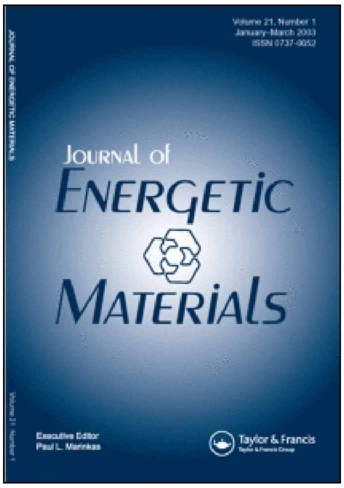

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Preparation and Explosive Properties of Tetraamminebis(3,5-Dinitro-1,2,4-Triazolato-N^1)Copper(II)

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The synthesis of tetraamminebis(3,5-dinitro-1,2,4-triazolato-N^1)copper(II) is reported along with its physical and sensitivity properties as well as crystal structure. In addition, the detonation velocity and CJ pressure have been determined at 0.5 inch diameter.

Keywords: energetic coordination compounds, 3,5-dinitro-1,2,4-triazolate, copper(II)

Introduction

Energetic metal coordination compounds have been used extensively as primaries and initiators for approximately 40 years. The most notable examples are pentaammine(5-cyano-1,2,3,4-tetrazolato-N^2)cobalt(III) perchlorate (CP) [1] and tetraamminebis(5-nitro-1,2,3,4-tetrazolato-N^2)cobalt(III) perchlorate (BNCP)

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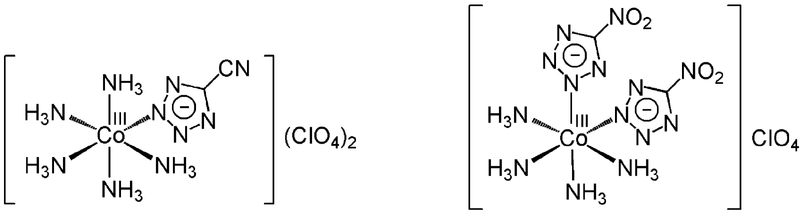


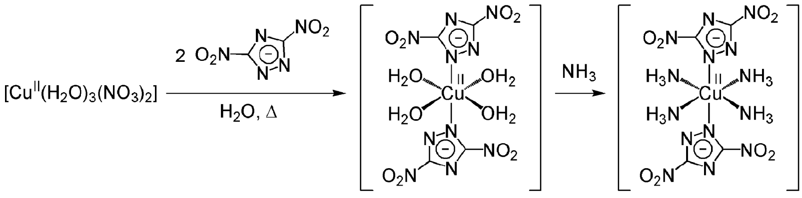
CP BNCP

Figure 1. Structure of CP and BNCP.

[2] (Figure 1). Several other energetic complexes have also been prepared utilizing various 1,2,3,4-tetrazolates substituted in the five-position [3]. Unlike typical primaries such as lead(II) azide or lead(II) styphnate, both CP and BNCP primary explosives are readily initiated thermally and transit to a detonation only if confined. BNCP is especially interesting as two very electron-deficient 5-nitro-1,2,3,4-tetrazolates are coordinated to cobalt(III). In this work, we wish to report the first complex made from another extremely electron deficient azolate: 3,5-dinitro-1,2,4-triazolate.

Results and Discussion

In contrast to 5-nitro-1,2,3,4-tetrazolate, which forms a large number of complexes with transition metal salts [4,5], 3,5-dinitro-1,2,4-triazolate (DNT) successfully coordinates only with copper(II). The water-soluble salts of iron(II), iron(III), cobalt (II), cobalt(III), nickel(II), and zinc(II) refused to coordinate to DNT even on extended refluxing in water. The cobalt(III) salt was in the form of tetraamminediaquacobalt(III) perchlorate, which readily coordinates to 5-nitro-1,2,3,4-tetrazolate to yield BNCP. With copper(II) solutions, the initial light blue of the hexaaqua complex turns green upon addition of ammonium 3,5-dinitro-1,2,4-triazolate (ADNT). This green complex does not precipitate, and it is thought to be tetraaquabis(3,5-dinitro-1,2,4-triazolato-N^1)copper(II) (**1**). Upon addition of concentrated ammonium hydroxide to this solution, a blue compound



(1) **(2)**

Figure 2. Synthesis scheme for tetraamminebis(3,5-dinitro-1,2,4-triazolato-N^1)copper(II) (**2**).

precipitates (**2**) (Figure 2). Infrared analysis definitely showed the presence of both ammonia and 3,5-dinitro-1,2,4-triazolate. Elemental analysis determined the stoichiometry as four ammonia and two 3,5-dinitro-1,2,4-triazolate ligands coordinated to a single copper. Single crystal X-ray diffraction (Figure 3) revealed two 3,5-dinitro-1,2,4-triazolate ligands in a transconfiguration and four ammonia in a square planar arrangement.[1] Only a single polymorph was found with density 1.860 g/cm^3. The bond length between the coordinating N in 3,5-dinitro-1,2,4-triazolate and Cu(II) (Cu1-N2 in Figure 3) was found to be extremely long at 2.655 Å. In a recent search of the Cambridge Crystallographic Data Base, this bond length appears to be the longest compared to all Cu(II)-N bonds ever measured for the coordinated N contained in an azole ring [6,7]. This extended bond length is indicative of the salt-like nature of this compound, much like a square planar Cu(II) tetraammine complex

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[1] Molecule (**2**) crystallizes in space group Pbca, with $a = 10.3333(5)$, $b = 10.7477(5)$, and $c = 14.397(1)$ Å, $V = 1598.9(2)$, and D(X-ray) = 1.860 g/cc; 1495 independent data were collected and routinely solved and refined to an $R = 0.057$. Other crystallographic data for (**5**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 248254. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK). Tel.: (+44)-1223-336-408, Fax: (+44) 1223-336-033, or E-mail: deposit@ccdc.cam.ac.uk

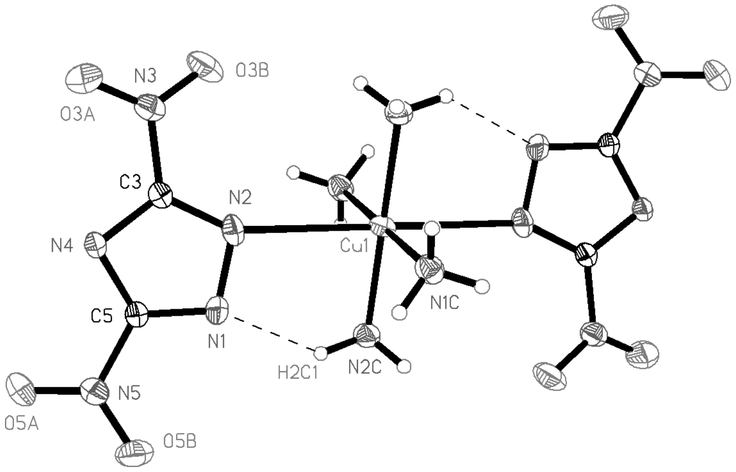

Figure 3. ORTEP of tetraamminebis(3,5-dinitro-1,2,4-triazolato-N^1)copper(II) (**2**). The Cu sits on a crystallographic center of symmetry. The ammine N atoms appeared clearly in the structure solution, but their hydrogen atoms did not (perhaps due to large thermal motions). In the final refinement, ammine hydrogen atoms were ‘‘placed’’ at idealized trigonal positions (i.e., restrained to have equal NH distances, equal HNH angles) in the refinement. The Cu-N2 distance and its centric equivalent are 2.655 Å, while the square planar set of ammines are 1.999 and 2.029 Å away.

containing two *trans* counterionic 3,5-dinitro-1,2,4-triazolate having extreme Jahn-Teller distortion.

The thermal, sensitivity, and performance properties of (**2**) were determined. The differential scanning calorimetry trace of (**2**) was somewhat complex, with the onset occurring at 206°C and three maxima. The first maximum at 240°C was broad, and the remaining two maxima at 257 and 315°C were sharper. Complex (**2**) was found to be insensitive to initiation by spark (0.36 J) and friction (>36 kg, BAM) and had a drop height of 42 cm (2.5 kg weight, HMX = 22 cm). When formulated with 5 weight percent LFC-1, the mixture maintained insensitivity to both spark and friction, and the drop height increased to 67 cm. The explosive performance of (**2**) was measured with a standard

0.5 inch rate stick/plate dent test with the formulated material pressed to a density of 1.81 g/cm^3. The detonation velocity was determined to be 7.21 ± 0.01 km/s with a CJ pressure of 246 kbar at this density.

Synthesis

Tetraamminebis(3,5-dinitro-1,2,4-triazolato-N^1)copper(II) (**2**). To 50 ml of deionized water are added $Cu(H_2O)_3(NO_3)_2$ (5.0 g, 20.7 mmol) and ammonium 3,5-dinitro-1,2,4-triazolate [8] (7.29 g, 41.4 mmol), and the mixture was refluxed with stirring for 2 hr to yield a homogeneous green solution. The volume of the solution was reduced to approximately 10 mL followed by the addition of 30 mL of concentrated ammonium hydroxide. The dark blue solid that formed was filtered, washed with the minimum amount of ice water, and air-dried. The combined filtrates were further reduced to ~20 mL, yielding a second crop. The combined yield was 8.80 g (95%). IR (Nujol mull) 3378, 3339, 3262, 3183, 1532, 1491, 1466, 1387, 1351, 1299, 1268, 1210, 1103, 1046, 845, 705, 667, 585 cm^{-1}. Elemental Analysis: calculated for $CuC_4H_{12}N_{14}O_8$: C, 10.83; H, 2.70; N, 43.79; O, 28.58. Found: C, 10.76; H, 2.69; N, 43.81; O, 28.06.

Acknowledgments

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