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Transition Metal Complexes of 3-Amino-1-nitroguanidine as Laser Ignitible Primary Explosives: Structures and Properties

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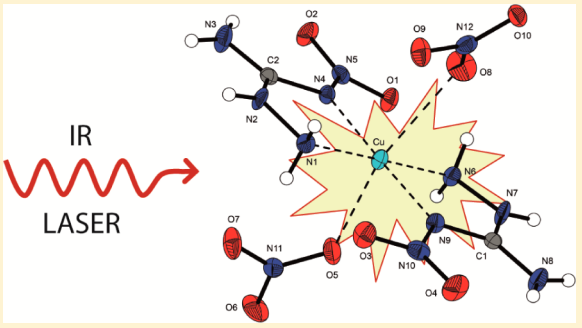
Supporting Information

ABSTRACT: 3-Amino-1-nitroguanidine (ANQ, **2**) was synthesized via hydrazinolysis of nitroguanidine. By dissolving **2** in solutions containing transition metal salts, several complexes $M^{2+}(ANQ)_2X_2(H_2O)_y$ with M^{2+} = Co, Ni, Cu, Zn as well as $M(ANQ)_2X(H_2O)_y$ with M = Ag could be isolated. In these cases, nitrate as well as perchlorate and chloride served as the respective anions X. Additionally, the ANQ complexes of Co, Ni, and Ag with dinitramide as the anion were synthesized from ANQ and silver dinitramide and by reacting the cobalt and nickel ANQ perchlorate complexes with ammonium dinitramide. The crystal structures of all described complexes were determined by low temperature single-crystal X-ray diffraction. Additionally, they were characterized using IR spectroscopy and elemental analysis. The decomposition temperatures were determined by differential scanning calorimetry and the sensitivities toward impact and friction were assessed using a BAM drophammer and a BAM friction tester (BAM = Bundesanstalt für Materialforschung und -prüfung). Additionally, the sensitivity toward electrostatic discharge was determined on a small-scale ESD device. The potential use of the nitrate, dinitramide and perchlorate containing species as primary explosives was investigated in a laser ignition test.



1. INTRODUCTION

In the continuous research toward new energetic materials, high-energy capacity transition metal complexes have become more and more popular.[1−3] These materials mostly combine facile syntheses and good thermal stabilities with energetic properties similar to that of the prominent primary explosive lead azide, which should be replaced because of its high toxicity. For the synthesis of energetic complexes, especially nitrogen-rich heterocycles[4] or guanidine-based ligands can be used.

The guanidine building block is one of the first structural moieties that has been known to the chemical and biological community and was discovered as early as 1866, when the first guanidine derivative was prepared by Hofmann.[5] Since then, guanidine chemistry has evolved into an extremely wide ranging field of applications starting from bioorganic chemistry and biochemistry[6] to inorganic chemistry, which most importantly can be traced back to a vast variability of derivatization of the guanidine moiety itself. Whereas a lot of correspondence can be found dealing with either aminated or nitrated guanidines such as aminoguanidine[7] or nitroguanidine,[8] only very few sources report on the synthesis[9] and use of the mixed 3-amino-1-nitroguanidine (ANQ, **2**), which is the only today known guanidine derivative containing both, an amine and a nitro substituent. Nevertheless, it has found application as a useful intermediate for cylization reactions yielding bis-nitramino-triazoles,[10] for the synthesis of 5-nitriminotetrazole, which proceeds via a diazotization reaction and following cyclization of nitroguanyl azide,[11] or as a cationic species in ionic energetic materials.[12]

Because of the considerable amount of electron density at its amine and nitramine substituent, it expectedly shows fairly good characteristics as a ligand in transition metals complexes, which have not been described in the literature before. Furthermore, although amine substituted guanidine derivatives are subject to oxidative decomposition in air, ANQ is stable under ambient conditions.

Ilyushin et al. report on the synthesis of a cobalt(III) complex bearing tetrazole as a ligand and perchlorate as the counterion and its use as nontoxic initiating explosive.[13] Bearing this in mind, the choice of counterions was directed to anions such as the nitrate, dinitramide, or perchlorate anion, which frequently have been reported as counterions in ionic energetic materials.[14,15] The first reported synthesis of a dinitramide compound was that of its ammonium salt.[16] To overcome the problems, which nowadays are discussed regarding the safe handling of commonly used primary explosives such as lead azide, which aside from being toxic has a high impact and friction sensitivity, a new class of initiating charges, which are laser-igitable primary explosives, are investigated.[17] If insensitive toward impact and friction, these materials can easily be ignited by a short but highly energetic laser pulse with a specific wavelength. This

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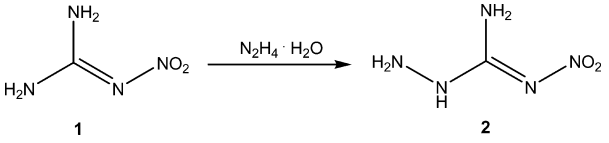
considerably reduces the probability of being accidentally ignited, which oftentimes happened while handling the commonly used impact and friction sensitive primary explosives. Here, the use of transition metal complexes has already been discussed, whereas the exact mechanism, by which transition metal containing complexes are ignited upon laser irradiation, is still under investigation.

As possible candidates for laser ignitable primary explosives, the ANQ complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ag^{+} with a choice of counterions (NO_3^-, $N(NO_2)_2^-$, ClO_4^-, Cl^-) were investigated including their synthesis and structure determination.

2. RESULTS AND DISCUSSION

2.1. Synthesis. 3-Amino-1-nitroguanidine (ANQ, **2**) was synthesized in aqueous solution employing a hydrazinolysis reaction of commercially available nitroguanidine (**1**, see Scheme 1), whereas it is important to control the temperature accurately.[18] The product itself shows fairly poor solubility in water and therefore can be recrystallized from hot water.

Scheme 1. Hydrazinolysis of Nitroguanidine[a]



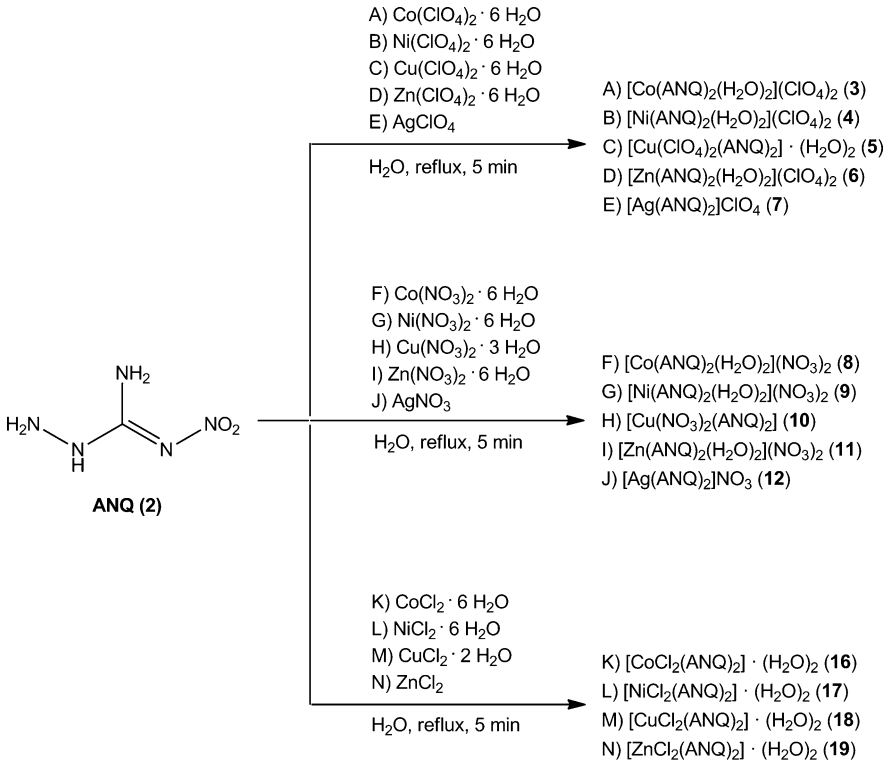
1 2

[a]Reaction conditions: stirring, 55 °C, 15 min.

The formation of the perchlorate, nitrate, and chloride-based 3-amino-1-nitroguanidinium complexes **3**–**7**, **8**–**12**, and **16**–**19** proceeds after dissolving the respective Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ag^{+} perchlorates, nitrates, or chlorides, as indicated in Scheme 2, in a boiling solution of ANQ. The stoichiometry of the reaction of ANQ: metal salt was chosen to be 1:1 instead of 2:1 (which is the stoichiometry found in the crystalline products), because poorly water-soluble ANQ tends to precipitate from the mixture upon cooling down. In some cases, precipitated ANQ indeed had to be filtered off from the mixture, before crystals of the complex began to grow, which especially was observed for the zinc(II) complexes. The yields of the described reactions were determined only of the first isolated fraction of crystals and lie between <10% and 49%, which presumably can be optimized by further evaporation of the mother liquors.

The ANQ complexes bearing a dinitramide counterion in the cases of the cobalt and nickel complexes **13** and **14** were synthesized from the respective metal perchlorate-containing solutions after addition of ammonium dinitramide in a stoichiometric ratio of metal perchlorate:ADN = 1:2 (see Scheme 3). The advantage of the perchlorate containing solutions as starting material over the nitrate or chloride containing solutions is the better solubility of the metal–ANQ perchlorates as compared to the nitrates or chlorides, so that they do not precipitate before the dinitramides were isolated from the mother liquors. Using potassium dinitramide instead is disadvantageous because of the simultaneous precipitation of both potassium perchlorate and the metal-ANQ dinitramides. The silver complex was formed after combining solutions of 3-amino-1-nitroguanidinium chloride[19] and acetonitrile-stabilized silver dinitramide[20] in a 1:1 stoichiometric ratio. After filtering off AgCl, the silver–ANQ dinitramide monohydrate crystallizes from the mother liquor in colorless needles.

Scheme 2. Formation of Perchlorate, Nitrate, and Chloride-Based 3-Amino-1-nitroguanidinium Complexes 3–7, 8–12, and 16–19



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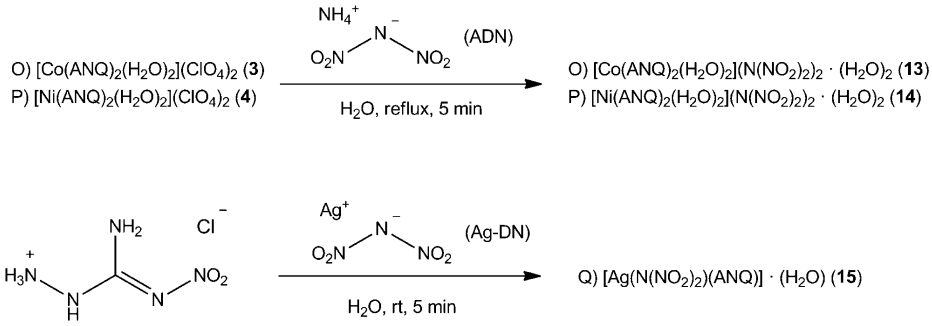
Scheme 3. Formation of Dinitramide-Based 3-Amino-1-Nitroguanidinium Complexes 13−15



2.2. Single-Crystal X-ray Structure Analysis. The low-temperature determination of the crystal structures of **3**−**19** was performed on a Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and reduction were carried out using the CrysAlisPro software.[21] The structures were solved either with SIR-92[22] or SHELXS-97,[23] refined with SHELXL-97[24], and finally checked using the PLATON[25] software integrated in the WinGX[26] software suite. The absorptions were corrected by a Scale3 Abspack multiscan method.[27] Selected data and parameter of the X-ray determinations are given in the Supporting Information in Tables S1−S3. Cif files have been deposited within the Cambridge Crystallographic Data Centre using the CCDC Nos. 900148 (**3**), 900144 (**4**), 900147 (**5**), 900149 (**6**), 900143 (**7**), 900142 (**8**), 900139 (**9**), 900141 (**10**), 900146 (**11**), 900140 (**12**), 900155 (**13**), 900154 (**14**), 900138 (**15**), 900152 (**16**), 900153 (**17**), 900151 (**18**) and 900156 (**19**)

The ANQ ligand shows a similar structure in all investigated complexes in this work. Recently we published the structure of neutral ANQ as well as some inorganic salts.[12,19] The ligand is almost planar. The C−N bonds are significantly shorter than C−N single bonds, with lengths between 1.28 and 1.38 Å. Coordination to the metal centers take place by the outer hydrazine nitrogen atom N4 and nitrogen atom N1. The coordination angles N1−M−N4 approximately increase with the following order. Ag (ca. 68°) < Zn = Co < Ni < Cu (ca. 80°).

$[Co(ANQ)_2(H_2O)_2](ClO_4)_2$ (**3**) crystallizes in the monoclinic space group $P2_1/c$ with two formula units in the unit cell. The molecular moiety is depicted in Figure 1. A similar coordination sphere has been described for diaqua-tetrakis-picoline cobalt(II) diperchlorate.[28]

The corresponding nickel complex $[Ni(ANQ)_2(H_2O)_2](ClO_4)_2$ (**4**) crystallizes in the orthorhombic space group $Pca2_1$ with four formula units in the unit cell. The molecular moiety is depicted in Figure 2. With the exception of the copper salt the densities of the perchlorates increase with rising atomic numbers (ρ [g cm^{-3}]: **3** (2.068) < **5** (2.128) < **4** (2.159) < **6** (2.193) < **7** (2.316)).

In agreement to all copper complexes investigated in this work, $[Cu(ANQ)_2(ClO_4)_2](H_2O)_2$ (**5**) also shows a Jahn−Teller[29] distorted octahedral coordination sphere due to the d^9 electron configuration (see Figure 3). The elongation of the octahedron is due to longer Cu−$OClO_3$ coordination bonds in comparison to the Cu−N coordination bonds which is similar described for dimethylethylendiamine bis-perchlorate.[30] The water molecules do not participate in metal coordination. The triclinic unit cell ($P\bar{1}$) contains one molecular moiety.

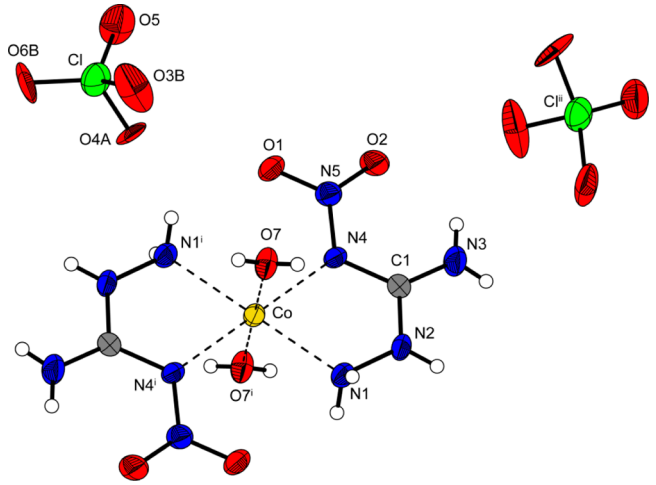


Figure 1. Molecular moiety of **3**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Perchlorate anions are strongly disordered. Only selected split positions are depicted. Selected coordination distances (Å): Co−O7 2.088(3), Co−N4 2.108(3), Co−N1 2.130(3); angles (deg): O7−Co−N4 89.24(11), O7−Co−N1 90.69(13), N4−Co−N1 75.76(11). Symmetry codes: (i) 1 − *x*, −*y*, −*z*; (ii) 1 − *x*, 0.5 + *y*, 0.5 − *z*.

The molecular structure of $[Zn(ANQ)_2(H_2O)_2](ClO_4)_2$ (**6**) is shown in Figure 4. The zinc(II) cations in **6**, which crystallizes in the monoclinic space group $P2_1/c$, have a centrosymmetric 6-fold coordination sphere.

The molecular moiety of $[Ag(ANQ)_2]ClO_4$ (**7**), which crystallizes in the triclinic space group $P\bar{1}$, is depicted in Figure 5. The silver cations are coordinated by four nitrogen atoms in square planar arrangement.

One formula unit of $[Co(ANQ)_2(H_2O)_2](NO_3)_2$ (**8**) shown in Figure 6 is incorporated in the centrosymmetric triclinic unit cell. The nirate anions do not participate in the coordination of the Co^{2+} centers.

Figure 7 is used exemplarily for the molecular structures of $[Ni(ANQ)_2(H_2O)_2](NO_3)_2$ (**9**) and $[Zn(ANQ)_2(H_2O)_2](NO_3)_2$ (**11**). The complexes are crystallizing isotypically in the triclinic space group $P\bar{1}$ showing almost the same unit cell dimensions (see Table S2 in the Supporting Information) and densities (ρ [g cm^{-3}]: **9** (2.011), **11** (1.992).

The copper complex $[Cu(ANQ)_2(NO_3)_2]$ (**10**) is shown in Figure 8. It crystallizes in the monoclinic space group $C2/c$ with a density of 2.171 g cm^{-3}. The Cu^{2+} cations reveal a distorted octahedral coordination sphere. This is indicated by the Cu−O bond lengths, which significantly differ from each other and the O5−Cu−O8 angle of ∼160°.

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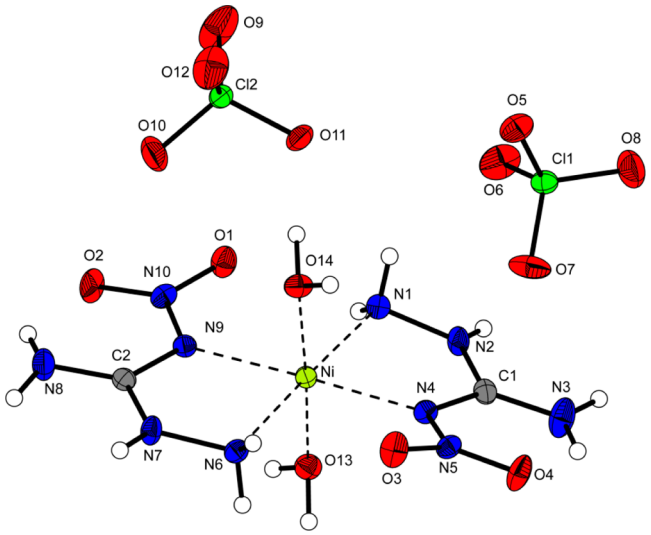

Figure 2. Molecular moiety of **4**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Ni–N4 2.0692, Ni–O14 2.0764, Ni–N6 2.0821, Ni–N9 2.0877, Ni–N1 2.0891, Ni–O13 2.125; angles (deg): N4–Ni–O14 94.8, N4–Ni–N6 101.9, O14–Ni–N6 86.6, O14–Ni–N9 87.0, N6–Ni–N9 77.5, N4–Ni–N1 76.7, O14–Ni–N1 95.0, N4–Ni–O13 88.4, N6–Ni–O13 93.9, N9–Ni–O13 89.8, N1–Ni–O13 84.5.

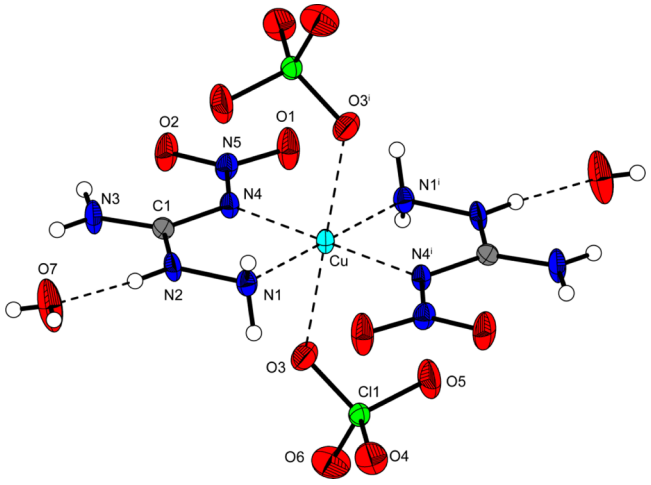

Figure 3. Molecular moiety of **5**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Cu–N1 1.982(2), Cu–N4 2.032(2), Cu–O3 2.4364(19), angles (deg): N1–Cu–N4 79.58(9), N1–Cu–O3 85.41(10), N4–Cu–O3 83.44(8). Symmetry codes: (i) $-x$, $1-y$, $-z$.

The density of complex $[Ag(ANQ)_2NO_3]$ (**11**) is considerably smaller (2.235 g cm^{-3}) than that observed for silver(I) nitrate (4.35 g cm^{-3}).[31] The silver cations in the structure of **11**, which crystallizes in the orthorhombic space group *Pbca*, are distorted tetrahedrally coordinated by only nitrogen atoms.

The dinitramide complexes **13** and **14** crystallize isotypically as tetrahydrates in the monoclinic crystal system within the space group $P2_1/c$. Two water molecules participate in the coordination sphere, while the others are connected to the dinitramide anions by formation of hydrogen bonds (see Figure 10). The density of the cobalt complex **13** is slightly lower (1.964 g cm^{-3}) than that of nickel complex **14** (1.982 g cm^{-3}).

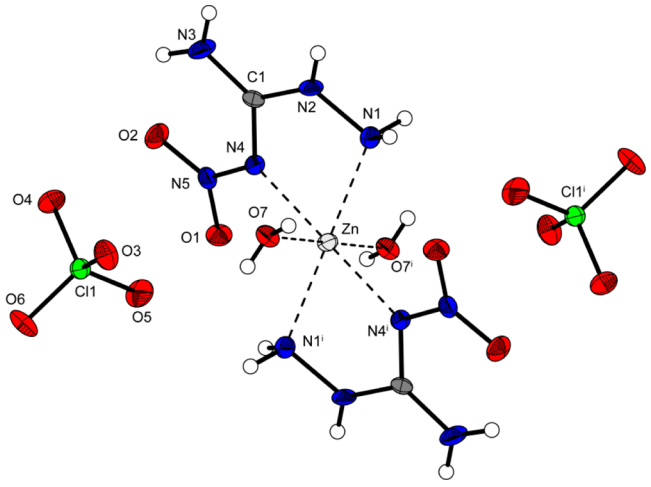

Figure 4. Molecular moiety of **6**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Zn–N4 2.106(2), Zn–N1 2.148(2), Zn–O7 2.164(2); angles (deg): N4–Zn–N1 74.70(8), N4–Zn–O7 88.51(8), N1–Zn–O7 84.43(10). Symmetry codes: (i) $-x$, $1-y$, $-z$.

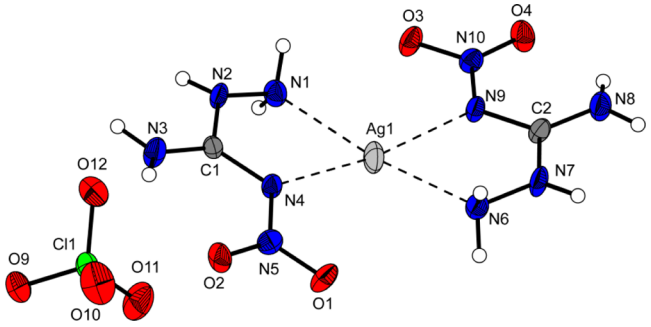

Figure 5. Molecular moiety of **7**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Ag1–N4 2.346(3), Ag1–N9 2.359(3), Ag1–N1 2.374(3), Ag1–N6 2.396(3); angles (deg): N4–Ag1–N9 175.12(8), N4–Ag1–N1 68.55(10), N9–Ag1–N1 116.31(10), N4–Ag1–N6 107.47(10), N9–Ag1–N6 67.88(10), N1–Ag1–N6 167.67(15).

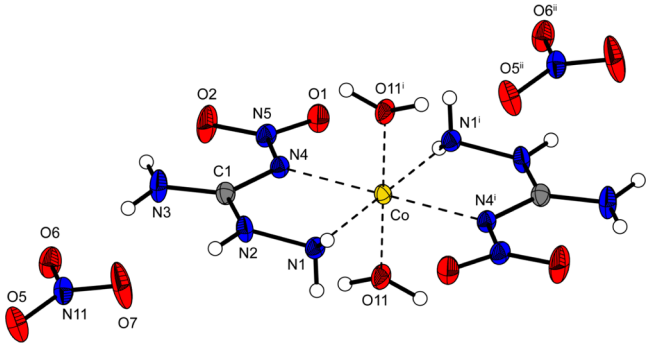

Figure 6. Molecular moiety of **8**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Co–O11 2.0623(11), Co–N1 2.1307(14), Co–N4 2.1543(13); angles (deg): O11–Co–N1 90.93(5), O11–Co–N4 88.74(5), N1–Co–N4 74.77(5). Symmetry codes: (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, $1-y$, $-z$.

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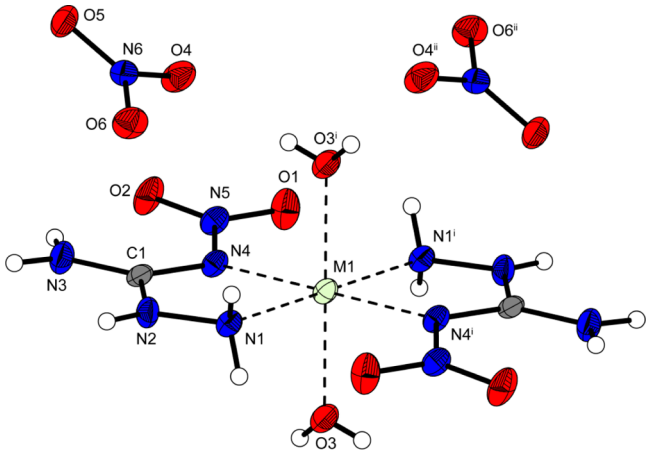

Figure 7. Molecular moiety of **9** (M1 = Ni) and **11** (M1 = Zn). Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): **9**: Ni–N1 2.0587(19), Ni–O3 2.0805(18), Ni–N4 2.1023(19); **11**: Zn–N1 2.1144(17), Zn–O3 2.1315(15), Zn–N4 2.1650(15); angles (deg) **9**: N1–Ni–O3 86.99(8), N1–Ni–N4 77.27(7), O3–Ni–N4 92.03(8); **11**: N1–Zn–O6 91.33(7), N1–Zn–N4 75.66(6), O6–Zn–N4 87.98(7). Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

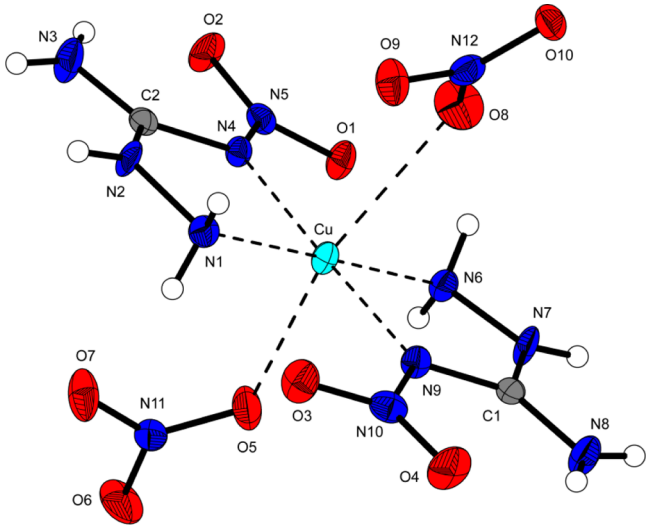

Figure 8. Molecular moiety of **10**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Cu–N6 1.982(2), Cu–N1 1.989(2), Cu–N4 2.0326(19), Cu–N9 2.0370(19), Cu–O5 2.3382(19); Cu–O8 2.586(2); angles (deg): N6–Cu–N1 178.8(1), N6–Cu–N4 99.67(8), N1–Cu–N4 79.69(8), N6–Cu–N9 79.02(9), N1–Cu–N9 101.65(9), N4–Cu–N9 178.13(8), N6–Cu–O5 84.27(9), N1–Cu–O5 94.70(9), N4–Cu–O5 94.28(7), N9–Cu–O5 86.93(8), O5–Cu–O8 160.18(7).

The dinitramide anions are not planar and follow the twisted structure observed for, for example, lithium and potassium dinitramide.[32]

The silver complex **15** could only be obtained crystalline (monoclinic, $P2_1/c$) as a monohydrate. The molecular motif is shown in Figure 11. The density of 2.456 g cm^{-3} is the highest observed in this work and is similar to that (2.488 g cm^{-3}) of silver dinitramide as its acetonitrile adduct.[33]

Remarkably, the chlorido complexes $[M(ANQ)Cl_2](H_2O)_2$ (**16** (M = Co^{2+}), **17** (M = Ni^{2+}) and **19** (M = Zn^{2+})

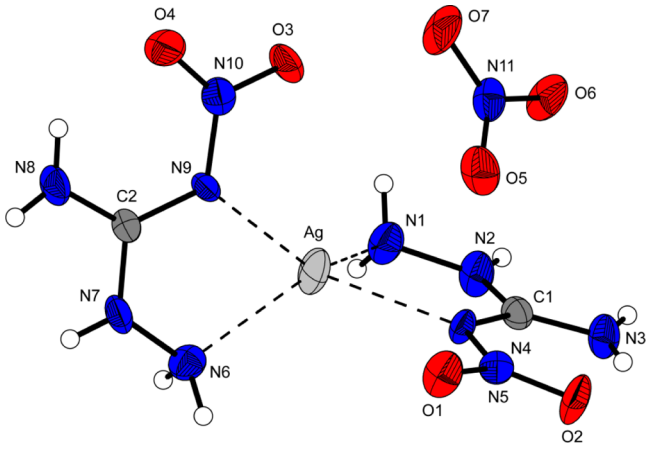

Figure 9. Molecular moiety of **12**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Ag–N6 2.344(4), Ag–N1 2.328(3), Ag–N9 2.301(3), Ag–N4 2.318(2); angles (deg): N9–Ag–N4 145.28(10), N9–Ag–N1 130.40(12), N4–Ag–N1 69.55(11), N9–Ag–N6 69.33(11), N4–Ag–N6 122.72(11), N1–Ag–N6 131.09(16).

investigated in this work crystallize isotypically in the monoclinic space group $P2_1/n$. Also, **18** shows very similar unit-cell dimensions; however, for the space group $P2_1/c$. The molecular unit for **16**, **17**, and **19** is depicted in Figure 12. In contrast to the crystal water molecules the chlorido anions are enclosed in coordination. The densities of **16** (1.927 g cm^{-3}), **17** (1.950 g cm^{-3}), **18** (1.945 g cm^{-3}), and **19** (1.944 g cm^{-3}) are similar and in total the lowest observed in this work.

As already observed for the coordination sphere of the cations in **16**, **17**, and **19**, the copper cations in **18** possess an elongated octahedral coordination sphere due to the Jahn–Teller effect (see Figure 13). The copper chlorine coordination bonds are much longer (~2.71 Å) than the Cu–O bonds in the previously described complexes **5** and **10**. This is in agreement to the recently published structure of dichlorido-tetrakis-1,2,4-triazole copper(II), where the Cu–Cl bonds are even longer (2.83 Å).[34]

2.3. IR Spectroscopy. The assignments of absorptions were undertaken referring to values reported in literature.[14,35] Strong absorptions are observed in all spectra in the region above 3000 cm^{-1}, indicating N–H and O–H valence vibrations. Here, the N–H valence vibration of the hydrazine moiety of the ligand is visible as a relatively sharp absorption band at 3430–3378 cm^{-1}. This is in contrast to the absorptions of O–H valence vibrations at around 3300–3200 cm^{-1} of the crystal water containing complexes, which are broadened because of hydrogen bond formation. In comparison to the IR absorptions of neutral, uncomplexed ANQ, the N–H valence vibrations are observed at somewhat lower energies if complexed (3551 cm^{-1} in ANQ). Other important absorptions are the antisymmetric and the symmetric N–O valence vibration of the nitramine moiety both of which are present as strong absorptions in all spectra at 1687–1651 cm^{-1} (asym) and 1297–1275 cm^{-1} (sym). For both absorptions, again lower wave numbers are observed as compared to uncomplexed ANQ, which reveals values of 1692 and 1329 cm^{-1} for the absorptions of the aforementioned vibrations. A relatively strong absorption at 1245–1203 cm^{-1} can be assigned to the N–N valence vibration of the nitramine moiety, whereas a second absorption at slightly lower energy (1139–1097 cm^{-1})

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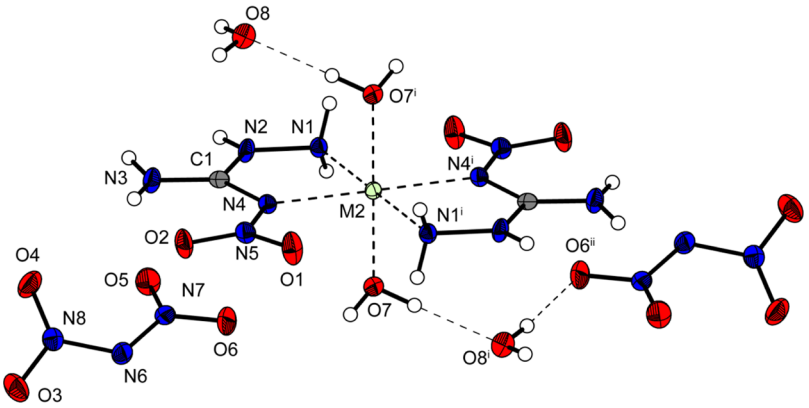

Figure 10. Molecular moiety of **13** (M2 = Co) and **14** (M2 = Ni). Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): **13**: Co−O7 2.0998(12), Co−N1 2.1128(14), Co−N4 2.1413(13); **14**: Ni−N1 2.0652(13), Ni−O7 2.0877(11), Ni−N4 2.1024(12); angles (deg) **13**: O7−Co−N1 89.87(6), O7−Co−N4 90.67(5), N1−Co−N4 76.44(5); **14**: N1−Ni−O7 90.76(5), N1−Ni−N4 78.19(5), O7−Ni−N4 89.47(5). Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$.

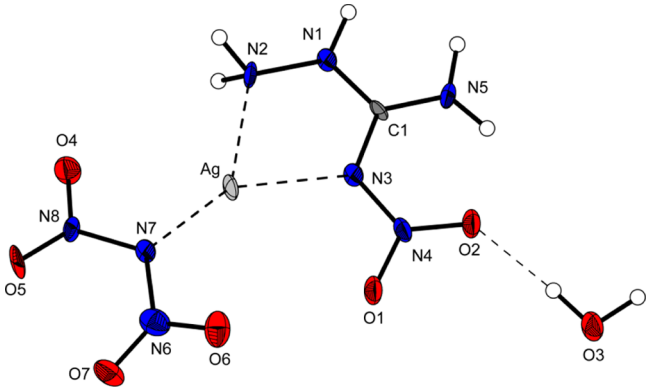

Figure 11. Molecular moiety of **15**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Ag−N7 2.147(9), Ag−N3 2.260(9), Ag−N2 2.340(10); angles (deg): N7−Ag−N3 147.4(4), N7−Ag−N2 142.3(3), N3−Ag−N2 70.1(3).

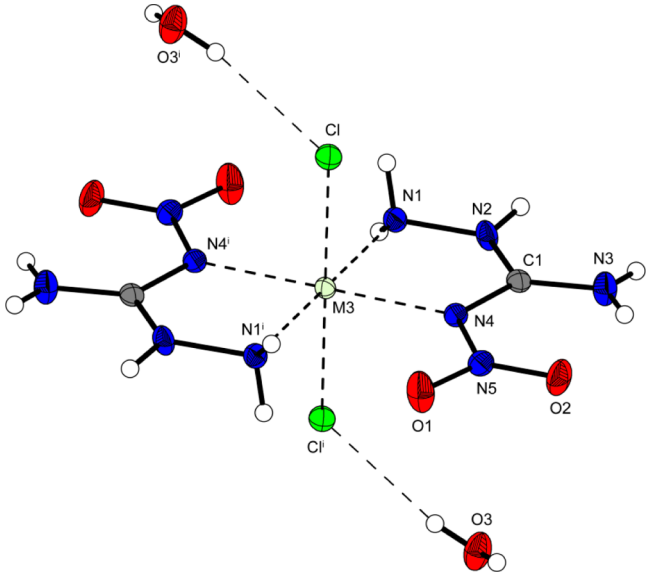

Figure 12. Molecular moiety of **16** (M3 = Co), **17** (M3 = Ni), and **19** (M3 = Zn). Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): **16**: Co−N1 2.1212(14), Co−N4 2.1305(13), Co−Cl 2.4810(4); **17**: Ni−N1 2.0651(13), Ni−N4 2.0949(12), Ni−Cl 2.4600(4); **18**: Cu−N1 1.997(2), Cu−N4 2.053(2), Cu−Cl 2.7155(7); **19**: Zn−N1 2.1071(15), Zn−N4 2.1439(14), Zn−Cl 2.5473(4); angles (deg) **16**: N1−Co−N4 75.69(5), N1−Co−Cl 90.66(4), N4−Co−Cl 90.61(4); **17**: N1−Ni−N4 77.66(5), N1−Ni−Cl 89.71(4), N4−Ni−Cl 89.46(3); **18**: N1−Cu−N4 79.14(8), N1−Cu−Cl 89.11(7), N4−Cu−Cl 89.90(6); **19**: N1−Zn−N4 76.18(6), N1−Zn−Cl 89.24(5), N4−Zn−Cl 89.41(4). Symmetry codes: (i) $1 - x$, $-y$, $1 - z$.

can be attributed to the N−N valence vibration of the hydrazine moiety of the ligand. Furthermore, the characteristic absorptions of the nitrate and the perchlorate anion at 1385−1382 and 1097−1083 cm^{-1} are observed in the respective IR spectra. The dinitramide anion can be detected by strong absorptions at 1539−1529 cm^{-1} (asymmetric in phase N−O valence vibration) and 1434−1431 cm^{-1} (asymmetric out of phase N−O valence vibration).

2.4. Sensitivities and Thermal Stability. The impact sensitivity tests were carried out according to STANAG 4489[36] modified instruction[37] using a BAM (Bundesanstalt für Materialforschung) drophammer.[38] The friction sensitivity tests were carried out according to STANAG 4487[39] modified instruction[40] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[41] Additionally, all compounds were tested upon the sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.[42] Because the described complexes are transition metal complexes with an energetic ligand together with energetic counterions such as nitrate, perchlorate, and dinitramide, we expect enhanced sensitivities toward outer stimuli. The perchlorates **3**−**7** are very sensitive toward impact, some of them (**5**, **7**) even bearing values of less than 1 J, which in the case of the silver complex is not least due to fact, that it crystallizes water free. Also the friction sensitivities are in a range between very sensitive (**3**−**6**) and extremely sensitive (**7**). The complexes bearing a nitrate counterion (**8**−**12**) at an average are less sensitive toward impact and friction than the perchlorate containing compounds, however they are still sensitive toward impact with two exceptions, the copper (**10**) and the silver (**12**) complex, which crystallize water free, again are very sensitive toward impact, a trend that has already been observed for the perchlorate containing compounds **5** and **7**.

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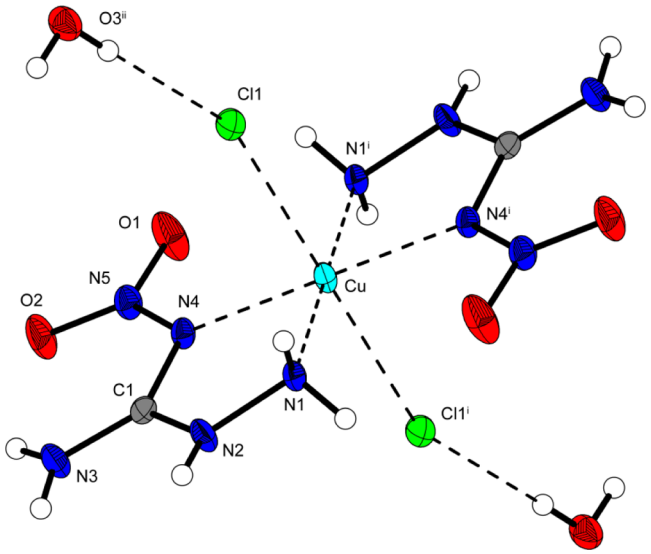

Figure 13. Molecular moiety of **18**. Thermal displacements of non-hydrogen atoms were set at 50% probability. Hydrogen atoms are shown as spheres of arbitrary radius. Selected coordination distances (Å): Cu−N1 1.997(2), Cu−N4 2.053(2), Cu−Cl 2.7155(7); angles (deg): N1−Cu−N4 79.14(8), N1−Cu−Cl 89.11(7), N4−Cu−Cl 89.90(6); Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $-x, -0.5 + y, 0.5 - z$.

Almost the same argumentation can be applied to the friction sensitivities of the nitrates. Interestingly, the dinitramides **13**−**15**, while still being comparatively sensitive, do not reach the high sensitivity levels of, for example, **7**, **10**, and **12** in terms of impact as well as friction sensitivity, presumably because of the inclusion of four (**13**, **14**) and one (**15**) molecule of crystal water per formula unit, respectively. Holding no energetic anion, the four chloride complexes **16**, **17**, and **19** show moderate impact sensitivity and are less sensitive toward friction. Unfortunately, the yields of **18** allowed no determination of sensitivities.

Differential scanning calorimetry (DSC) measurements to determine the dehydration- and decomposition temperatures of **3**−**17** and **19** (about 1.5 mg of each energetic material) were performed in covered Al-containers containing a hole in the lid and a nitrogen flow of 20 mL min^{-1} on a Linseis PT 10 DSC[43] calibrated by standard pure indium and zinc at a heating rate of 5 °C min^{-1}. All decomposition temperatures are given as absolute onset temperatures, whereas dehydration temperatures are set at the minimum of the endothermic peak in the DSC curve.

Several interesting trends can be observed while comparing the decomposition temperatures of the complexes **3**−**17** and **19**. The nickel complexes reveal the highest decomposition temperatures if compounds bearing the same anion are compared to each other (e.g., **4**: 230 °C). For the perchlorates and nitrates, the zinc complexes follow the nickel complexes (e.g., **6**: 198 °C) having the second highest decomposition temperatures again followed by the cobalt complexes (e.g., **3**: 176 °C). The silver and especially the copper complexes decompose at relatively low temperatures oftentimes even below 100 °C (e.g., **5**: 134 °C, **10**: 77 °C). Comparing complexes with the same metal ion, the perchlorates have higher decomposition temperatures as the nitrates (e.g., **7**: 148 °C, **12**: 142 °C). Most of the chlorides show decomposition at even higher temperatures as the perchlorates except for the zinc complex (**19**: 172 °C). The dinitramides expectedly decompose at relatively low temperatures (**13**: 118 °C, **14**: 142 °C), whereas the trend of higher decomposition temperatures of the nickel complexes is again confirmed. A detailed list of all decomposition and dehydration temperatures as well as the sensitivities toward impact, friction, and electrostatic discharge can be found in Table 1.

Table 1. Sensitivities and thermal Behavior of 3−19

	IS (J)	FS (N)	ESD (J)	T_{dehydr} (°C)	T_{dec} (°C)[#]
3	3	10	0.03	170[a]	176
4	3	10	0.04	162	230
5	<1	16	0.50	120[a]	134
6	3	28	0.30	108, 154	198
7	<1	<5	0.01	[b]	148
8	9	80	0.70	[c]	139
9	4	120	0.08	160[a]	186
10	<1	<5	0.50	[b]	77
11	5	120	0.50	119	181
12	<1	<5	0.01	[b]	142
13	5	80	0.70	85	118
14	3	80	0.60	138[a]	142
15	2	7	0.10	71	108
16	10	360	0.70	144	186
17	10	360	0.70	150	250
19	10	360	0.70	104	172

[a]Decomposition (exothermic) occurs immediately after dehydration (endothermic). [b]No crystal water contained. [c]No dehydration (endothermic event) observed before decomposition (exothermic event). [#]Exothermic decomposition of the water free or dehydrated compounds.

Most of the crystal water containing complexes can be dehydrated after heating (**4**, **6**, **11**, **13**, **14**−**16**, **19**), indicated by an endothermic peak in the DSC curve, which is well-separated from the exothermic decomposition event. Some of the complexes decompose immediately after they start to lose their crystal water (**3**, **5**, **9**, **14**), whereas for **8**, no endothermic event before decomposition can be observed, although it crystallizes as a dihydrate.

2.5. UV−Vis−NIR Spectroscopy and Laser Ignition Tests. Further, the synthesized metal complexes **3**−**5**, **7**−**10**, as well as **13** and **14** were investigated upon their behavior toward single pulsed laser irradiation at a wavelength of 940 nm and a pulse length of 100 μs. The cobalt(II) complex **3**, copper(II) complex **5**, and also the silver(I) complex **7** could be initiated by a single pulse laser beam and led to detonation of samples, which previously to the experiment were pressed into pellets of approximately 8 mm diameter and 2 mm thickness. The nickel(II) complex **4** and all corresponding nitrate complexes **8**−**10** as well as even the complexes holding the highly energetic dinitramide anion **13**−**14** did not show any response to laser irradiation. The laser initiation mechanism (electronically, thermally, etc.) of transition metal complexes is still unknown. Related to that, the UV−vis−NIR reflectance of the solid samples **3** ($[Co(ANQ)_2(H_2O)_2](ClO_4)_2$), **4** ($[Ni(ANQ)_2(H_2O)_2](ClO_4)_2$), **5** ($[Cu(ANQ)_2(ClO_4)_2](H_2O)_2$), and **7** ($[Ag(ANQ)_2]ClO_4$) were measured on a *Varian Cary 500* spectrometer in a wavelength range of 350−1300 nm. The measured diffuse reflectance R [%] was transformed after applying the Kubelka−Munk eq 1 to give the absorption function $F(R)$ (no unit).[44]

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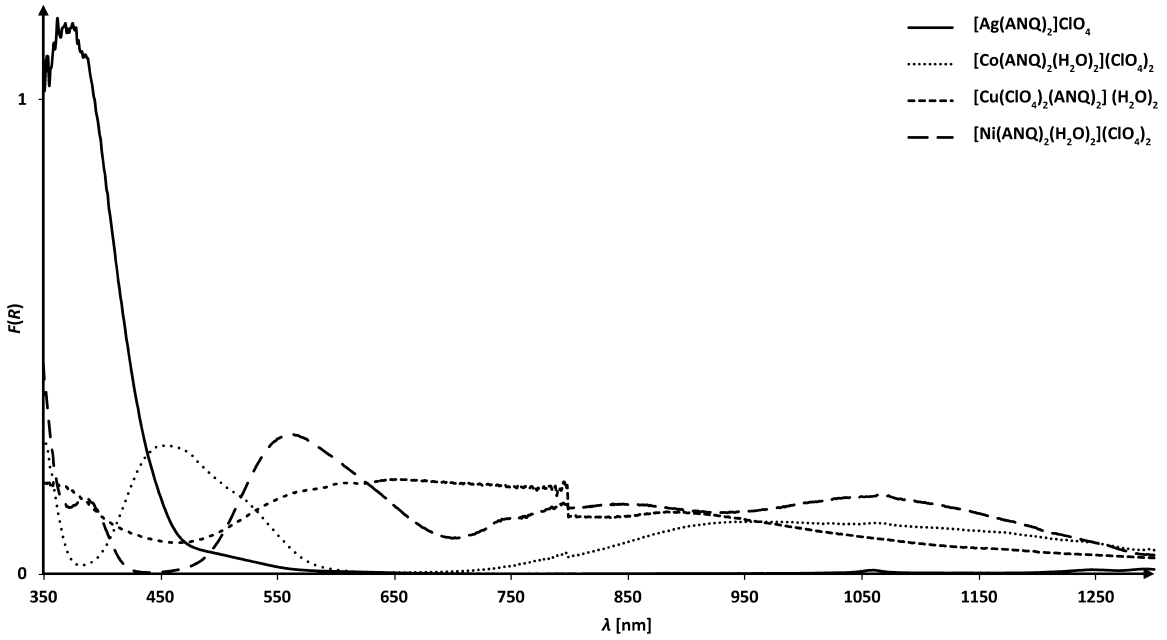

Figure 14. UV−vis−NIR spectra of complexes **3**−**5** and **7**. The absorption function $F(R)$ is obtained after applying the Kubelka−Munk equation.

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

Where K is the absorption component, S the scattering component, and R_∞ the reflectance of an infinite thick sample.

The step in the absorption intensity $F(R)$ at 800 nm in Figure 14 is caused by a detector change. The spectra have only qualitative character. Due to technical limits no quantitative information about the absorption intensity can be obtained from the spectra. Commonly, R_∞ is technically approximated by a sample layer thick enough that the measuring instrument cannot detect differences in the thickness-dependent diffuse reflectance. However, not all samples could be coated on the object plate thick enough that there were no differences detectable anymore.

The information obtained from the UV−vis−NIR spectra essentially is, that the four samples considerably differ in their absorption only at wavelengths in the visible and near UV region of the electromagnetic spectrum, what we would expect of four obviously differently colored samples. However in the NIR region, the samples **3**−**5** equally absorb radiation, especially at 940 nm, which is the wavelength of the laser beam used for laser initiation experiments. However, the silver complex shows no absorption at this wavelength.

Considering, that all metal perchlorates **3**−**5** except the silver(I) complex **7** were light absorbing at 940 nm together with the initiation results it seems that there is no relation between optical absorption properties and the photosensitivity toward pulsed laser irradiation, which is in agreement with the laser initiation experiments made by Ilyushin et al.[13,45] The fact that only perchlorate compounds and no nitrates could be initiated fits to the literature claimed initiation mechanism where an active perchlorate radical is formed by a one-electron transfer from the perchlorate anion to the metal cation induced by the laser beam.[45]

Consequently, it seems, that the initiation of energetic materials by a short pulsed laser beam rather is an electronic process than a thermal one, especially when comparing the decomposition temperatures of the samples with their laser ignitability. For example, $[Cu(ANQ)_2(NO_3)_2]$ (**10**) could not be initiated by the laser beam but shows the lowest thermal stability ($T_{dec.}$ = 77 °C) of the investigated compounds.

The role of the nature of the ligand in the laser initiation process is not yet fully understood and therefore under current investigation.

3. CONCLUSION

From the experimental study of energetic complexes based on 3-amino-1-nitroguanidine the following conclusions can be drawn:

- Combining boiling solutions of 3-amino-1-nitroguanidine (ANQ) and a transition metal (M = Co, Ni, Cu, Zn, Ag) perchlorate (X = ClO_4) or nitrate (X = NO_3) affords complexes $M^{2+}(ANQ)_2(X^-)_2(H_2O)_n$ (n = 0, 2) in the case of Co, Ni, Cu, and Zn or $M^+(ANQ)_2(X^-)$ in the case of Ag, which readily crystallize from their aqueous mother liquors, but in minor yields. For Co, Ni, Cu, and Zn, the respective chlorides $M^{2+}(ANQ)_2(X^-)_2(H_2O)_2$ were also isolated following the same procedure.
- Complexes $M^{2+}(ANQ)_2(X^-)_2(H_2O)_4$ with X = $N(NO_2)_2$ were isolated in the case of M = Co and Ni starting from the rescpective perchlorate containing complexes upon addition of ammonium dinitramide to the solutions. $Ag(ANQ)(N(NO_2)_2)(H_2O)$ crystallized after combining solutions of silver dinitramide and 3-amino-1-nitroguanidinium chloride (ANQ^+Cl^-).
- The complexes crystallize in the space groups $P\bar{1}$ (**5**, **7**−**9**, **11**), $P2_1/c$ (**3**, **6**, **13**−**15**, **18**), $P2_1/n$ (**16**, **17**, **19**), $C2/c$ (**10**), $Pca2_1$ (**4**) and $Pbca$ (**12**) with densities between 1.927 (**16**) and 2.456 (**15**), whereas perchlorates, if hydrated, reveal higher densities than nitrates and chlorides. The highest densities are observed for the silver complexes.
- All perchlorate, nitrate, and chloride containing complexes crystallize as dihydrates, except for the silver complexes **7** and **12** and the copper complex **10**, which

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crystallize water free. The dinitramides crystallize as tetrahydrates (**13**, **14**) and monohydrate (**15**), respectively. Most of the crystal water containing complexes can be dehydrated (**4**, **6**, **11**, **13**, **15**−**19**) without decomposition.

- Nickel complexes generally show the highest decomposition temperatures (**17**: 250 °C), whereas copper and silver complexes decompose at relatively low temperatures (**10**: 77 °C). Also a trend of higher decomposition temperatures for chlorides and perchlorates as compared to nitrates and dinitramides is observed.
- All complexes bearing energetic counterions show enhanced sensitivities toward impact and friction, which especially applies to the solvate water free silver and copper complexes **7**, **10**, and **12** with values of <1 J (IS) and <5 N (FS).
- Selected perchlorate, nitrate and dinitramide containing complexes were tested upon their laser ignitability with a 100 μs laser pulse at 940 nm. Only the perchlorate containing complexes **3**, **5**, and **7** could successfully be initiated.
- UV−vis−NIR spectra of the perchlorate containing complexes **3**−**5** and **7** were recorded and show, that there is no relationship between their absorption behavior at the designated wavelength of the laser beam (940 nm) and their initiation properties.

4. EXPERIMENTAL SECTION

Caution! The herein described metal complexes of ANQ are energetic materials with increased sensitivities toward shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds. All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^{1}H and ^{13}C and ^{15}N NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N). To determine the melting and decomposition temperatures of the described compounds a Linseis PT 10 DSC (heating rate 5 °C min^{-1}) was used. Infrared spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd:YAG-Laser (1064 nm) and a LN-Ge diode as detector. Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 using FAB technique. To measure elemental analyses, we employed a Netsch STA 429 simultaneous thermal analyzer.

3-Amino-1-nitroguanidine (2). Commercially available nitroguanidine (20% H_2O, 25 g, 192 mmol) was dispended in 250 mL of water and the mixture was heated to 55 °C. Hydrazine hydrate (10.5 mL, 216 mmol) was added dropwise over a period of 15 min and the temperature was kept at 55 °C for a further 15 min under constant stirring. After the mixture turned to a clear, orange solution, it was cooled to room temperature in an ice bath and the reaction was quenched with conc. hydrochloric acid (pH 7). 3-Amino-1-nitroguanidine starts to precipitate after the solution was cooled to 4 °C overnight. The product was separated by filtration and recrystallized from hot water. Yield: 10.3 g (86 mmol, 45%).

DSC (5 °C min^{-1}, °C): 184 °C (dec 1), 200 °C (dec.2); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3551 (s), 3411 (s), 3234 (s), 2025 (w), 1692 (m), 1637 (s), 1616 (vs), 1545 (m), 1502 (m), 1443 (m), 1384 (m), 1329 (m), 1134 (m), 1108 (m), 1088 (m), 1031 (m), 1005 (w), 963 (w), 870 (w), 772 (w), 745 (w), 696 (w), 622 (m), 571 (w), 482 (m). Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3319 (4), 3255 (13), 1659 (5), 1616 (4), 1580 (32), 1381 (13), 1287 (32), 1190 (5), 1111 (39), 1019 (5), 961 (100), 770 (27), 483 (30), 419 (33), 378 (10), 248 (13). ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.29 (s, 1H, NH), 8.23 (s, 1H, C−NH_AH$_B$), 7.52 (s, 1H, C−NH$_A$$H_B$), 4.64 (s, 2H, N−NH$_2$). ^{13}C NMR (DMSO-$d_6$, 25 °C, ppm) δ: 161.5 (C(NNO$_2$)(N$_2$H$_4$)(NH$_2$)). ^{15}N NMR (DMSO-d_6, 25 °C, ppm) δ: −13.3 (*N*O$_2$), −146.3 (*N*NO$_2$), −276.4 (*N*H/*N*H$_2$), −301.8 (*N*H/*N*H$_2$), −327.9 (*N*H/*N*H$_2$). MS (FAB$^-$): m/z = 117.99 [M−H] $^-$. EA ($CH_5N_5O_2$, 119.08) calcd: C 10.09, H 4.23, N 58.81%; found: C 10.51, H 4.32, N 58.90%. BAM drophammer: 20 J; friction tester: 144 N; ESD: 0.15 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)diaquacobalt(II) Perchlorate (3). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) was dissolved in 20 mL of boiling water. Cobalt(II) perchlorate hexahydrate (1.548 g, 4.23 mmol) was added and the mixture was boiled until a clear solution resulted. The clear solution was filtered and slowly cooled to room temperature. After a few days, the product started to crystallize as red blocks. Yield: 35% (788 mg, 1.48 mmol). The crystal density was 2.068 g cm^{-3}.

DSC (5 °C min^{-1}, °C): 176 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3548 (m), 3407 (s), 3321 (s), 3303 (s), 2964 (w), 2615 (w), 2231 (w), 2135 (w), 2059 (w), 1660 (s), 1579 (w), 1508 (m), 1480 (m), 1424 (m), 1385 (m), 1278 (s), 1211 (s), 1097 (vs), 938 (m), 820 (w), 808 (w), 779 (m), 717 (w), 671 (w), 663 (w), 627 (m), 599 (m), 520 (m). EA ($C_2H_{14}Cl_2N_{10}O_{14}Co$, 532.03) calcd: C 4.52, H 2.65, N 26.33%; found: C 3.96, H 2.60, N 23.03%. BAM drophammer: 3 J; friction tester: 10 N; ESD: 0.03 J (at grain size 500−1000 μm).

Bis(3-amino-1-nitroguanidine)diaquanickel(II) Perchlorate (4). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) was dissolved in 20 mL of boiling water. Nickel(II) perchlorate hexahydrate (1.547 g, 4.23 mmol) was added and the mixture was boiled until a clear solution resulted. The clear solution was filtered and slowly cooled to room temperature. After a few days, the product started to crystallize as light purple blocks. Yield: 21% (467 mg, 0.88 mmol).

DSC (5 °C min^{-1}, °C): 230 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3527 (m), 3439 (s), 3401 (s), 3307 (s), 3247 (s), 2774 (w), 2626 (w), 2510 (w), 2219 (w), 2219 (w), 2054 (w), 2021 (w), 1657 (s), 1613 (s), 1569 (m), 1511 (s), 1492 (m), 1459 (m), 1412 (m), 1390 (m), 1283 (s), 1207 (s), 1108 (vs), 1083 (s), 938 (m), 814 (w), 776 (m), 716 (m), 672 (m), 625 (m), 600 (m), 515 (m). EA ($C_2H_{14}Cl_2N_{10}O_{14}Ni$, 531.79) calcd: C 4.52, H 2.65, N 26.34%; found: C 4.72, H 2.50, N 25.98%. BAM drophammer: 3 J; friction tester: 10 N; ESD: 0.04 J (at grain size 500−1000 μm).

Bis(3-amino-1-nitroguanidine)diperchloratocopper(II) Dihydrate (5). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Copper(II) perchlorate hexahydrate (1.567 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled down to room temperature. After 1 h, the product starts to crystallize in blue blocks. Yield: 6.5% (137 mg, 0.27 mmol).

DSC (5 °C min^{-1}, °C): 134 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3500 (m), 3406 (s), 3285 (m), 3203 (m), 3076 (m), 1651 (s), 1610 (m), 1558 (w), 1511 (m), 1495 (s), 1432 (w), 1385 (m), 1322 (m), 1281 (s), 1212 (s), 1135 (s), 1108 (vs), 1083 (vs), 935 (m), 820 (w), 773 (w), 735 (w), 707 (w), 653 (w), 622 (m), 606 (m), 521 (m). EA ($C_2H_{14}Cl_2N_{10}O_{14}Cu$, 536.64) calcd: C 4.48, H 2.63, N 26.10%; found: C 4.73, H 2.50, N 25.85%. BAM drophammer: 1 J; friction tester: 16 N; ESD: 0.50 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)diaquazinc(II) Perchlorate (6). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Zinc(II) perchlorate hexahydrate (1.575 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. Slow evaporation of the solvent affords **5** as colorless crystals. Yield: 21% (441 mg, 0.82 mmol).

DSC (5 °C min^{-1}, °C): 198 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3531 (m), 3487 (m), 3430 (s), 3338 (s), 3312 (s), 1655 (s), 1630 (m), 1576 (m), 1519 (m), 1495 (m), 1413 (m), 1384 (m), 1288 (s), 1217 (m), 1139 (s), 1090 (vs), 936 (m), 815 (w), 778 (m), 720 (w), 636 (m), 626 (m), 592 (w), 544 (w), 468 (w). EA ($C_2H_{14}Cl_2N_{10}O_{14}Zn$, 538.49) calcd: C 4.46, H 2.62, N 26.01%; found: C 4.48, H 2.67, N

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24.33%. BAM drophammer: 3 J; friction tester: 28 N; ESD: 0.30 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)silver(I) Perchlorate (7). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Silver(I) perchlorate (0.877 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. A fine gray precipitate, which forms upon standing of the solution after several hours, is removed by filtration, whereafter light yellow fascicular crystals began to grow. Slow evaporation of the solvent affords **6** in 22% yield (407 mg, 0.91 mmol).

DSC (5 °C min^{-1}, °C): 148 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3400 (s), 3305 (s), 3228 (s), 1656 (s), 1623 (s), 1583 (m), 1504 (m), 1460 (m), 1401 (m), 1291 (s), 1203 (m), 1095 (vs), 1023 (m), 1001 (m), 923 (m), 801 (w), 774 (w), 704 (w), 624 (m), 584 (m), 485 (w). EA ($C_2H_{10}ClN_{10}O_8Ag$, 445.48) calcd: C 5.39, H 2.26, N 31.44%; found: C 5.68, H 2.94, N 31.31%. BAM drophammer: <1 J; friction tester: <5 N; ESD: 0.01 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)diaquacobalt(II) Nitrate (8). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Cobalt(II) perchlorate hexahydrate (1.231 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled down to room temperature. **7** starts to crystallize in red blocklike crystals after 30 min. Yield: 47% (910 mg, 1.99 mmol).

DSC (5 °C min^{-1}, °C): 139 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3409 (s), 3329 (m), 3273 (s), 3237 (m), 3196 (m), 1666 (s), 1638 (m), 1588 (m), 1524 (s), 1486 (s), 1384 (vs), 1340 (s), 1315 (m), 1275 (s), 1219 (s), 1111 (s), 1044 (m), 1028 (m), 937 (m), 825 (w), 814 (w), 780 (m), 694 (m), 647 (w), 616 (w), 597 (w), 523 (m). EA ($C_2H_{14}N_{12}O_{12}Co$, 457.14) calcd: C 5.25, H 3.09, N 36.77%; found: C 5.59, H 2.94, N 36.51%. BAM drophammer: 7 J; friction tester: 240 N; ESD: 0.50 J (at grain size 500−1000 μm).

Bis(3-amino-1-nitroguanidine)diaquanickel(II) Nitrate (9). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Nickel(II) nitrate hexahydrate (1.230 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. After a few minutes, the product starts to crystallize as light purple plates. Yield: 49% (950 mg, 2.08 mmol).

DSC (5 °C min^{-1}, °C): 186 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3412 (s), 3274 (s), 2637 (w), 2417 (w), 2296 (w), 2225 (w), 2142 (w), 2060 (w), 1972 (w), 1766 (m), 1662 (s), 1635 (s), 1522 (m), 1489 (s), 1385 (vs), 1278 (s), 1220 (s), 1111 (s), 1031 (m), 938 (m), 825 (w), 817 (w), 776 (m), 688 (m), 647 (w), 598 (w), 532 (m). EA ($C_2H_{14}N_{12}O_{12}Ni$, 456.90) calcd: C 5.26, H 3.09, N 36.79%; found: C 5.57, H 2.94, N 36.07%. BAM drophammer: 4 J; friction tester: 120 N; ESD: 0.08 J (at grain size 500−1000 μm).

Bis(3-amino-1-nitroguanidine)dinitratocopper(II) (10). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Copper(II) nitrate trihydrate (1.022 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. After 1 h, the product starts to crystallize as deep blue, blocklike crystals. Yield: 15% (274 mg, 0.64 mmol).

DSC (5 °C min^{-1}, °C): 77 °C (dec.). IR (KBr, cm^{-1}):~;ν = 3439 (m), 3412 (m), 3280 (m), 3126 (m), 1665 (s), 1629 (m), 1500 (m), 1382 (vs), 1281 (s), 1212 (s), 1141 (m), 1111 (m), 1045 (w), 943 (w), 820 (w), 773 (w), 724 (w), 705 (w), 653 (w), 603 (w), 565 (w), 480 (w). EA ($C_2H_{10}N_{12}O_{10}Cu$, 425.72) calcd: C 5.64, H 2.37, N 39.48%; found: C 6.00, H 2.24, N 37.98%. BAM drophammer: <1 J; friction tester: <5 N; ESD: 0.50 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)diaquazinc(II) Nitrate (11). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Zinc(II) nitrate hexahydrate (1.258 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. Slow evaporation of the solvent affords **10** as colorless crystals. Yield: 25% (492 mg, 1.06 mmol).

DSC (5 °C min^{-1}, °C): 181 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3414 (s), 3272 (s), 3240 (s), 3176 (s), 2763 (w), 2643 (w), 2426 (w), 2295 (w), 2223 (w), 2147 (w), 2064 (w), 1766 (w), 1663 (s), 1590 (m), 1526 (m), 1487 (s), 1384 (vs), 1280 (s), 1221 (s), 1114 (s), 1044 (m), 1030 (m), 935 (m), 827 (w), 813 (w), 780 (m), 745 (w), 696 (m), 638 (w), 584 (w), 527 (m). EA ($C_2H_{14}N_{12}O_{12}Zn$, 463.60) calcd: C 5.18, H 3.04, N 36.26%; found: C 5.48, H 2.83, N 36.09%. BAM drophammer: 5 J; friction tester: 120 N; ESD: 0.50 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine) Silver(I) Nitrate (12). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 20 mL of boiling water. Silver(I) nitrate (0.719 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The clear solution is filtered and slowly cooled to room temperature. After 15 min, the product starts to crystallize as colorless blocks, which turn gray after several hours if not isolated and dried. Yield: 26% (448 mg, 1.10 mmol).

DSC (5 °C min^{-1}, °C): 142 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3432 (s), 3401 (s), 3313 (s), 3219 (s), 3104 (m), 3010 (m), 2923 (m), 1665 (s), 1618 (s), 1580 (m), 1522 (m), 1473 (s), 1382 (s), 1355 (vs), 1292 (vs), 1245 (s), 1179 (s), 1108 (m), 1028 (m), 960 (m), 919 (m), 831 (w), 820 (w), 795 (w), 776 (w), 735 (w), 696 (m), 600 (m), 578 (m), 540 (m), 482 (w); EA ($C_2H_{10}N_{11}O_7Ag$, 408.04) calcd: C 5.89, H 2.47, N 37.76%; found: C 6.25, H 2.28, N 37.30%. BAM drophammer: 1 J; friction tester: <5 N; ESD: 0.01 J (at grain size <100 μm).

Bis(3-amino-1-nitroguanidine)diaquacobalt(II) Dinitramide Dihydrate (13). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Cobalt(II) perchlorate hexahydrate (1.55 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. Ammonium dinitramide (1.05 g, 8.46 mmol) is added to the solution and dissolved. The resulting solution is allowed to slowly cool to room temperature. The product crystallizes in flat orange prisms in 46% yield (1.13 g, 1.94 mmol).

DSC (5 °C min^{-1}, °C): 118 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3597 (m), 3406 (s), 3302 (s), 3244 (s), 1658 (s), 1630 (m), 1612 (m), 1529 (s), 1512 (s), 1454 (s), 1434 (s), 1390 (m), 1344 (m), 1281 (s), 1204 (vs), 1178 (s), 1123 (m), 1099 (s), 1031 (s), 952 (m), 936 (m), 827 (w), 808 (w), 778 (w), 761 (w), 732 (m), 688 (w), 640 (w), 594 (w), 507 (m); EA ($C_2H_{18}N_{16}O_{16}Co$, 581.20) calcd: C 4.13, H 3.12, N 38.56%; found: C 4.65, H 2.78, N 38.68%. BAM drophammer: 5 J; friction tester: 80 N; ESD: 0.70 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)diaquanickel(II) Dinitramide Dihydrate (14). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Nickel(II) perchlorate hexahydrate (1.55 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. Ammonium dinitramide (1.05 g, 8.46 mmol) is added to the solution and dissolved. The resulting solution is allowed to slowly cool to room temperature. The product crystallizes in light purple plates in 36% yield (0.888 g, 1.53 mmol).

DSC (5 °C min^{-1}, °C): 142 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3405 (s), 3302 (s), 3243 (s), 1658 (s), 1612 (m), 1539 (s), 1512 (s), 1454 (s), 1434 (s), 1388 (m), 1344 (m), 1283 (s), 1205 (vs), 1178 (s), 1122 (m), 1099 (s), 1022 (s), 952 (w), 936 (m), 827 (w), 808 (w), 778 (w), 761 (m), 749 (w), 732 (m), 688 (m), 640 (w), 593 (w), 509 (m); EA ($C_2H_{18}N_{16}O_{16}Ni$, 580.96): calcd C 4.13, H 3.12, N 38.58%; found: C 4.57, H 2.99, N 38.09%. BAM drophammer: 3 J; friction tester: 80 N; ESD: 0.60 J (at grain size 100−500 μm).

3-Amino-1-nitroguanidinedinitramidosilver(I) Hydrate (15). Ten milli,oles of silver dinitramide acetonitrile adduct was prepared according to the literature.[20] 1-Amino-3-nitroguanidinium chloride[19] (1.00 g, 6.4 mmol) was dissolved in 10 mL of boiling water. After the solution was cooled to about 60 °C, the silver dinitramide acetonitrile adduct, dissolved in 5 mL of acetonitrile, was added to the solution. After which the mixture was stirred under the exclusion of light at 35 °C for a further 2 h. The mixture was filtrated and **15** crystallizes from the clear filtrate in colorless needles. Yield: 0.61 g (2.50 mmol, 39%).

DSC (5 °C min^{-1}, °C): 71 °C (dehydr.), 108 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3398 (m), 3304 (m), 3218 (m), 1671 (m), 1622 (m), 1580 (m), 1539 (s), 1431 (s), 1344 (m), 1297 (s), 1205 (vs), 1176 (vs), 1108 (w), 1031 (s), 951 (w), 827 (w), 761 (w), 732 (w), 706 (w), 594

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(w), 484 (w), 470 (w). ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.31 (s, 1H, NH), 8.19 (s, 1H, C−NH_AH$_B$), 7.69 (s, 1H, C−NH$_A$$H_B$), 4.76 (s, 2H, N−NH$_2$), 3.36 (s, 2H, H$_2$O). ^{13}C NMR (DMSO-$d_6$, 25 °C, ppm) δ: 160.9 (C(NNO$_2$)(N$_2$H$_4$)(NH$_2$)). ^{14}N NMR (DMSO-d_6, 25 °C, ppm) δ: −11.0 (NO$_2$), −14.5 (*N*NO$_2$). *m*/*z* (FAB$^+$): 120.1 [C(NNO$_2$)(N$_2$H$_3$)(NH$_2$)+H$^+$], 107.0 [Ag$^+$]; *m*/*z* (FAB$^-$): 106.0 [N(NO$_2$)$_2^-$]; EA (AgCH$_7$N$_8$O$_7$, 244.12) calcd: C 3.42, H 2.01, N 31.93%; found: C 3.31, H 1.80, N 31.61%; BAM drophammer: 2 J; friction tester: 7 N; ESD: 0.10 J.

Bis(3-amino-1-nitroguanidine)dichlorocobalt(II) Dihydrate (16). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Cobalt(II) chloride hexahydrate (1.006 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The solution is allowed to slowly cool to room temperature. The product starts to crystallize in red blocklike crystals in 32% yield (0.555 g, 1.37 mmol).

DSC (5 °C min^{-1}, °C): 186 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu} \cong$ 3457 (s), 3393 (vs), 3295 (s), 3245 (s), 3029 (m), 2963 (m), 1667 (s), 1626 (s), 1577 (m), 1521 (m), 1491 (s), 1430 (m), 1384 (m), 1277 (vs), 1217 (s), 1106 (s), 1015 (w), 931 (m), 777 (w), 748 (w), 705 (m), 594 (m). EA (C$_2$H$_{14}$Cl$_2$N$_{10}$O$_6$Co, 404.04) calcd: C 5.95, H 3.49, N 34.67%; found: C 5.93, H 3.47, N 34.42%. BAM drophammer: 10 J; friction tester: 360 N; ESD: 0.70 J (at grain size 100−500 μm).

Bis(3-amino-1-nitroguanidine)dichloronickel(II) Dihydrate (17). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Nickel(II) chloride hexahydrate (1.005 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The solution is allowed to slowly cool to room temperature. The product starts to crystallize in light blue blocklike crystals in 42% yield (0.722 g, 1.79 mmol).

DSC (5 °C min^{-1}, °C): 250 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3378 (s), 3303 (s), 3245 (s), 2963 (m), 2923 (m), 2549 (m), 2457 (m), 1687 (vs), 1626 (m), 1519 (w), 1494 (m), 1432 (w), 1379 (m), 1277 (m), 1217 (m), 1196 (m), 1120 (m), 1094 (m), 1037 (m), 975 (m), 935 (m), 775 (w), 746 (w), 728 (w), 705 (w), 562 (m), 537 (m). EA (C$_2$H$_{14}$Cl$_2$N$_{10}$O$_6$Ni, 403.80) calcd: C 5.95, H 3.49, N 34.69%; found: C 6.04, H 3.28, N 34.91%. BAM drophammer: 10 J; friction tester: 360 N; ESD: 0.70 J (at grain size <100 μm).

Bis(3-amino-1-nitroguanidine)dichlorocopper(II) Dihydrate (18). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Copper(II) chloride dihydrate (0.721 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The solution is allowed to slowly cool to room temperature. Eventually precipitating 3-amino-1-nitroguanidine is filtered off. The product starts to crystallize in deep blue blocklike crystals in minor yield. Unfortunately, no analytical data except the crystal structure could be obtained, because ANQ started to precipitate immediately after the isolation of a single crystal of **18**.

Bis(3-amino-1-nitroguanidine)dichlorozinc(II) Dihydrate (19). 3-Amino-1-nitroguanidine (0.50 g, 4.23 mmol) is dissolved in 15 mL of boiling water. Zinc(II) chloride (0.577 g, 4.23 mmol) is added and the mixture is boiled until a clear solution results. The solution is allowed to slowly cool to room temperature. 3-amino-1-nitroguanidine precipitates as a colorless solid first, which is filtered off. The product starts to crystallize after several days in colorless blocks in minor yield.

DSC (5 °C min^{-1}, °C): 172 °C (dec.). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3388 (s), 3244 (s), 3030 (m), 2961 (m), 1665 (s), 1628 (s), 1580 (m), 1521 (m), 1494 (s), 1432 (m), 1284 (vs), 1219 (s), 1111 (s), 1017 (w), 931 (m), 778 (m), 752 (w), 706 (m), 598 (m). EA (C$_2$H$_{14}$Cl$_2$N$_{10}$O$_6$Zn, 410.48) calcd: C 5.85, H 3.44, N 34.12%; found: C 6.02, H 3.27, N 33.49%. BAM drophammer: 10 J; friction tester: 360 N; ESD: 0.70 J (at grain size <100 μm).

■ ASSOCIATED CONTENT

Supporting Information

Tables of X-ray diffraction data and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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