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A Novel DDT Explosive**

John Fronabarger, Alex Schuman,
Robert D. Chapman, Wayne Fleming,
and William B. Sanborn

Pacific Scientific Company,
Energy Dynamics Division
Chandler, AZ

Tom Massis

Sandia National Laboratories
Albuquerque, NM

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CHEMISTRY AND DEVELOPMENT OF BNCP, A NOVEL DDT EXPLOSIVE

John Fronabarger*, Alex Schuman†, Robert D. Chapman‡,
Wayne Fleming‡, and William B. Sanborn
Pacific Scientific, Energy Dynamics Division, Chandler, AZ

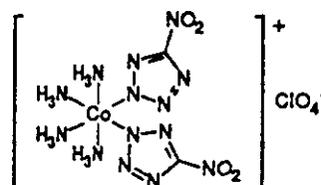
Tom Massis
Sandia National Laboratories, Albuquerque, NM

ABSTRACT

Tetraammine-cis-bis(5-nitro-2H-tetrazolato-N²)cobalt (III) perchlorate (BNCP) is a deflagration-to-detonation (DDT) explosive structurally similar to CP, a 5-cyanotetrazolotocobalt complex used in national defense applications since 1979. BNCP is a more powerful explosive and undergoes DDT more rapidly than CP. The synthesis of its two precursors as well as the preparation of BNCP will be described. Analytical characterization regarding chemical structure and purity will be presented. This will include elemental and functional group analysis as well as the results of spectroscopic techniques such as IR, UV-Visible-NIR and NMR. Also the chemical structure by single crystal X-ray diffraction will be described. Other characterization includes sensitivity properties (impact, friction, electrostatic discharge and ignition by flame) thermal analysis and density determination. Finally a brief review will be made of BNCP performance in detonator configurations.

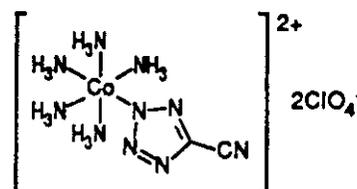
GENERAL

Since the early 1970's, it has been known that certain 5-substituted pentaammine-tetrazolotocobalt(III) perchlorates would undergo deflagration-to-detonation transition (DDT) under the appropriate confinement. Of this series the 5-cyanotetrazolato complex, known as CP, has been used in DOE weapons systems since



BNCP

Tetraamminebis(5-nitro-2H-tetrazolato-N²)cobalt(III) perchlorate



CP

Pentaammine(5-cyano-2H-tetrazolato-N²)cobalt(III) perchlorate

Figure 1

*Author to whom correspondence should be addressed. †Currently at TPL, Inc., Albuquerque, NM ‡Currently at Universal Propulsion Company, Inc., Phoenix, AZ

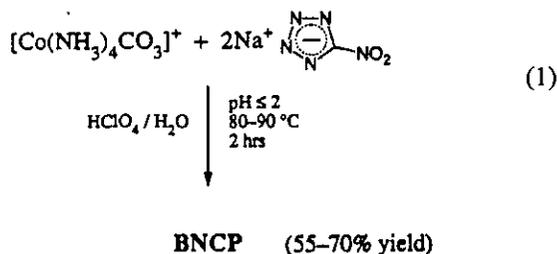
1979. More recently CP detonators have been used in oil field completion work, and are continually being investigated for DOD applications.

In 1986 L. R. Bates of RARDE reported a related compound, tetraamminebis(5-nitro-2*H*-tetrazolato-*N*²)cobalt(III) perchlorate, as a possible replacement for lead azide and other priming materials.¹ At the time of the Bates paper, Pacific Scientific Energy Dynamics Division, formerly Unidynamics/Phoenix, had the need for an alternative to CP, specifically an explosive capable of undergoing DDT in a smaller configuration. Lead azide was considered undesirable for the particular application. Subsequently small quantities of the Bates compound, now referred to as BNCP, were prepared and found to undergo DDT in smaller and less confining configurations than required for CP. BNCP also exhibited a higher explosive yield than CP as indicated by witness block testing and later by the VISAR method.

Shortly thereafter Sandia National Laboratories became interested in the explosive and has been supporting work on BNCP at the Albuquerque laboratories and Pacific Scientific. The chemical structures for BNCP and CP are illustrated in Figure 1.

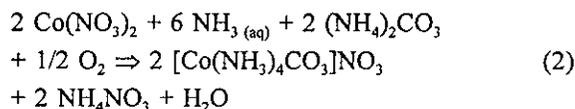
SYNTHESIS OF BNCP

The synthesis of BNCP is accomplished via a typical anation reaction, Equation 1.



Currently, the process has been scaled to produce 250 grams of recrystallized BNCP. Plans are being made to scale to larger batch sizes.

Preparation of the precursors sodium 5-nitrotetrazolate dihydrate ($\text{NaTzNO}_2 \cdot 2\text{H}_2\text{O}$) and tetraamminecarbonatocobalt(III) nitrate (CTCN) represent somewhat greater synthesis challenges than the final BNCP preparation. For many years, the cobalt bearing precursor CTCN has been prepared by a well known procedure, Equation 2.^{2,3}



However, a detailed examination of the products obtained using the reported procedures often resulted in the presence of pentaamminecarbonatocobalt(III) nitrate (CPCN, a CP precursor).

This conclusion is based on ultraviolet/visible spectrophotometry and DMSO solubility studies. The spectra for CTCN, CPCN and a sample of CTCN containing CPCN impurity are shown in Figure 2.

The acceptability of CTCN is currently best identified from the ratio the relative absorbances of the peak at 361 nm and the minimum at 327 nm. This method allows for a rapid screening of the material, however, it has not yet been quantified.

A simple quantitative method has been devised that is based upon the solubility of CTCN and the insolubility of CPCN in DMSO. Small percentages (<10%) of CPCN can be detected in CTCN using this characteristic. Further analytical techniques are currently being pursued by Sandia.

The crucial step in preparing pure CTCN appears to be the addition of the ammonium carbonate during the evaporation of the reaction solution. Failure to add

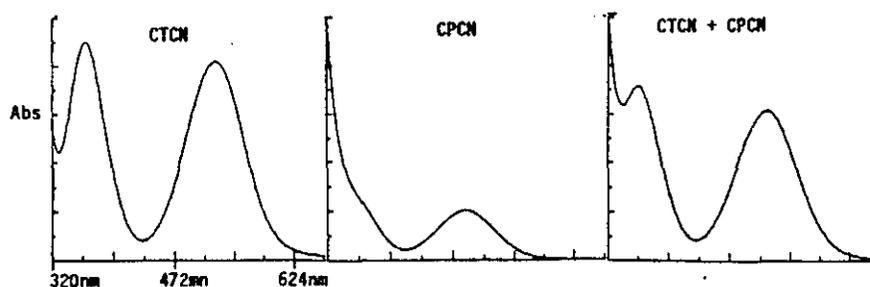
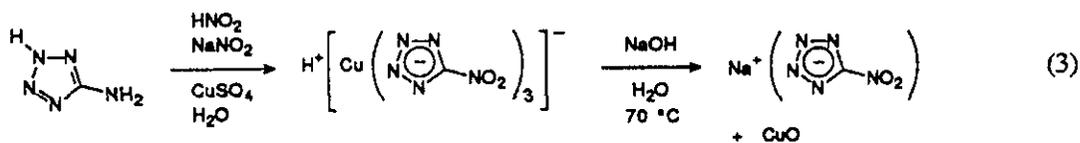


FIGURE 2



this material properly will result in appreciable quantities of the CPCN impurity.

The other precursor is sodium 5-nitrotetrazolate dihydrate. The degree of hydration has been confirmed by thermogravimetric analysis. Further studies have confirmed Gilligan/Kamlet's observation of the variability of this hydration as a function of relative humidity.⁴ The dihydrate appears to be a minimum under normal temperatures and increases with humidity. Methods of preparation have been modifications of previously reported procedures.^{4,5} The basic series of reactions is found in Equation 3.

One major concern with this synthesis is isolation of the sodium salt. Sodium 5-nitrotetrazolate dihydrate is quite water-soluble and is cumbersome to isolate from the other water soluble salts, e.g., sodium nitrate. Some consideration is being given to using a

concentrated NaTzNO_2 solution directly, thus eliminating the tedious crystallization procedure. However, the effect of the remaining solution impurities may pose problems. Also a previously reported extraction procedure involving the isolation of the ammonium salt and conversion to the sodium salt is being pursued.⁵

Another reported problem which has been observed at Pacific Scientific is the occurrence of "microdetonations" during the diazotization reaction.⁴ This can be alleviated, at least to some extent, by the use of a small concentration of copper sulfate in the aminotetrazole addend solution. This prevents gaseous nitrogen oxides from reacting with the aminotetrazole to build up a concentration of the tetrazole diazonium ion which can detonate in solution.⁴ Also proper reactor design can alleviate much of the problem.

STRUCTURE OF BNCP

BNCP is a yellow-gold crystalline solid which is typical for octahedral cobalt(III) complexes having six coordinating nitrogens (as is the case with CP). The electronic spectrum is typical with a d-d transition (${}^1T_{1g} \leftarrow {}^1A_{1g}$) at 456 nm, $\epsilon = 74 \text{ L cm}^{-1} \text{ mole}^{-1}$. The higher frequency ${}^1T_{2g} \leftarrow {}^1A_{1g}$ band is obscured by the strong nitrotetrazole charge transfer band.

Regarding the vibrational modes of BNCP, the infrared spectrum is as would be expected; typical bands for coordinated ammonias, nitro groups, tetrazole ring and perchlorate anion are observed.

The composition and structure elucidation of BNCP has been approached by several means. Elemental combustion analysis for carbon, hydrogen and nitrogen provided acceptable results for the empirical formula $\text{C}_2\text{H}_{12}\text{CoClN}_{14}\text{O}_8$. A perchlorate gravimetric analysis using tetrapentylammonium bromide confirmed the presence of a single anion per molecular formula. Structurally, the ${}^1\text{H}$ NMR spectrum was consistent with the nitrotetrazoles in a cis configuration as evidenced by two equivalent ammonia proton resonances at 3.79 ppm and 4.29 ppm relative to an internal TMS standard as shown in Figure 3.⁶

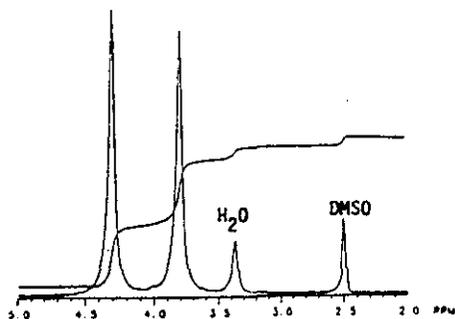


Figure 3

A single crystal x-ray diffraction analysis by Morosin revealed that BNCP crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 10.032(5)\text{\AA}$, $b = 10.547(6)\text{\AA}$, $c = 14.861(10)\text{\AA}$, $\beta = 109.09(4)^\circ$, and $Z = 4$.⁷ The crystal structure determination readily confirmed the cis relationship of the tetrazolato ligands as deduced from NMR analysis. These ligands displayed N-2 bonding to the cobalt ion with Co-N bonds of $1.924(4)$ and $1.933(4)\text{\AA}$ while the ammine metal distances ranged 1.950 - 1.974\AA . The experimental and calculated densities are in close agreement at approximately 2.03 g/mL . Several of the oxygen atoms associated with the ClO_4^- anions appear to be slightly disordered.

PROPERTIES OF BNCP

Various properties of BNCP have been investigated, including several important functional characteristics. Thermal response (DSC) and safety data are compiled in the following Table with corresponding values for CP given as comparisons.

As indicated above, BNCP is slightly more sensitive to impact and friction than CP and exhibits ESD sensitivity similar to CP. Also BNCP responds to a DSC gradient of $20^\circ\text{C}/\text{minute}$ at about 20°C lower than CP. This may be a slight disadvantage for BNCP regarding hot wire detonator no-fire characteristics, but a slight advantage for hot wire all-fire and laser initiation applications.

Explosive output data determined for BNCP include steel witness plate and detonator closure disk ($0.005''$) velocity data as determined by VISAR, refer to Table II.

As mentioned previously, BNCP undergoes the DDT process more rapidly and in a shorter distance than CP under steel confinement. Further, BNCP will DDT moderately well under aluminum confinement and to a lesser extent under plastic (Lexan)

Table I - COMPARISON OF PROPERTIES OF BNCP AND CP

	BNCP	CP
DENSITY, g -cm ⁻³	2.03	1.98
IMPACT SENSITIVITY, cm (2 kg, 10% FIRE LEVEL)	50	55-70 LOT DEPENDENT
FRICTION SENSITIVITY, JULIUS PETERS BAM TESTER, THRESHOLD, g	600	>1000
ELECTROSTATIC DISCHARGE SENSITIVITY, kV (600 pF, 500-Ω series) LOOSE POWDER CONFINED, 0.020" GAP	>25 4.8 (79% TMD) 8.5 (89% TMD)	>25 5.2 (82% TMD) 8.0 (86% TMD)
DIFFERENTIAL SCANNING CALORIMETRY (DSC), 20°C/MIN EXOTHERM ONSET, °C EXOTHERM PEAK(S), °C	269 276, 301	289 333

Table II - EXPLOSIVE OUTPUT CHARACTERIZATION

TEST	BNCP (%TMD)	CP (%TMD)
STEEL WITNESS PLATE (DEPTH OF DENT), IN	0.026 (80)	0.018 (76)
VISAR (VELOCITY INTERFEROMETER SYSTEM FOR ANY REFLECTOR), mm/μs	3.2 (80)	2.7 (76)

confinement. CP does not DDT well using these two materials for confinement.

APPLICATIONS

Several uses of BNCP have been envisioned and investigated in the area of ordnance applications.

A number of these activities are briefly described and it is to be noted these investigations are still in progress.

The ability of BNCP to achieve detonation with a very short column length made development of an extremely small (0.24" diameter, 0.21" long)

semiconductor bridge detonator possible. This device, designed for a DoD application, utilized a total charge weight of 13 mg of BNCP loaded in two increments to initiate PBXN-301. A small particle BNCP ignition load weighing 3 mg was consolidated at 20,000 psi against the SCB and was followed by 10 mg output load of larger particle size BNCP pressed at 10,000 psi. The SCB was adhesively bonded to a 2 pin commercial glass-to-metal sealed transistor header to which a stainless steel charge holder was welded. The application required that the firing pulse be 3.5 A with rise time slowed to 50 μ s. For the SCB used, this firing pulse resulted in marginal condition for plasma creation which under low temperature conditions caused the SCB to fire in the regime between the plasma and hot-wire modes. Nevertheless, function times were typically 120 μ s over the temperature extremes.

At Sandia BNCP based SCB detonators have been designed and studied using the capacitor discharge firing mode. For example, a function time of 10.4 μ s was realized using a 20 μ F capacitor charged to 28V.⁸

The use of BNCP in optical ordnance has been investigated particularly in regard to laser diode initiated detonators. Studies at Sandia and Pacific Scientific have been shown the concept to be quite feasible. For example, work at Sandia has shown that carbon doped (1%) BNCP is somewhat more sensitive to the diode laser output (~800nm) than comparably doped CP.⁹ Using a 100 micron optical fiber at the explosive interface the BNCP charge exhibited an ignition threshold of about 0.5 millijoules at a power level of 0.2 watts whereas a CP charge required approximately 0.75 millijoules for threshold at the same power level. These results do correlate with the lower temperature response of BNCP as compared to CP (see previous table of BNCP and CP properties). It has been demonstrated that optical approaches to ordnance provide safety enhancement with respect to electrostatic discharge, electromagnetic radiation and

stray optical sources.

As mentioned previously, BNCP and CP are DDT type explosives requiring short distances to achieve steady state detonation. It has been further demonstrated that in very short columns, these explosives will promote DDT in organic explosives such as HMX and BTF (benzotrifuroxan) much more effectively than a rapid burning pyrotechnic such as titanium/potassium perchlorate. It is to be mentioned that in these short columns the propagation rate of BNCP and CP was considerably below detonation velocities, i.e., about 400 to over 500 m/s for BNCP and 250-300 m/s for CP. Corresponding rates for Ti/KClO₄ were estimated to be in the 60-70 m/s range.¹⁰ The hot wire mode was used to ignite the BNCP, CP, and Ti/KClO₄ charges.

CONCLUSIONS:

- An energetic coordination compound, BNCP, has been developed which undergoes DDT more readily and is more powerful in the detonating mode than CP.
- BNCP possesses sensitivity and stability characteristics that should render it applicable for detonator applications.
- The chemical structure of BNCP has been fully elucidated.
- Methods have been developed for the preparation of moderate amounts of BNCP. It is anticipated BNCP can be prepared in kilogram or larger quantities.
- BNCP has been shown to be feasible for ordnance applications.

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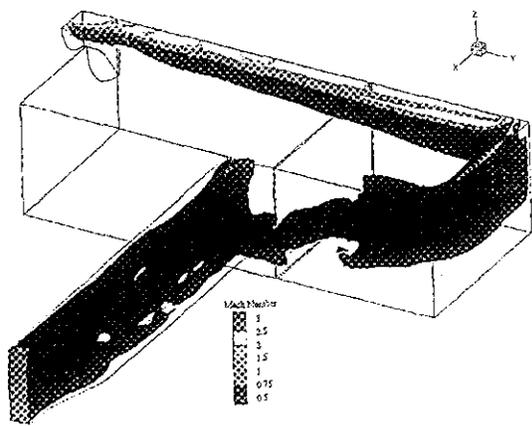


Figure 7. NPARC Simulation Mach Number Iso-surfaces.

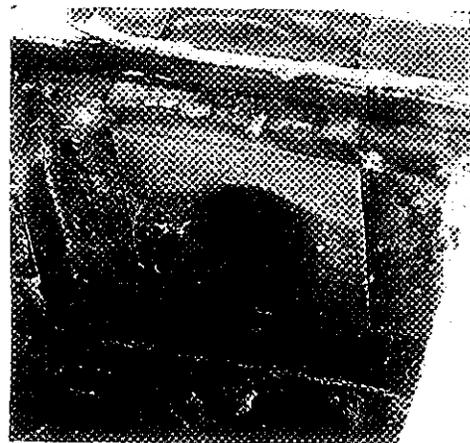


Figure 8. Post-test View of a Plenum Backplate

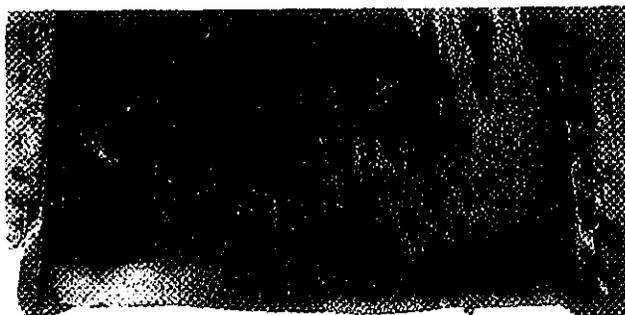


Figure 9. Post-test View of One side of an Exhaust Duct Detailing Front Edge Erosion.

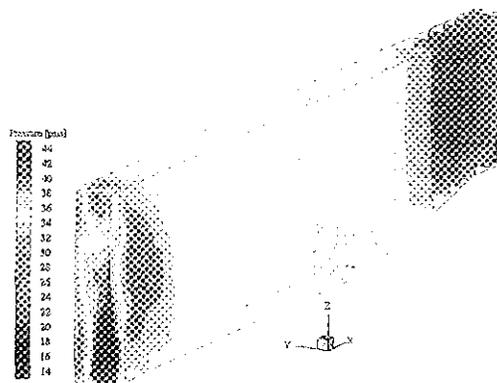


Figure 10. Pressure Iso-surfaces in the Exhaust Duct

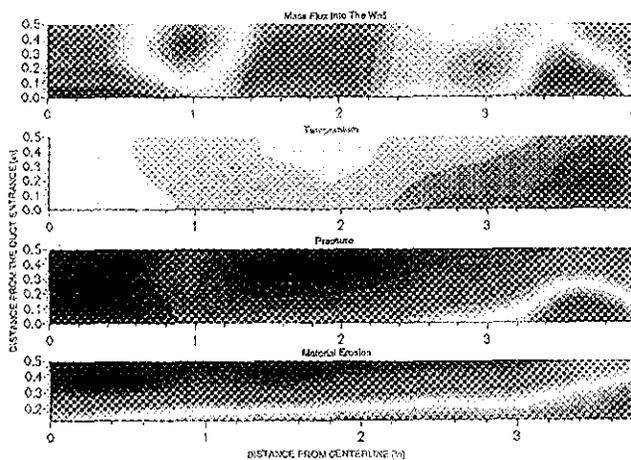


Figure 11. Comparison of Simulation Flowfield with Measured Erosion in the Exhaust Duct Entrance.

*See Figure 4 for Location of Displayed Region.