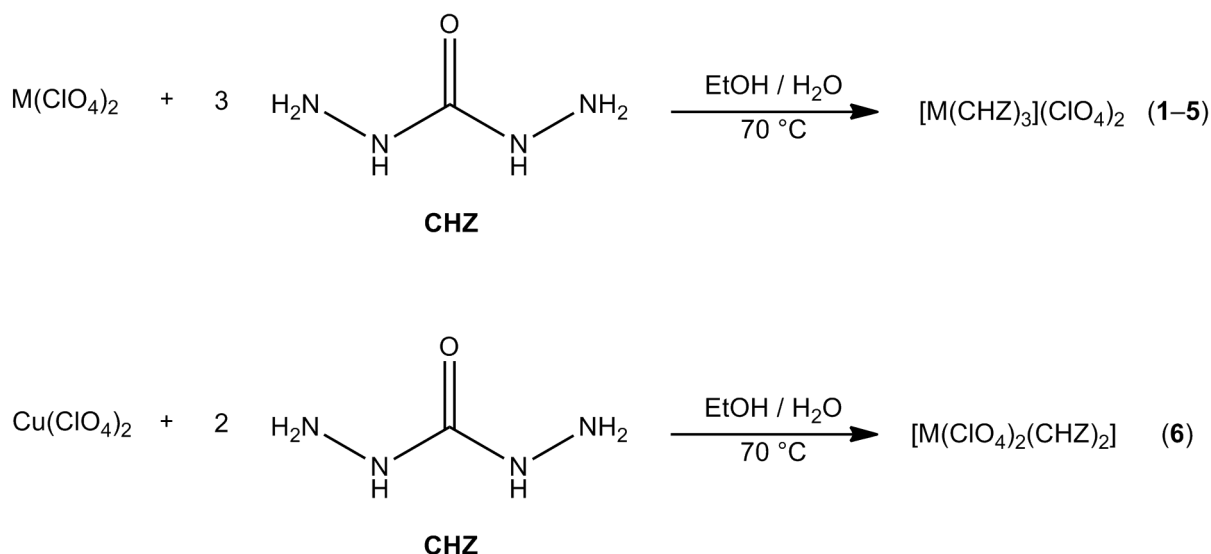
Scheme 1. Synthesis of complexes **1**–**6**.

ty to laser radiation [6]. The 5-hydrazino-1*H*-tetrazolemercury(II) perchlorate (HTMP) is one example for such a laser-sensitive explosive with an initiation energy of 1×10^{-5} J at a pulse length of 30 ns [6]. Other interesting complexes with low initiation thresholds are the bis(3-hydrazino-4-amino-1,2,4-triazole)metal(II) perchlorates, whereas especially copper(II) showed a very high photosensitivity [7]. Metal(II) complexes with 5-(1-methylhydrazinyl)-1*H*-tetrazole (HMHT) and 1,2-bis[5-(1-methylhydrazinyl)tetrazol-1-yl)]-ethane (BMHTE) as ligand have been synthesized and investigated toward laser irradiation by our research group [8]. Amongst others, it was shown that the metal(II) perchlorates (Co, Ni, and Cu) with BMHTE showed a high sensitivity to laser radiation and could all be initiated by a 100 μs pulse of a common diode laser at 940 nm. But not only hydrazinoazoles are suitable ligands for laser-sensitive coordination compounds. For example, various metal perchlorates (Co^{2+}, Ni^{2+}, Cu^{2+}, and Ag^+) with the hydrazine-derivative 3-amino-1-nitroguanidine as ligand were prepared and their behavior upon laser irradiation tested by our research group [9]. In the case of cobalt, copper, and silver, the initiation by a 100 μs pulse at 940 nm was successful.

Although laser initiation of energetic materials is extensively investigated, the initiation mechanism is still not completely understood. A photothermal mechanism and a photochemical one are discussed in literature, though the thermal one is the most prominent [5b, 10]. According to literature [4a, 11], it is stated that in case of a photothermal mechanism, light absorbing particles like carbon black decrease the initiation energy threshold.

Based on the previous results, further investigations to the laser initiation mechanism are necessary. To investigate the influence of the metal center on the laser ignitability it would be wise to have complexes of same formula and structure. Suitable energetic coordination compounds are

the literature-known [12] tris(carbohydrazide)metal(II) perchlorate complexes [*M*(CHZ)$_3$](ClO$_4$)$_2$, which all crystallize in the monoclinic space group *P*2$_1$/*n* and the bis(carbohydrazide)diperchloratocopper(II), whose crystal structure is still unknown. In this work, the literature known carbohydrazide perchlorate complexes with Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} were tested upon laser irradiation. Further, the influence of activated carbon as light absorbing additive and magnesium oxide as light scattering additive was investigated.

2 Results and Discussion

2.1 Synthesis

Carbohydrazide was synthesized according to the literature procedure from dimethylcarbonate and hydrazine [13]. Further, aqueous metal(II) perchlorate solutions were combined with hot carbohydrazide solutions in ethanol. Owing to the use of ethanol as solvent, the products precipitated fast and as fine powders from the reaction mixture. The prepared coordination compounds **1**–**6** (Scheme 1) are all literature-known [12].

2.2 IR Spectroscopy

IR spectra of the ligand CHZ and all perchlorate complexes **1**–**6** were recorded. Carbohydrazide vibrations were assigned according to Ref. [14]. The free ligand exhibits typical N—H valence vibrations in the range between 3353 and 3094 cm^{-1}. The absorption bands are sharp due to the formation of hydrogen bonds in the solid state. Further, a very strong band at 1629 cm^{-1}, with shoulders at 1681, 1648, and 1637 cm^{-1}, can be observed for the N—H deformation vibrations and the C=O stretching vibration. The very

Table 1. Wavenumbers [cm^{-1}] of selected infrared active vibrations for complexes **1–6**.

Vibration[a]	1[b]	2[b]	3[b]	4[b]	5[b]	6[b]
ν(N–H)	3405			3405		
	3392	3391	3389	3389	3389	3368
	3353	3348	3350	3344	3350	
	3317	3324	3327	3328	3329	
	3307	3308	3299	3308	3304	3303
	3232	3235	3228	3232	3225	3263
						3187
δ(N–H)	1645	1645	1645	1645	1645	1670
+ν(C=O)						1635
						1616
δ(N–H)	1546	1548	1541	1544	1541	1503
+ν(C–N)	1544	1541			1538	
ν(Cl–O)	1066	1062	1066	1065	1067	1075
						1061

a) Vibration assignment according to Refs. [14, 15]. b) Experimental data

Table 2. Sensitivities and thermal stability of complexes **1–6**.

	Tonset [°C]	IS[a,b] [J]	FS[a,b] [N]	ESD[a] [J]
[Mg(CHZ)$_3$](ClO$_4$)$_2$	239	2.5	60	0.20
[Mn(CHZ)$_3$](ClO$_4$)$_2$	263	2	24	0.50
[Co(CHZ)$_3$](ClO$_4$)$_2$	243	1	≤ 5	0.035
[Ni(CHZ)$_3$](ClO$_4$)$_2$	273	1	≤ 5	0.30
[Zn(CHZ)$_3$](ClO$_4$)$_2$	268	1.5	20	0.70
[Cu(ClO$_4$)$_2$(CHZ)$_2$]	186	3	<< 5	0.02

a) At grain sizes < 100 μm for all samples. b) According to BAM standard methods (IS: BAM Drophammer; FS: BAM friction tester).

strong band at 1531 cm^{-1} is a vibrational combination of an N–H bend and a C–N stretching vibration. At 1447 cm^{-1} an N–H bend vibration and at 1340 and 1318 cm^{-1} rocking vibrations are observed in strong intensity. Between 1209 and 693 cm^{-1} further vibrational combinations of carbohydrazide are detected.

Compared to the free carbohydrazide, the CHZ ligand vibrations are shifted and changed in the complexes due to coordination. An overview is given in Table 1. The vibrations of the complexes **1–5** are nearly identical, which is in agreement with the crystal structures. In contrast, the structure and formula of the copper complex **6** is different, which is also indicated by the deviating wavenumbers and the presence of different vibrations than in the spectra of **1–5**.

2.3 Energetic Properties and Laser Initiation

The sensitivities toward impact, friction, and electrostatic discharge were determined for the complexes **1–6** by standard methods. Further, the temperature stability was determined with differential thermal analysis. The compounds were classified according the UN Recommendations on the Transport of Dangerous Goods [16]. An overview about the sensitivities and temperature stabilities is given in Table 2.

All complexes **1–6** are classified as very sensitive in terms of impact. Further, the magnesium (**1**), manganese (**2**), and zinc (**5**) complexes are classified as very sensitive toward friction, whereas the cobalt (**3**), nickel (**4**), and copper (**6**) compounds are extremely sensitive. Complex **6** showed the highest friction sensitivity and once detonated accidentally by positioning a small amount on the porcelain plate during the preparation for the friction test.

The copper complex **6** further shows the highest sensitivity toward electrostatic discharge followed by the cobalt compound **3**. The zinc compound **5** exhibited the lowest ESD sensitivity. The temperature stability of the metal complexes **1–6** decreases in the following series:

$$Ni^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Mg^{2+} > Cu^{2+}$$
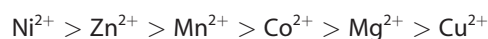
The low temperature stability of the copper compound **6** may also be a result of its different structure ([Cu(ClO$_4$)$_2$(CHZ)$_2$]) compared to **1–5**.

Laser initiation tests were performed with a single-pulsed diode laser at a wavelength of 940 nm and a pulse length of 400 μs. The laser power was in the order of 10^5 W cm^{-2} and kept constant for all tests. Multiple samples of each complex were tested under constant parameters. The samples consisted of powders of the complexes **1–6** and

Table 3. Laser initiation results and average function times t_f of complexes **1**–**6**.

	$F(R)$ at 940 nm	$t_f^{a)}$ [s]	$tf^{b)}$ [s]
[Mg(CHZ)$_3$](ClO$_4$)$_2$	0.01	no init.	no init.
[Mn(CHZ)$_3$](ClO$_4$)$_2$	$<$0.01	no init.	no init.
[Co(CHZ)$_3$](ClO$_4$)$_2$	0.03	40.1×10^{-5}	4.3×10^{-5}
[Ni(CHZ)$_3$](ClO$_4$)$_2$	0.37	13.6×10^{-5}	1.7×10^{-5}
[Zn(CHZ)$_3$](ClO$_4$)$_2$	0.01	no init.	no init.
[Cu(ClO$_4$)$_2$(CHZ)$_2$]	$<$0.01	6.5×10^{-5}	0.8×10^{-5}

a) No addition of activated carbon. b) Addition of 1% activated carbon ($F(R)_{940nm} = 0.76$).

5 wt% polyethylene as binder. Additional, to half of the samples 1 wt% powdered activated carbon was added to investigate the influence of light absorbing particles on the initiation threshold. Sample bulks of 180 mg were further pressed to pellets of a bulk-density of 1.5 g cm^{-3}, confined with an aluminum shell and placed on an aluminum witness plate for detection of detonation. In case of a successful initiation, the function time [3b] as the sum of the ignition delay time (time from beginning irradiation to beginning of decomposition) and the propagation of the reaction zone (time from beginning of the self-sustained decomposition reaction until "breakout" at the end of the device) was measured. Thereby, the beginning of irradiation was detected by an electric signal and the end of reaction by an optical output signal due to a light emission accompanied with the detonation. For function times in the order of 10^{-4} s and under the assumption of a process time for DDT of 2–10$\times$10^{-6} s, the measured function time can nearly be supposed as the ignition delay time [4a]. For faster function times in magnitude of 10^{-6}–10^{-5} s, it would be necessary to directly measure the ignition delay time similar to the method by Hafenrichter et al [4a]. However, under the assumption that the required time for the DDT process is similar in magnitude for the complexes **1**–**6**, it would be sufficient to measure the function time to obtain a trend for the laser ignitability related to the metal cation.

The results of the laser initiation are listed in Table 3. The complexes **1**, **2**, and **5** could not be initiated by the laser pulse in our experiments what is in agreement with the Vis/NIR spectra, which show nearly no absorption (Figure 1). Even under addition of 1 wt% activated carbon, the samples of the complexes **1**, **2**, and **5** could not be initiated. Contrary, the complexes **3** (401 μs), **4** (136 μs), and **6** (65 μs) were successfully initiated and the function times measured. Regarding the solid Vis/NIR spectra (Figure 2), it appears plausible that the nickel compound **4** has a lower initiation energy threshold according to its higher light absorption at 940 nm than the cobalt compound **3**. However, the copper(II) complex **6** exhibits nearly no absorption at 940 nm but showed the lowest ignition delay of the undoped samples. One reason might be the found in the lowest auto-ignition temperature ($T_{onset} = 186$ °C) for **6** of the herein investigated complexes, although this could not be the only explanation under the assumption that the ini-

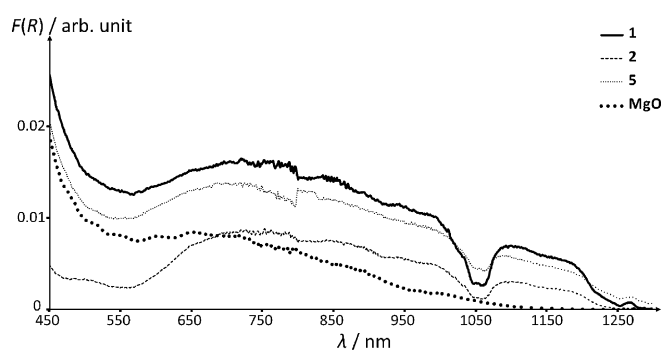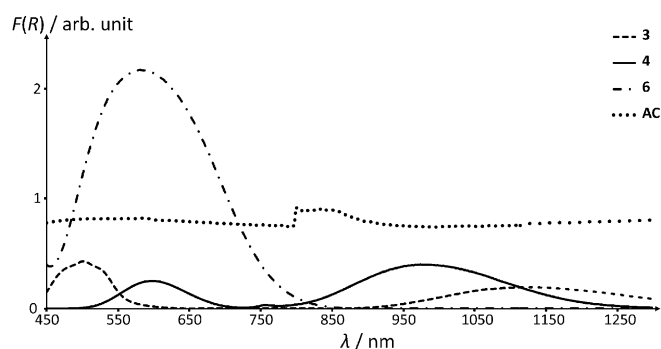**Figure 1.** Vis/NIR spectra of the colorless complexes **1**, **2**, **5**, and MgO.

Figure 2. Vis/NIR spectra of the colored complexes **3**, **4**, **6**, and activated carbon (AC).

tiation follows a thermal mechanism. Further parameters like thermal conductivity, heat capacity or other yet disregarded might play an important role.

By adding 1 wt% activated carbon ($R_{@940nm} = 31$%) to the samples to decrease the light reflection R (%), the function time and correlated to it the energy threshold could be decreased by approximately factor ten for **3**, **4**, and **6**. Thus it can be concluded, that the main amount of laser radiation is absorbed by the carbon particles independent of the absorptivity of the metal complex itself and that heating of carbon particles and heat transfer to energetic particles is the influential process. This is also an indication for a thermal initiation mechanism.

A further proof for a thermal mechanism and not a photochemical one was given by mixing 1 wt % of magnesium oxide ($R_{@940nm} = 107\%$) instead of carbon to a sample of **6**. In case of a photochemical process according to literature [10a], light scattering particles like MgO should decrease the initiation energy threshold by an increase of irradiated volume resulting in an enhancement of probability for electronic excitation. However, the opposite is observed. The function time of **6** is lengthened from 65 µs to 126 µs. This can be explained by the increase of reflection and the enlargement of irradiated volume by light scattering. Due to the consequential lowering of energy density, more energy is necessary to reach the auto-ignition temperature, which is finally achieved by a longer irradiation time at constant power P.

3 Experimental Section

Caution! The perchlorate complexes **1**–**6** are energetic materials, which show increased sensitivities toward various stimuli (e.g. impact, friction, electrostatic discharge, heat). Proper protective measures (safety glasses, face shield, leather coat, earthed equipment, conductive floor and shoes, Kevlar gloves, and ear plugs) are recommended when handling these materials [17]. The handled scales should be kept small. Especially, the cobalt (**3**), nickel (**4**) and copper (**6**) compounds are extremely sensitive toward impact and friction.

All chemicals were used as supplied by ABCR, Acros Organics, AppliChem, Fluka, Sigma-Aldrich, and VWR. The impact and friction sensitivity tests were performed according to standard methods by using a BAM (Bundesanstalt für Materialforschung und -prüfung) drop hammer and a BAM friction tester [18]. The sensitivity toward electrostatic discharge was tested by using an OZM Research electric spark tester ESD 2010 EN [19]. Decomposition temperatures were determined by differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 C min^{-1} and in a range of room temperature to 400 °C [19, 20]. The determination of the carbon, hydrogen and nitrogen contents was carried out by combustion analysis with an Elementar Vario EL [21]. IR spectra were recorded with a Perkin-Elmer BXII FT-IR system with a Smith DuraSamplIR II diamond ATR unit [22]. The Vis/NIR reflectance of solid samples (powders) was determined with a Varian Cary 500 spectrometer in the wavelength range of 450–1300 cm^{-1} [23]. The relative reflectance R (%) was transformed by the Kubelka-Munk equation to the absorption intensity $F(R)$ (arbitrary units). A reflectance of $R >$ 100 % is possible because the values are relative to the background reflection of blank samples [24].

The tris(carbohydrazide)metal(II) perchlorates **1**–**5** and the bis(carbohydrazide)diperchloratocopper(II) (**6**) have all been prepared in a similar way. A concentrated aqueous solution of the corresponding metal(II) perchlorate (2.2 mmol) was added to a 70 °C warm solution of carbohydrazide (**1**–**5**: 6.0 mmol, 0.54 g; **6**: 4.0 mmol, 0.36 g) in ethanol (45 mL) whilst stirring. The resulting clear solution was cooled down to room temperature whilst stirring. The product precipitated in form of a fine powder (**1**: colorless; **2**: colorless; **3**: intense red; **4**: intense blue; **5**: colorless; **6**: dark blue) within 1 h. Detailed experimental data can be found in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Detailed experimental data.

4 Conclusions

The literature known carbohydrazide (CHZ) complexes with perchlorate as anion and magnesium (**1**), manganese (**2**), cobalt (**3**), nickel (**4**), zinc (**5**), and copper (**6**) as metal(II) cations were synthesized by fast precipitation from ethanol solutions. The complexes were characterized by Vis/NIR and infrared spectroscopy as well as elemental analysis. Further, the sensitivities toward mechanical, electrical, and thermal stimuli were determined. Especially the copper(II) complex **6** was extremely sensitive toward friction, whereas the magnesium complex exhibited the lowest mechanical sensitivity. Additional, laser initiation experiments were made. The copper (**6**) compound exhibited the shortest ignition delay time followed by nickel (**4**) and cobalt (**3**). The complexes **1**, **2**, and **5** could not be ignited. By addition of powdered activated carbon (decrease of initiation threshold) and alternatively magnesium oxide (increase of initiation threshold), it could be shown that the initiation of explosives by monopulsed diode laser radiation presumably is a thermal process which is also in agreement with the literature [4a, 5b, 25]. However, it is not understood, which parameter mainly influences the initiation energy threshold.

Future investigations should proof if the initiation energy threshold is decreased for laser wavelengths, at which the absorptance of the corresponding coordination compound is higher e.g. for **6** [$F(R)_{@635nm} = 1.94$] under use of a AlGaInP diode laser or for **3** [$F(R)_{@1064nm} = 0.17$] under use of a Nd:YAG laser.

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