Inorganic Chemistry

Article

pubs.acs.org/IC

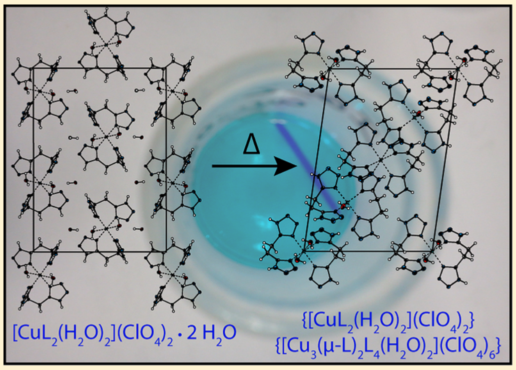
Cocrystallization of Photosensitive Energetic Copper(II) Perchlorate Complexes with the Nitrogen-rich Ligand 1,2-Di(1*H*-tetrazol-5-yl)ethane

Jürgen Evers, Ivan Gospodinov, Manuel Joas, Thomas M. Klapötke,* and Jörg Stierstorfer

Department of Chemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich, Butenandtstr. 5−13, 81377 Munich, Germany

Supporting Information

ABSTRACT: Two recently introduced concepts in the design of new energetic materials, namely complexation and cocrystallization, have been applied in the synthesis and characterization of the energetic copper(II) compound "$[Cu(dt\text{-}5\text{-}e)_2(H_2O)](ClO_4)_2$," which consists of two different complex cations and can be described as a model energetic ionic cocrystal. The presence of both the N-rich 1,2-di(1*H*-tetrazol-5-yl)ethane ligand and oxidizing perchlorate counterion results in a new type of energetic material. The ionic complex cocrystal consists of a mononuclear and a trinuclear complex unit. It can be obtained by precipitation from perchloric acid or by dehydration of the related mononuclear coordination compound $[Cu(dt\text{-}5\text{-}e)_2(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ at 70 °C in the solid state. The transformation starting at 60 °C was monitored by X-ray powder diffraction and thermal analysis. The energetic ionic cocrystal was shown to be a new primary explosive suitable for laser ignition. The different coordination spheres within the ionic cocrystal (octahedral and square pyramidal) were shown by UV/vis/NIR spectroscopy to result in excellent light absorption.



INTRODUCTION

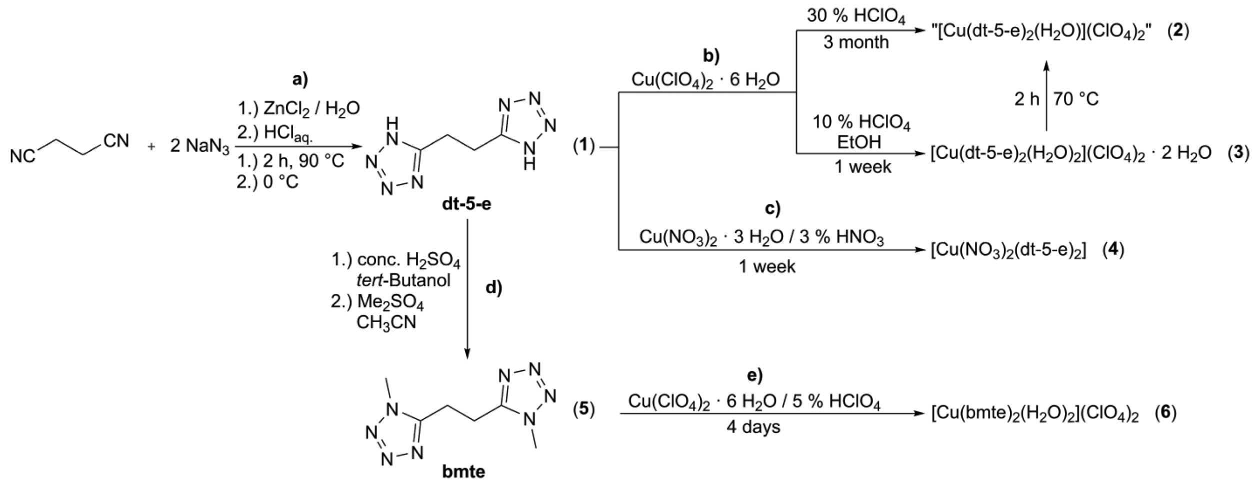
The improvement of the performance, safety, and environmental compatibility of energetic materials (EMs) is a major goal for energetic material researchers around the world.[1−4] Not only due to the European REACH regulations from 2007, the replacement of toxic, carcinogenic, and hazardous energetic materials like 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), monomethylhydrazine (MMH), or lead azide (LA) by "green" alternatives is a main object.[5−7] Strategies for the development of new EMs include increasing the nitrogen content, introducing ring strain, or oxidation of the molecule backbone.[8] An interesting and recent approach is the synthesis of energetic coordination compounds (ECCs), which offers the advantage of allowing selective design, since the metal center, energetic ligand, and oxidizing anion can be varied.[9] This is an extremely important possibility since it allows the development of EMs with specific, defined, and targeted properties. Two of the most powerful coordination compounds of this type which have been reported are tris(hydrazine)cobalt(II) perchlorate (CHP) and tris(hydrazine)nickel(II) perchlorate (NHP), which show detonation energies in the range of those of secondary explosives.[10] Unfortunately, both of these compounds are too sensitive and not suitable for any application. Probably the best investigated and most promising ECC is tetraammine-*cis*-bis(5-nitro-2*H*-tetrazolato)cobalt(III) perchlorate (BNCP).[11]

Another trend in the improvement of EMs is the synthesis and investigation of energetic cocrystals. In such compounds, usually secondary explosives such as 2,4,6-trinitrotoluene (TNT),[12] octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX),[13] or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)[12,13] are used for cocrystallization. Investigations have shown that the cocrystallization of two energetic compounds can decrease the sensitivity but (crucially) maintain the performance. An important example of this are 2:1 cocrystals of Cl-20/HMX.[13]

While cocrystals of (nonenergetic) coordination compounds are well-known in inorganic chemistry,[14] to the best of our knowledge, cocrystals of compounds containing energetic complexes have not yet been described. The concept of combing both the formation of a coordination compound and the introduction of an ionic cocrystal to develop a new class of EMs has been used in this work, and the synthesis and characterization of the energetic ionic complex cocrystal abbreviated as "$[Cu(dt\text{-}5\text{-}e)_2(H_2O)](ClO_4)_2$" (**2**) containing 1,2-di(1*H*-tetrazol-5-yl)ethane (dt-5-e, **1**)[15−17] as a neutral coordinating ligand and the perchlorate anion as a counterion has been achieved. The ionic cocrystal (**2**) consists of a mononuclear ($[Cu(dt\text{-}5\text{-}e)_2(H_2O)_2](ClO_4)_2$) and a trinuclear ($[(dt\text{-}5\text{-}e)(H_2O)Cu(\mu\text{-}dt\text{-}5\text{-}e)Cu(dt\text{-}5\text{-}e)_2(\mu\text{-}dt\text{-}5\text{-}e)Cu(dt\text{-}5\text{-}$

Received: August 19, 2014
Published: October 13, 2014

Scheme 1. (a) Literature Synthesis of the Ligand 1,2-di(1*H*-tetrazol-5-yl)ethane,[15] (b) Reaction of dt-5-e Forming the Copper(II) Compounds 2 and 3, (c) Reaction of 1 Forming the Nitrato Compound 4, (d) Methylation of 1 According to Literature,[18] (e) Further Reaction of 5 Forming Compound 6



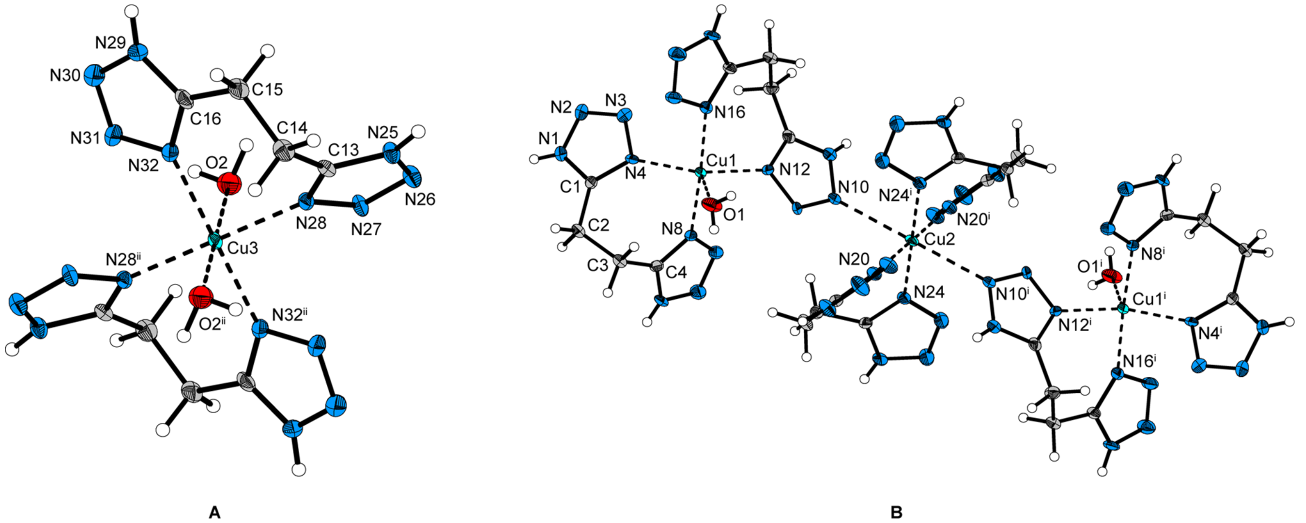


Figure 1. Crystal structures of the ionic cocrystal **2** showing the mononuclear (A) and trinuclear (B) copper units. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. The perchlorate counterions were omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−N4 2.006(3), Cu1−N8 2.009(3), Cu1−N12 2.002(3), Cu1−N16 2.022(3), Cu1−O1 2.172(3), Cu2−N10 2.5674(31), Cu2−N20 2.013(3), Cu2−N24 2.014(3), Cu3−N28 1.997(3), Cu3−N32 2.049(3), Cu3−O2 2.411(3), N25−C13 1.328(5), Cl1−O3 1.411(4), N4−Cu1−N8 87.58(12), N12−Cu1−N8 91.89(12), N8−Cu1−N16 176.15(12), N4−Cu1−O1 98.35(13), N8−Cu1−O1 91.84(13), N12−Cu1−N4 149.41(13), N20−Cu1−N24 88.09(12), N10−Cu2−N20 85.94(11), N10−Cu2−$N10^{i}$ 180.00, N20−Cu2−$N20^{i}$ 180.00, N24−Cu2−$N24^{i}$ 180.00, N28−Cu3−N32 89.97(12), N28−Cu3−O2 83.94(12), N28−Cu3−$N28^{ii}$ 180.00, N32−Cu3−$N32^{ii}$ 180.00, O2−Cu3−$O2^{ii}$ 180.00, C13−N25−N26−N27 0.1(4), C1−C2−C3−C4 57.2(4), C13−C14−C15−C16 67.1(4). Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) 1 − *x*, 2 − *y*, −*z*.

e)(H_2O)](ClO_4)$_6$) complex unit. Additionally, two mononuclear coordination compounds with dt-5-e as a ligand and perchlorate (**3**) and nitrate (**4**) as counterions as well as the mononuclear perchlorate coordination compound with 1,2-bis(1-methyltetrazol-5-yl)ethane as a ligand (**6**) were prepared, characterized, and compared to the ionic cocrystal **2**.

RESULTS AND DISCUSSION

Synthesis. Preparation of ligand **1** (dt-5-e) was similar to the method of Demko and Sharpless in yields of 30%.[15] Compound **2** can be obtained two ways (Scheme 1a,b): (i) by extremely slow evaporation (three months) of a concentrated solution of $Cu(ClO_4)_2·6H_2O$ and **1** in perchloric acid or (ii) by dehydration of the similar—but more accessible—mononuclear coordination compound [Cu(dt-5-e)$_2$(H_2O)$_2$](ClO_4)$_2$·$2H_2O$ (**3**) in the solid state at 70 °C. The mononuclear coordination compound **3** is obtained within a few days by precipitation of the product due to the addition of ethanol to the reaction mixture (diluted perchloric acid). Treating **1** with copper(II) nitrate in nitric acid yields the nitrato compound **4** with the formula [Cu(NO_3)$_2$(dt-5-e)$_2$] (Scheme 1c). Methylation of **1** using the method of Ivashkevich et al. resulted in the formation of 1,2-bis(1-methyltetrazol-5-yl)ethane (bmte, **5**),[18] which can react with $Cu(ClO_4)_2·6H_2O$ to form the mononuclear coordination compound **6** (Scheme 1d,e).

Crystal Structures. The structures of **2**, **3**, **4**, and **6** were determined using single crystal X-ray diffraction. In contrast to **3**, compound **2** does not only show a mononuclear octahedral coordination sphere. Instead, an atypical and rare energetic ionic cocrystal consisting of a mononuclear and a trinuclear

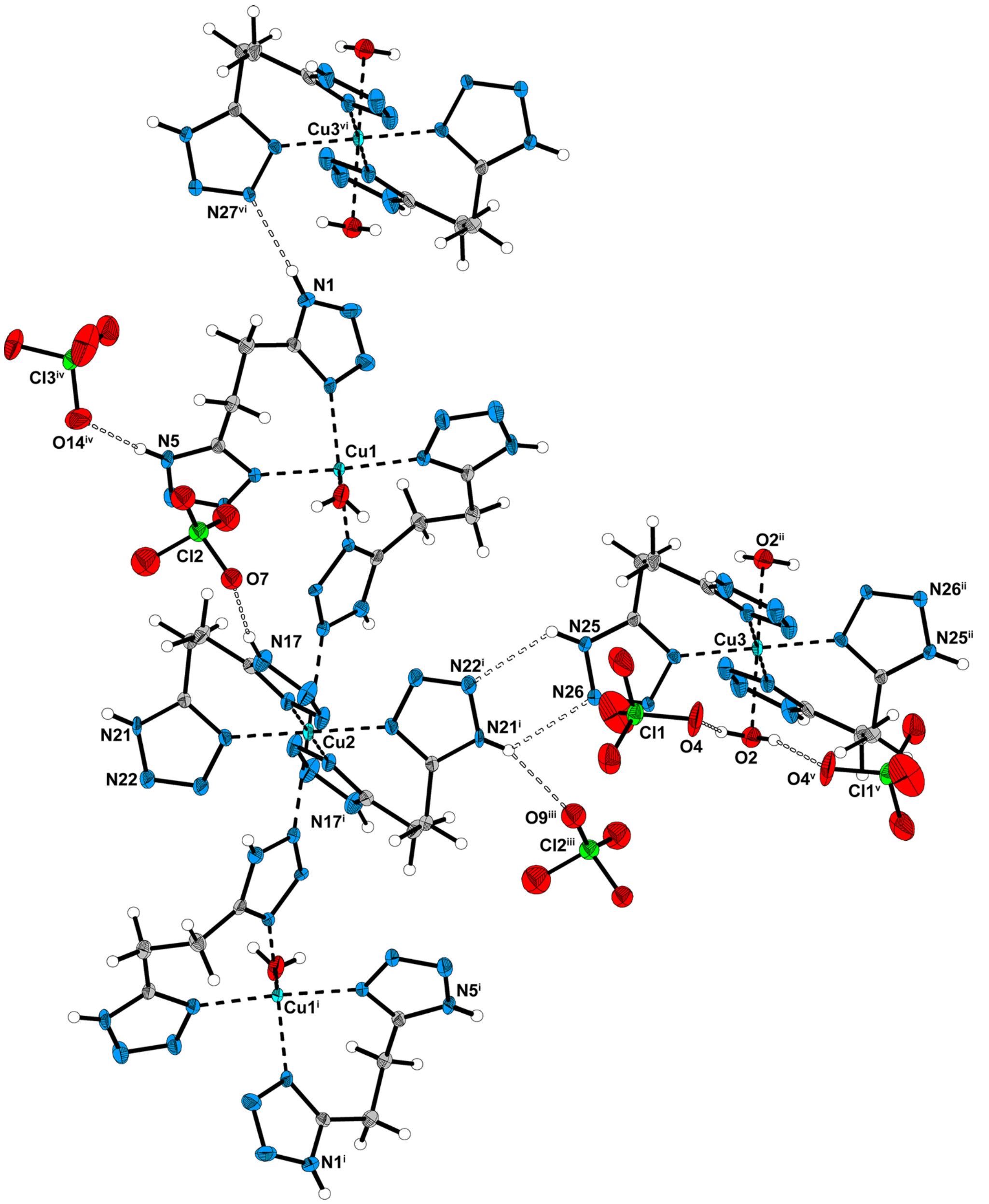


Figure 2. Selected hydrogen bonds in **2**. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) 1 − *x*, 2 − *y*, −*z*; (iii) *x*, 1 + *y*, *z*; (iv) 1 − *x*, −*y*, 1 − *z*; (v) −*x*, 2 − *y*, −*z*; (vi) 1 + *x*, −1 + *y*, *z*.

complex unit is formed (Figure 1). Compound **2** crystallized as blue rod ($20 \times 2 \times 1$ mm^3) in the triclinic space group $P\overline{1}$ with a density of 1.908 cm^{-3} at 173 K. The mononuclear unit shows the expected Jahn−Teller distorted octahedral coordination sphere, as is also observed for compound **3**.

The angles and Cu−N and Cu−O bond lengths of the mononuclear unit are in the expected range for typical Jahn−Teller distorted octahedral copper(II) complexes.[19] The trinuclear copper complex consists of two pentacoordinated copper centers which are connected through a six-coordinated octahedral unit. The coordination sphere of the pentacoordinated copper center is between those of a trigonal-bipyramid and a square-pyramid (Addison parameter $\tau = 0.45$).[20] Due to the similar N positions and an Addison parameter $\tau < 0.5$, the structure is described as square-pyramidal. All of the equatorial positions of the two symmetric square-pyramids are occupied by nitrogen atoms (Cu−N 2.00−2.02 Å similar to literature values)[14,18] of two bidentate dt-5-e ligands (N12−Cu1−N4 149.41(13)° and N8−Cu1−N16 176.15(12)°). The apical position is occupied by the oxygen atom of an aqua ligand. The Cu−O bond (Cu1−O1 2.172(3) Å) is slightly elongated compared to the equatorial Cu−N bonds but is still shorter than the values reported for Cu−O bonds in similar square-pyramidal copper complexes in the literature.[14] The two dt-5-e ligands differ in their coordination mode. One is bidentate only, whereas the other is bidentate and additionally μ-bridging at the N10 position to Cu2. The copper center Cu2 is surrounded by six nitrogen atoms arranged in a Jahn−Teller distorted octahedron (Cu2−N20 2.013(3), Cu2−N24 2.014(3), and Cu2−N10 2.5674(31) Å). Two dt-5-e ligands coordinate in a terminal bidentate mode (equatorial positions), while the axial positions are occupied by N atoms of μ-bridging dt-5-e ligands of neighboring copper units. The bond lengths and angles of the dt-5-e ligand in **2** are similar to those observed for the two polymorphs of the free ligand **1** and other 5-substituted tetrazoles.[16−19]

In compound **2**, numerous hydrogen bonds are formed between the neutral dt-5-e ligands of the mononclear and trinuclear unit, the aqua ligands, and the perchlorate counterions (Figure 2). The distances and angles of selected hydrogen bonds are given in Table 1. Most notable are the hydrogen bonds between N1 and N27^{vi}, N21^{i} and N26, as well as N22^{i} and N25, which clearly show the connections between the mononuclear and the trinuclear complex units (symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (vi) 1 + *x*, −1 + *y*, *z*).

Table 1. Distances and Angles of Selected Hydrogen Bonds in 2

D−H···A[a]	D−H/Å	H···A/Å	D···A/Å	D−H···A/deg
N1−H1···N27^{vi}	0.76(5)	2.12(5)	2.878(5)	175(6)
O2−H2C···N4^{v}	0.79(7)	2.06(7)	2.829(5)	166(7)
O2−H2D···N4	0.87(7)	2.19(6)	2.922(5)	141(5)
N5−H5···O14^{iv}	0.73(4)	2.12(4)	2.824(5)	161(4)
N17−H17···O7	0.89(4)	1.97(4)	2.855(6)	170(4)
N21^{i}−H21^{i}···N26	0.75(4)	2.49(4)	2.969(5)	123(4)
N21^{i}−H21^{i}···O9^{iii}	0.75(4)	2.34(4)	3.022(7)	152(4)
N25−H25···N22^{i}	0.84(4)	2.46(4)	3.000(4)	123(3)

[a] Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (iii) *x*, 1 + *y*, *z*; (iv) 1 − *x*, −*y*, 1 − *z*; (v) −*x*, 2 − *y*, −*z*; (vi) 1 + *x*, −1 + *y*, *z*.

The mononuclear coordination compound **3** crystallizes in the orthorhombic space group *Pbc*2$_1$ with four formula units per unit cell and a calculated density of 1.881 g cm^{-3} at 173 K. The copper(II) center is coordinated by two bidentate dt-5-e ligands at the equatorial positions and by two aqua ligands at the axial positions (Figure 3). The coordination sphere is octahedral and similar to the mononuclear complex unit of compound **2**. Jahn−Teller distortion can be observed along the O1−Cu1−O2 axis. Further, the structure contains two crystal water molecules which are disordered. The bond lengths and angles are in a typical range.

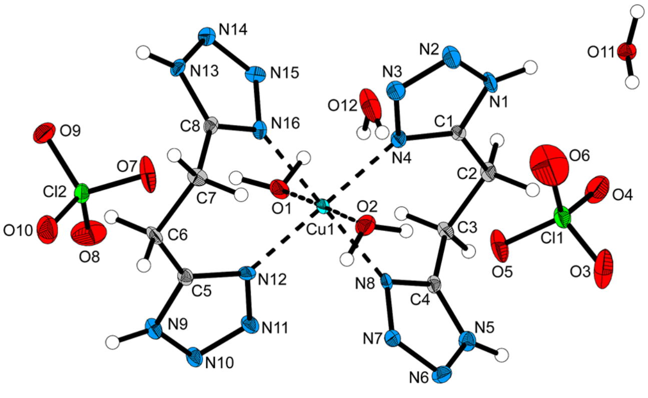


Figure 3. Crystal structure of the mononuclear coordination compound **3**. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Cu1−N4 2.016(3), Cu1−N8 1.992(3), Cu1−N12 2.009(3), Cu1−N16 1.993(3), Cu1−O1 2.7471(28), Cu1−O2 2.6453(29), N1−C1 1.320(5), Cl1−O3 1.432(3), N8−Cu1−N4 90.86(11), N8−Cu1−N12 89.45(13), N12−Cu1−N4 179.68(14), N8−Cu1−N16 178.01(14), O2−Cu1−O1 178.76(9), O3−Cl1−O4 108.43(17), N1−C1−N4 107.4(3), C4−C3−C2−C1−62.5(4).

Coordination compound **4** crystallizes in the triclinic space group *P*1̅ with a calculated density of 1.948 g cm^{-3} (at 100 K). Compound **4** is the only compound of the herein investigated ones which crystallizes in a water-free form. As expected, the copper center exhibits a Jahn−Teller distorted octahedral coordination sphere with nitrato anions in the axial position and bidentate dt-5-e ligands in the equatorial (Figure 4). The equatorial positions are occupied by the N4 atoms of the two bidentate dt-5-e ligands with typical Cu−N bond lengths of 1.9672(16) and 2.0856(16) Å. The bidentate dt-5-e forms a seven-membered ring with the copper center. The axial positions are occupied by the O1 atoms of the two nitrato ligands. The Cu−O bond is strongly elongated with 2.4180(14) Å.

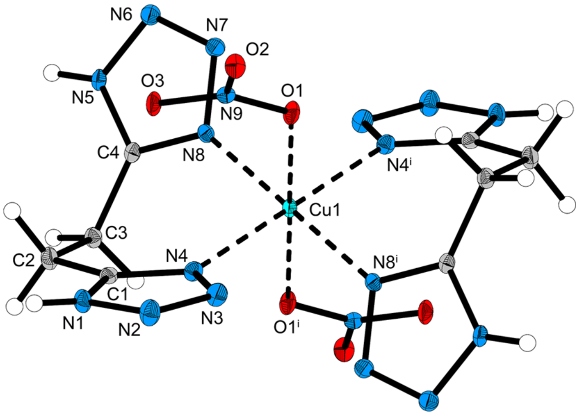


Figure 4. Crystal structure of the mononuclear coordination compound **4**. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Cu1−N8 1.9672(16), Cu1−N4 2.0856(16), Cu1−O1 2.4180(14), N1−C1 1.332(2), O1−N9 1.262(2), N8−Cu1−N4 90.75(6), N8−Cu1−O1 88.84(6), O1−Cu1−O1^{i} 180.00, N4−Cu1−N4^{i} 180.00, N8−Cu1−N8^{i} 180.00(7). Symmetry code: (i) −*x*, 1 − *y*, 1 − *z*.

The obtained copper(II) perchlorate coordination compound **6** with **5** as a ligand forms the expected mononuclear octahedron with two bidentate bmte ligands in the equatorial and two aqua ligands in the axial positions (Figure 5) showing the typical Jahn−Teller distortion (Cu1−O1 2.4387(13)). The bond lengths and angles are very similar to the mononuclear complex unit of compound **2**. The ECC **6** crystallizes in the monoclinic space group *P*2$_1$/*c* with two formula units per unit cell and a calculated density of 1.790 g cm^{-3} (at 100 K).

Powder Diffraction. Due to the mixed coordination mode, compound **2** shows superior laser absorption. Therefore, the formation of **2** by thermal transition of the mononuclear coordination compound **3** was investigated by X-ray powder diffraction. Gunier diffractograms (Figures S1 and S2) with Mo Kα1 radiation (λ = 0.7093 Å) were performed in the 2θ range between 4 and 34° with **3** (orthorhombic) and **2** (triclinic). In addition, a series of Gunier diffractograms was obtained for orthorhombic **3**, which was heated for 2 h at 50, 60, 70, and 80 °C. At 50 °C the diffractogram showed only the phase-pure diffraction pattern of **3**. At 60 °C, equal amounts of **3** and **2** were observed, whereas at 70 °C, a diffraction pattern containing only phase-pure **2** was obtained. In addition to infrared spectroscopy and elemental analysis, powder diffraction proved that the mononuclear, octahedral compound **3** transforms into the mono- and trinuclear coordination

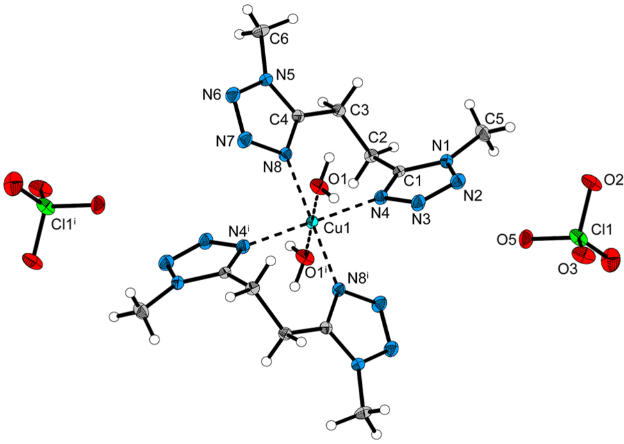


Figure 5. Crystal structure of the mononuclear coordination compound **6**. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Cu1−N4 1.9998(14), Cu1−N8 2.0294(14), Cu1−O1 2.4387(13), N1−C1 1.335(2), N4−Cu1−N8 89.66(6), N4−Cu1−O1 85.91(5), O1−Cu1−O1^{i} 180.00, N4−Cu1−N4^{i} 180.00(6), N8−Cu1−N8^{i} 180.00, C1−N1−N2−N3−0.40(18), C1−C2−C3−C4 62.7(2). Symmetry code: (i) −*x*, −*y*, −*z*.

compound **2** by a solid state thermal dehydration and migration process.

Due to the dehydration which occurs, the copper centers rearrange within the unit cell to saturate the free coordination sites which arise and which were originally occupied by aqua ligands. Saturation of the copper coordination sites is achieved by the new coordination modes of the dt-5-e ligand which are observed (μ_2, κ^3N^2,N^4,$N^{4\prime}$ instead of only κ^2N^4,$N^{4\prime}$) and the new coordination spheres which are formed (square-pyramidal instead of only octahedral). The cell parameters (see Table S1) change slightly due to the loss of water (e.g., **3**, V = 2355.3 Å → **2**, V = 2132.9 Å).

Infrared Spectroscopy. In addition to the powder diffractions of **2** and **3**, infrared spectra were recorded for all compounds **1**−**6**. A comparison of the infrared spectra of the free ligand **1** with the coordination compounds **2** and **3** shows that both coordination compounds exhibit the ligand vibrations of **1**, although in **2** and **3** they are shifted owing to coordination to the Cu^{2+} center (Figure S3 and S4). For example, the C═N stretching vibration of the free ligand **1** at 1583 cm^{-1} is shifted to 1564 cm^{-1} for **3** and to 1571, 1562, and 1557 cm^{-1} for **2**. The three C═N vibration bands in the spectra of **2** also indicate that different coordination modes of ligand **1** are present in compound **2**, which is in agreement with the crystal structure. The IR spectra of the mononuclear octahedral coordination compounds **3** and **6** show similar vibration bands and agree with the crystal structures of $[CuL_2(H_2O)_2](ClO_4)_2$. For compound **3**, an additional broad vibration band at approximately 3490 cm^{-1} is observed which can be assigned to uncoordinated crystal water. The spectra of compounds **2**, **3**, and **6** also show the typical perchlorate vibration bands (**2**, 1071 cm^{-1}; **3**, 1073 cm^{-1}; **6**, 1087 cm^{-1}), while in the spectrum of **4** split nitrate vibrations are observed, which is due to the coordination of the nitrate ion (**4**, 1333 and 1323 cm^{-1}).

Table 2. Energetic Properties of 2, 3, 4, and 6

	2	**3**	**4**	**6**
IS/J^{a}	1	3	4	4
FS/N^{a}	5	14	160	80
grain size/μm	100−500	500−1000	<100	500−1000
hot needle^{b}	det.^{c}	defl.^{d}	decomp.^{e}	defl.^{d}
laser init.^{f}	det.^{c}			defl.^{d}
function time/μs	67			292
$F(R)_{@940nm}$^{g}	1.35	0.04		0.09

^{a}According to BAM standard methods. ^{b}The hot needle test was performed by penetrating the sample, which is confined by adhesive tape, with the hot tip of a needle. ^{c}Detonation. ^{d}Deflagration. ^{e}Decomposition. ^{f}Wavelength of the diode laser λ = 940 nm at constant power density on the order of 10^{5} W cm^{-2}. ^{g}Relative light absorption [arbitrary units] as a function of the reflectance at 940 nm.

Energetic Properties and Laser Ignition. The metal coordination compounds were also investigated for their potential use as primary explosives, and selected parameters are summarized in Table 2. As expected (in contrast to the nitrato coordination compound **4**), the perchlorate compounds show an increased sensitivity toward mechanical stimuli. The coordination compound **2** in particular shows sensitivities and performance corresponding to that of a primary explosive. Despite this, however, it can be handled appropriately. The thermal stabilities of the compounds were determined by differential thermal analysis using a heating rate of 5 °C min^{-1}. The mononuclear compound **3** can be dehydrated at about 70 °C and is transformed to **2** in the solid state. Compound **2** is thermally stable up to 188 °C at which temperature dehydration occurs followed by exothermic decomposition. The dehydration of **6** occurs in a similar range, although the resulting compound is stable up to 278 °C. However, only compound **2** shows energetic properties comparable with those of a primary explosive. Without confinement, **2** only deflagrates by thermal ignition while with confinement it detonates if exposed to shock, thermal, or laser ignition. Due to the high light absorption over a broad range (500 to 1200 nm; Figure 6) compound **2** shows an outstanding response toward laser radiation.

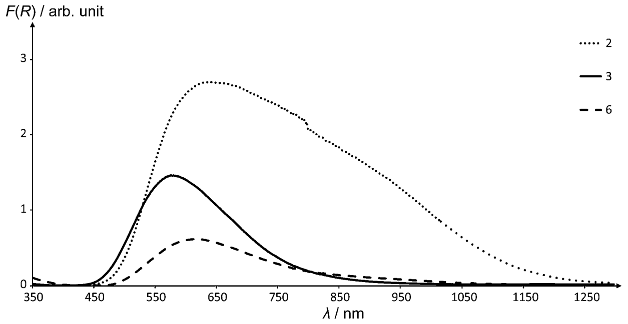


Figure 6. UV/vis/NIR spectra of compounds **2**, **3**, and **6**.

The UV/vis/NIR spectra of **3** and **6** are very similar, indicating the same electronic transitions occur (from the xy orbital to the $x^2 - y^2$ and from xz/yz to $x^2 - y^2$), which are typical for a Jahn−Teller distorted d^{9} complex. Owing to the different coordination spheres present in compound **2** (octahedral and square-pyramidal), **2** absorbs in a much larger range than the mononuclear, octahedral coordination compounds **3** and **6**. Compound **2** is therefore more suitable for laser ignition because the use of radiation sources emitting in the near-infrared (∼800−1100 nm) is preferred for technical reasons. Confined samples of **2** and **6** were irradiated with a monopulsed laser beam at 940 nm and a pulse length of 400 μs.

Compound **2** detonated, while the less powerful compound **6** only deflagrated. The energy output was measured qualitatively by an aluminum witness plate (Figure 7) and indicated detonation for **2**. For compound **6**, no dent was observed in the witness plate. Furthermore, the function times t_f (time delay between beginning irradiation and complete reaction) were determined and showed a 4 times faster value for **2** ($t_f = 67\ \mu s$) than for **6** ($t_f = 292\ \mu s$). This is in agreement with the higher absorption by **2** at 940 nm (Table 2). Values for the function time in the low-microsecond range are essential for potential alternatives for fast-functioning electric type detonators such as exploding-bridge wires.[21]

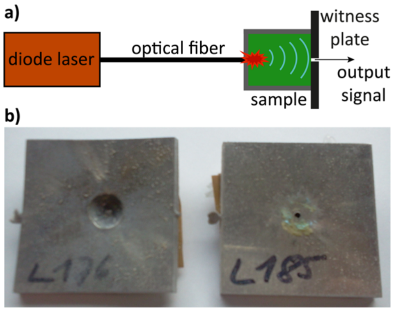


Figure 7. (a) Laser ignition setup. (b) Witness plates after laser ignition of coordination compounds **2** (left) and **6** (right).

CONCLUSION

In conclusion, the successful combination of the synthesis of energetic coordination compounds with the concept of cocrystallization was achieved in the synthesis and characterization of the mono- and trinuclear copper(II) perchlorate coordination compound **2** using dt-5-e as a flexible ligand. This represents a new concept in the design of energetic materials and offers the possibility to prepare highly photosensitive explosives. Furthermore, it was shown that the mono- and trinuclear coordination compound **2** can be obtained in a facile method by the dehydration of its mononuclear homologue **3** in the solid state. Due to the three different copper(II) coordination spheres in **2**, light is absorbed over a broad range with high intensity making **2** suitable for advanced laser initiated explosive devices.

EXPERIMENTAL SECTION

Caution! *The prepared copper(II) compounds are energetic materials with increased sensitivity to various stimuli (e.g., friction, impact, or heat). Proper protective measures (face shield, ear protection, leather coat, earthed equipment, conductive floor and shoes, Kevlar gloves) should be used at all time. Only small amounts of the compounds* **2** *and* **3** *should be handled.*

The impact and friction sensitivity tests were performed according to standard methods by using a BAM (Bundesanstalt für Materialforschung and -prüfung) drop hammer and a BAM friction tester.[22,23] Decomposition temperatures were measured via 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.[24,25] The determination of the carbon, hydrogen, and nitrogen contents was carried out by combustion analysis using an Elementar Vario EL.[26] Infrared (IR) spectra were recorded on a PerkinElmer BXII FT-IR system with a Smith DuraSamplIR II diamond ATR unit.[27] The UV/vis/NIR reflectance of solid samples (powders) was determined with a Varian Cary 500 spectrometer in the wavelength range of 350−1300 cm^{-1}.[28] 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.[29]

The crystal structures were determined on an Oxford Diffraction Xcalibur 3 diffractometer with a Sapphire CCD detector, four circle kappa platform, enhanced molybdenum Kα radiation source (λ = 71.073 pm), and Oxford Cryosystems Cryostream cooling unit.[28] Data collection and reduction were performed with the CrysAlisPro software.[30,31] The structures were solved with SIR97 or SIR2004.[32,33] The refinement was performed with SHELXL-97.[34] The CIF files were checked at the checkCIF Web site.[35] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically if not calculated.

X-ray powder experiments were performed on a Gunier diffractometer (Huber G644) with Mo Kα1 radiation (λ = 0.7093 Å; quartz monochromator) in Lindemann capillaries (0.7 mm diameter). The angle calibration was performed with electronic grade germanium. In the 2θ range between 4 and 34° with an increment of 0.04°, 750 data points were collected with a counting rate of 10 s for each increment. The Rietveld parameters were analyzed with the program FullProf.[36] The Rietveld data set contained 106 crystallographic independent atoms for the triclinic compound **2** and 59 crystallographic independent atoms for the orthorhombic compound **3**. Due to excessive peak overlapping, calculating diffractograms with FullProf was only possible in the 2θ range between 4 and 16°.

All chemicals were used as purchased. The ligands 1,2-di(1*H*-tetrazol-5-yl)ethane (dt-5-e, **1**) and 1,2-bis(1-methyltetrazol-5-yl)ethane (bmte, **5**) were synthesized similar to the literature procedures.[15,18]

{[Cu(dt-5-e)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$}{[(dt-5-e)(H$_2$O)Cu(μ-dt-5-e)-Cu(dt-5-e)$_2$(μ-dt-5-e)Cu(dt-5-e)(H$_2$O)](ClO$_4$)$_6$} (2) Abbreviated as "[Cu(dt-5-e)$_2$(H$_2$O)](ClO$_4$)$_2$". (a) The nitrogen-rich compound **1** (166 mg, 1.00 mmol) was dissolved in perchloric acid (30%, 5.0 mL) at 60 °C. Under stirring, a solution of copper(II) perchlorate hexahydrate (186 mg, 0.5 mmol) in perchloric acid (30%, 1.0 mL) was added, and the resulting blue reaction mixture cooled to room temperature and left for crystallization. After three months, one single crystal in the form of a blue rod (20 × 2 × 1 mm^3) suitable for X-ray diffraction was obtained. The crystal was filtered off and dried under ambient conditions for 1 h. Yield: 76 mg (0.04 mmol, 12%). (b) Drying of compound **3** (333 mg, 0.50 mmol) at 70 °C in the oven for 2 h yielded 306 mg (0.13 mmol, 100%) of **2**. DTA (5 °C min^{-1}) onset: 188 °C (dehydration), 206 °C (decomposition); IR (ATR): $\tilde{\nu}$ = 3527 (w), 3476 (vw), 3317 (w), 3153 (w), 1571 (w), 1562 (m), 1557 (m), 1415 (w), 1394 (w), 1101 (s), 1091 (s), 1071 (s), 1051 cm^{-1} (vs). Elem anal. ($C_{32}H_{56}Cl_8Cu_4N_{64}O_{36}$, 2451.17 g mol^{-1}) calcd.: C 15.68, H 2.30, N 36.57%. Found: C 15.98, H 2.44, N 36.29%. BAM impact: 1 J. BAM friction: ≤ 5 N (at grain size 100−500 μm).

[Cu(dt-5-e)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·2H$_2$O (3). Compound **1** (330 mg, 2.00 mmol) was dissolved in diluted perchloric acid (10%, 6.0 mL) at 60 °C. A solution of copper(II) perchlorate hexahydrate (372 mg, 1.00 mmol) in water was added under stirring and the blue reaction mixture cooled to room temperature. After 2 days, ethanol (3.0 mL) was added and the solution left for crystallization for further 3 days. Single crystals in the form of violet blocks were obtained, filtered off, washed with a small amount of ether, and dried under ambient conditions. Yield: 454 mg (0.68 mmol, 68%). DTA (5 °C min^{-1}) onset: 77 °C (dehydration). IR (ATR): $\tilde{\nu}$ = 3490 (m), 3153 (w), 1564 (m), 1417 (w), 1403 (w), 1071 (vs), 1054 cm^{-1} (vs). Elem anal. ($C_8H_{20}Cl_2CuN_{16}O_{12}$, 666.80 g mol^{-1}) calcd.: C 14.41, H 3.02, N 33.61%. Found: C 14.68, H 3.17, N 33.22%. BAM impact: 3 J. BAM friction: 14 N (at grain size 500−1000 μm).

$[Cu(NO_3)_2(dt\text{-}5\text{-}e)_2]$ (4). Compound **1** (330 mg, 2.00 mmol) was dissolved in 0.5 M nitric acid (7.0 mL) at 60 °C. A solution of copper(II) nitrate trihydrate (247 mg, 1.00 mmol) in water (1.0 mL) was added under stirring. The blue solution was cooled to room temperature and left for crystallization. After 1 week, X-ray suitable single crystals in the form of blue blocks were obtained. The crystals were filtered off, washed with a small amount of ethanol, and air-dried. Yield: 495 mg (0.95 mmol, 95%). DTA (5 °C min^{-1}) onset: 180 °C (decomposition). IR (ATR): $\tilde{\nu}$ = 3177 (w), 3136 (w), 1559 (s), 1426 (s), 1390 (s), 1333 (vs), 1323 (vs), 1051 cm^{-1} (vs). Elem anal. ($C_8H_{12}CuN_{18}O_6$, 519.84 g mol^{-1}) calcd.: C 18.48, H 2.33, N 48.50%. Found: C 18.74, H 2.32, N 47.95%. BAM impact: 4 J. BAM friction: 160 N (at grain size <100 μm).

$[Cu(bmte)_2(H_2O)_2](ClO_4)_2$ (6). The nitrogen-rich compound **5** (390 mg, 2.00 mmol) was dissolved in diluted perchloric acid (5%, 8.0 mL) at 60 °C. A solution of copper(II) perchlorate hexahydrate (372 mg, 1.00 mmol) in diluted perchloric acid (5%, 1.0 mL) was added under stirring. The reaction mixture was cooled to room temperature and left for crystallization. Within 4 days, X-ray suitable single crystals were obtained in the form of blue blocks. The crystals were filtered off, washed with a small amount of water, and dried under ambient conditions. Yield: 428 mg (0.62 mmol, 62%). DTA (5 °C min^{-1}) onset: 190 °C (dehydration), 278 °C (decomposition). IR (ATR): $\tilde{\nu}$ = 3593 (vw), 3509 (vw), 1619 (w), 1543 (w), 1420 (w), 1087 cm^{-1} (vs). Elem anal. ($C_{12}H_{24}Cl_2CuN_{16}O_{10}$, 686.87 g mol^{-1}) calcd.: C 20.98, H 3.52, N 32.63%. Found: C 21.11, H 3.43, N 32.70%. BAM impact: 4 J. BAM friction: 80 N (at grain size 500−1000 μm).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Single crystal X-ray and powder diffraction data, IR spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

* tmk@cup.uni-muenchen.de.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL) under grant no. W911NF-09-2-0018, the Armament Research, Development and Engineering Center (ARDEC) under grant nos. W911NF-12-1-0467 and W911NF-12-1-0468, and the Office of Naval Research (ONR) under grant nos. ONR.N00014-10-1-0535 and ONR.N00014-12-1-0538 is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Sućeska (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) for many inspired discussions. The authors thank Stefan Huber for assistance while performing the sensitivity and laser ignition tests.

■ REFERENCES

(1) Haiges, R.; Schneider, S.; Schroer, T.; Christe, K. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 4919.

(2) Gao, H.; Shreeve, J. M. *Chem. Rev.* **2011**, *111*, 7377.

(3) Fronabarger, J. W.; Williams, M. D.; Sanborn, W. B.; Bragg, J. G.; Parrish, D. A.; Bichay, M. *Propellants, Explos., Pyrotech.* **2011**, *36*, 541.

(4) Sabatini, J. J.; Moretti, J. D. *Chem.—Eur. J.* **2013**, *19*, 12839.

(5) Giles, J. *Nature* **2004**, *427*, 580.

(6) Vogel, S. Defense Dept. Standards On Lead Exposure Faulted. *Washington Post*, Dec 4, 2012; p 23.

(7) Brinck, T. *Green Energetic Materials*, 1st ed.; John Wiley & Sons Ltd: Chichester, U. K., 2014.

(8) Klapötke, T. M. *Chemie der Hochenergetischen Materialien*, 1st ed.; Walter de Gruyter: Berlin, 2009.

(9) Sinditskii, V. P.; Seurshkin, V. V. *Defence Science Journal* **1996**, *46*, 371.

(10) Bushuyev, O. S.; Brown, P.; Maiti, A.; Gee, R. H.; Peterson, G. R.; Weeks, B. L.; Hope-Weeks, L. J. *J. Am. Chem. Soc.* **2012**, *134*, 1422.

(11) Fronabarger, J. W.; Sanborn, W. B.; Massis, T. *Proceedings of the 22nd International Pyrotechnics Seminar*; Fort Collins, CO, Jul 15−19, 1996; p 645.

(12) Bolton, O.; Matzger, A. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 8960.

(13) Bolton, O.; Simke, L. R.; Pagoria, P. F.; Matzger, A. J. *Cryst. Growth Des.* **2012**, *12*, 4311.

(14) El Bakkali, H.; Choquesillo-Lazarte, D.; Dominguez-Martin, A.; Perez-Toro, M. I.; Lezama, L.; Gonzalez-Perez, J. M.; Castineiras, A.; Niclos-Gutierrez, J. *Cryst. Growth Des.* **2014**, *14*, 889.

(15) Demko, Z. P.; Sharpless, K. B. *J. Org. Chem.* **2001**, *66*, 7945.

(16) Shen, L.; Yang, J.; Yang, G.-W.; Li, Q.-Y.; Tang, X.-Y.; Zhou, F.; Miao, Z.-F.; Jin, J.-N.; Shen, W. *Inorg. Chim. Acta* **2011**, *370*, 150.

(17) Qiao, C.-F.; Zhou, C.-S.; Wei, Q.; Xia, Z.-Q. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2012**, *68*, o989.

(18) Ivashkevich, D. O.; Lyakhov, A. S.; Pytleva, D. S.; Voitekhovich, S. V.; Gaponik, P. N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *C59*, m221.

(19) Joas, M.; Klapötke, T. M.; Stierstorfer, J.; Szimhardt, N. *Chem.—Eur. J.* **2013**, *19*, 9995.

(20) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(21) Hafenrichter, E. S.; Marshall, B. W.; Fleming, K. J. *41st Areospace Sciences Meeting and Exhibit*, Reno, NV, Jan 6−9, 2003; pp 1−11.

(22) *NATO Standardization Agreement 4489*, September 17, 1999.

(23) *NATO Standardization Agreement 4487*, October 29, 2009.

(24) OZM Research s.r.o. Home Page. http://www.ozm.cz (accessed March 13, 2014).

(25) *NATO Standardization Agreement 4515*, August 23, 2002.

(26) Elementar Analysensysteme GmbH Home Page. http://www.elementar.de/ (accessed March 13, 2014).

(27) PerkinElmer Inc. Home Page. http://www.perkinelmer.de/ (accessed March 13, 2014).

(28) Agilent Technologies Inc. Home Page. http://www.agilent.com/ (accessed March 13, 2014).

(29) Kubelka, P.; Munk, F. *Z. Technol. Physik* **1931**, *1*, 593.

(30) *CrysAlisPro 1.171.36.24*; Oxford Diffraction Ltd.: Abingdon, U. K., 2012.

(31) *CrysAlisPro 1.171.37.31*; Oxford Diffraction Ltd.: Abingdon, U. K., 2014.

(32) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(33) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381.

(34) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112.

(35) checkCIF/PLATON Home Page. http://journals.iucr.org/services/cif/checkcif.html (accessed June 27, 2014).

(36) Rodriguez-Carvajal, J. R. *Abstracts of the Satellite Meeting on Powder Diffration of XV Congress of the IUCr*, Toulouse, France, 1990; p 127.