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Technical Report ARMET-TR-12013

SYNTHESIS OF BIS(1-METHYL-3-PROPYL-4-NITRO)IMIDAZOLIUM DODECAHYDRODODECABORATE AND BIS(1-METHYL-3-PROPYL-5-NITRO)IMIDAZOLIUM DODECAHYDRODODECABORATE SALTS: A NEW CLASS OF ENERGETIC FUELS

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Paul Anderson

February 2013

U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER

Munitions Engineering Technology Center

Picatinny Arsenal, New Jersey

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14. ABSTRACT

Two new salts that ionically bind nitroimidazolium cations with the dodecahydro-*closo*-dodecaborane anion are reported from the synthesis of the corresponding nitrate, iodide, and potassium salts. These salts represent a category of tailorable energetic oxidizer-fuel compounds that can be synthesized in the aqueous environment under normal atmospheric conditions. Spectroscopic data - including single crystal x-ray diffraction, Fourier transform infrared (FTIR), melting points, and densities - are provided along with thermal gravimetric analysis of each compound.

15. SUBJECT TERMS

Boron Metathesis Energetic cation Energetic fuel Boron oxidation Dodecaborate Decaborate

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INTRODUCTION

Dodecahydro-*closo*-dodecaborate [*closo*-$B_{12}H_{12}]^{2-}$ and decahydro-*closo*-decaborate [*closo*-$B_{10}H_{10}]^{2-}$ salts are caged boron analogues of aromatic hydrocarbons (fig.1). Due to both their thermal stability up to 800°C and high energy release upon combustion compared to their hydrocarbon analogues the *closo*-borate species are a promising class of compounds or energetic and burn rate enhancement research.

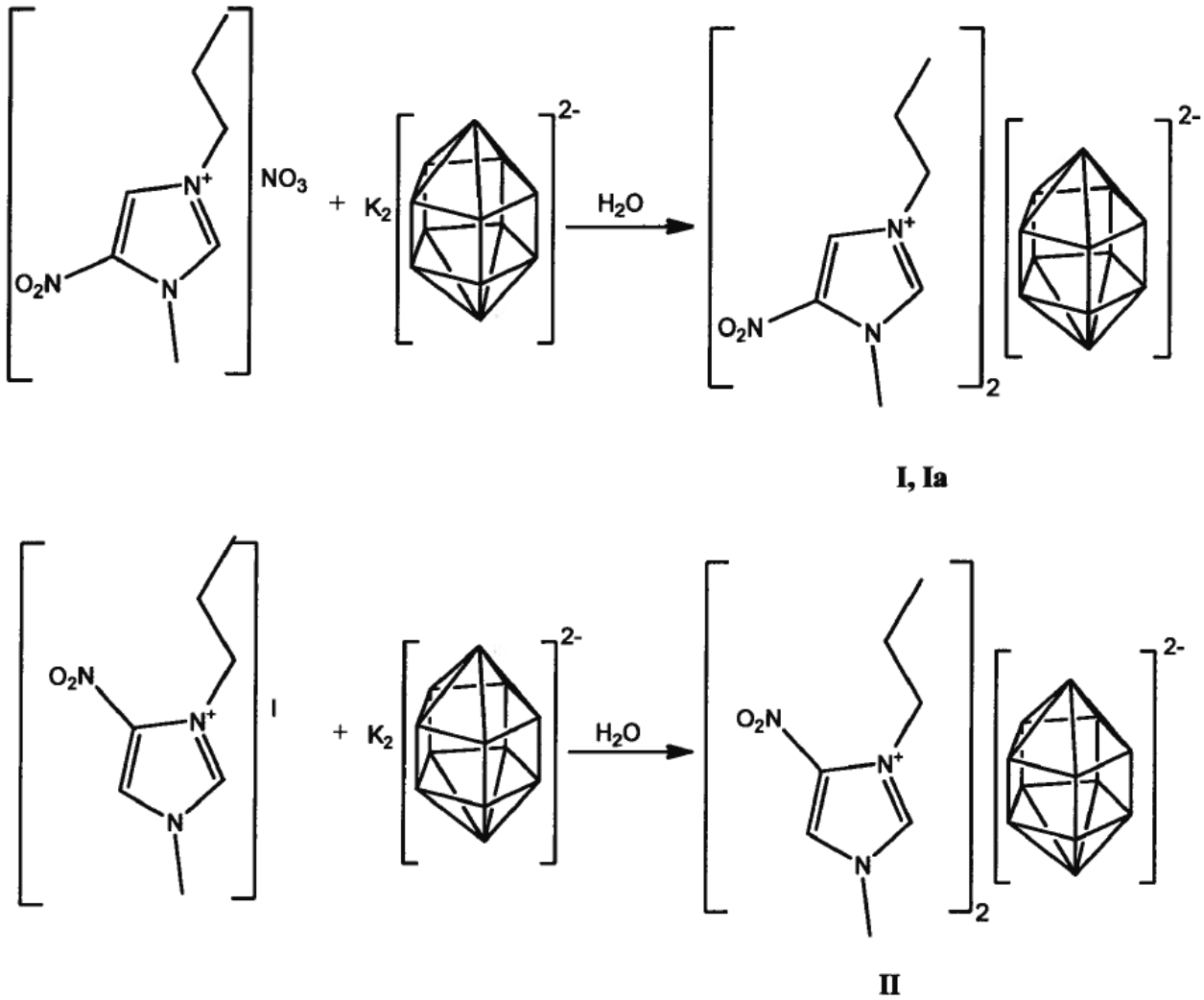

Figure 1
Metathesis reaction of dipotassium dodecahydro-*closo*-dodecaborate salt, [closo-$B_{12}H_{12}]^{2-}$, with 1-methyl-5-nitro-propyl imidazolium iodide and with 1-methyl-4-nitro-propyl imidazolium iodide to form the corresponding methylnitroimidazolium dodecaborate salts **I**, **Ia**, and **II** (all vertices are boron)

BACKGROUND

Despite having a high gravimetric and volumetric energy density, energetic boron research has been limited due to both kinetic and thermodynamic impediments: a kinetic bottleneck experienced during oxidation, and a solid phase oxide layer that encompasses the particle surface, requires high temperatures to remove and consequentially causes ignition difficulties (ref. 1). During combustion in an oxygenated environment, boron is oxidized first to boric acid, then to metaboric acid (HOBO), and finally to diborontrioxide with energy being released during each of the oxidative stages (fig. 2).

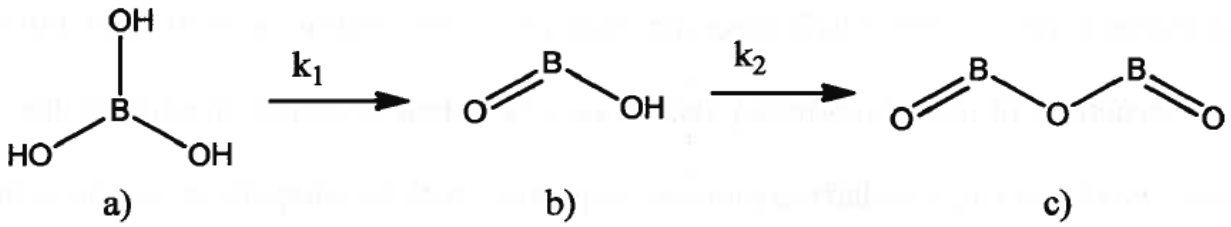

Figure 2
Equilibrium of (a) boric acid, (b) metaboric acid, and (c) diborontrioxide

Due to the thermal stability of metaboric acid (HOBO), the rate of reaction of k_1 is far greater than the rate of k_2, thus, the energy release associated with metaboric acid oxidation during combustion is often not realized because of a kinetic bottleneck in the oxidation pathway. Thermodynamically, boron is inhibited by particle diffusion during combustion. In an oxygen-containing atmosphere, boron as a free metal, is surrounded by a fully oxidized diborontrioxide (B_2O_3) layer, which during ignition restricts further oxidation (ref. 2). At temperatures above the B_2O_3 melting point of 723 K, B_2O_3 liquefies and allows some oxygen to slowly diffuse and react with the boron particle surface. This reaction, though, produces more B_2O_3 that cools, condenses back to the boron surface, and further retards the boron particle combustion.

Closo-borate compounds such as dodecahydrododecaborate (DDB) and decahydro-decaborate (DB) are *closo*-polyhedral boron cages with 12 and 10 vertices, respectively. The DDB and DB possess the stability of benzene in a spherical orientation and are considered amongst the most stable compounds yet indentified. The DDB and DB cages exhibit a negative two charge across the surface of the molecule and are susceptible to metathesis chemistry with singly and doubly charged cations. They are not metalloids like boron particulates, and thus effects of the oxide passivation layer typically present on boron particles is not a factor. Recently, Shackelford and coworkers used DDB and carboborane DDB to co-precipitate in aqueous solution salts of various triazolium moieties (ref. 3). The reactions proceeded with high yields. The group also showed that open-air bench-top synthesis is possible even with perfluoronated versions of the DDB caged structure (ref. 4). In this follow-on work, they used *cis* and *trans* structures of triazolium-based derivatives of a butane structure. In concept, they effectively produced a molecularly engineered explosive, with an energetic molecule in direct contact with a fuel system.

It is in these regards that bis(1-methyl-3-propyl-4-nitro)imidazoluim dodecahydro-dodecaborate salt [MP4NI (DDB)] and bis(1-methyl-3-propyl-5-nitro)imidazolium dodecahydro-dodecaborate salt [MP5NI (DDB)] were successfully synthesized. These new compounds represent a category of materials in which an energetic cation is ionically bound to a boron rich fuel. This is the first known synthesis of a molecule with an oxidative moiety (nitrate) directly bound to the fuel system (borate). The energetic properties of the compounds can be tuned by the use of different energetic cations to vary characteristics, such as oxygen or nitrogen balance and density. Use of DDB or DB eliminates the effect of the oxide layer on boron particulate combustion. This is due to

the simultaneous energy release from intimate contact energetic cation and DDB or DB fuel. The oxidation could proceed without inhibition by diffusion limitations associated with the sluggish metaboric and HOBO formation.

TEST METHODS

Materials

Potassium [*closo*-$B_{12}H_{12}$]$^{2-}$ was obtained from the University of Missouri at Columbia. Pure MP5NI iodide salt, MP4NI iodide salt, and MP5NI nitrate salt were synthesized at the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, New Jersey. They were used without further purification and analyzed by melting point and Fourier Transform Infrared (FTIR). This data can be seen in the appendix A.

Synthesis of Compound (I), (Ia), and (II)

An aqueous solution of the methylnitroimidazolium salt (2.27 mmol in 2 mL DI H_2O) is added drop wise with stirring to an aqueous solution of potassium [*closo*-$B_{12}H_{12}$]$^{2-}$ salt (1.14 mmol in 1 mL DI H_2O) at ambient temperature (fig. 2). A white crystalline solid precipitates out of solution and is filtered and rinsed with excess DI H_2O to remove potassium iodide (KI) or potassium nitrate (KNO_3). The solid is then analyzed thermogravametrically and spectrophotometrically.

Analysis

Single crystal x-ray diffraction spectroscopy of **I** and **II** synthesized from the iodide imidazolium salts was solved and refined using the Bruker SHELXTL software package at the University of Missouri in Columbia. X-ray crystallographic analysis of **Ia** prepared from the nitrate salt was obtained from the Naval Research Laboratory using SHELXTL-*plus* system of programs.

Infrared absorption data was recorded as nujol mulls suspensions on a Perkin Elmer Spectrum 100 FTIR in the range of 400 to 4000 cm^{-1} at ambient temperature and analyzed using Perkin Elmer Spectrum software.

Thermogravimetric analysis (TGA) thermograms were recorded from a Perkin Elmer Diamond TGA using ceramic boats. The temperature was increased at a rate of 5°C/min from 50 to 400°C in argon. The argon was passed over a molecular sieve and oxygen traps to ensure it was highly pure. Decomposition and melting points were determined by subtracting the thermogram of the ceramic boat from that of the corresponding borate salt.

RESULTS

Three new crystal structures were reported. MP4NI(DDB) and MP5NI(DDB) were synthesized from MP4NI iodide and MP5NI iodide, respectively, in high yield. MP5NI(DDB) was also synthesized from the corresponding nitrate salt. Crystal spectra for each of the materials are in appendix B. The MP4NI(DDB) and MP5NI(DDB) are white crystalline solids that are insoluble in water.

Traditional use of FTIR or nuclear magnetic resonance proved futile as the results were unable to show the difference between a mixture of the corresponding starting materials and the desired product. To overcome this obstacle, the materials were observed under both FTIR and digital scanning calorimeter.

Dodecaborate is identified in FTIR spectra by boron-hydrogen (B-H) stretching vibrations in the range of 2400 cm^{-1}, and bending bands at 1000 and 700 cm^{-1} (ref. 5). To determine the exact wavelength of this particular dipotassium dodecaborate salt used in the reaction raw material was analyzed in a nujol mulls suspension and the corresponding FTIR spectrum indicated B-H stretching at 2485 cm^{-1} and 1075 cm^{-1}. The FTIR spectra of the reactant imidazolium salts were analyzed and compared to the metathesized DDB product. In all cases, the absorbance of the imidazolium moiety became less intense and the B-H stretch was apparent in the spectrum (app. A). A B-H stretch, in particular the strong, sharp peaks at 2485 cm^{-1} and 1075 cm^{-1}, shifts to the right indicating that there is a molecular attraction between the organic cation and *closo*-dodecaborate salt.

The use of FTIR along with a change in melting point was considered sufficient to determine that the metathesis reaction was successful. Both MP4NI(DDB) and MP5NI(DDB) are high melting point organic salts; TGA of the materials shows melting points at 203.0°C and 214.9°C after background subtraction (app. A). Melting of both compounds seems to occur almost simultaneously with gas evolution and decomposition shortly after. A shift to a single higher melting point from the starting materials, along with FTIR analysis, was used to indicate that a reaction proceeded and single crystal x-ray analysis was then obtained. The structures are shown in appendix B.

CONCLUSIONS

Bis(1-methyl-3-propyl-4-nitro)imidazoluim dodecahydrododecaborate and bis(1-methyl-3-propyl-5-nitro(imidazolium dodecahydrododecaborate are two new organic *closo*-dodecaborate salts synthesized for potential energetic purposes. They represent a class of materials in which an energetic cation is in intimate contact with a borate fuel. They are a tailorable class of compounds through variation of the chemical properties of the energetic cations.

RECOMMENDATIONS

A thermogravimetric analysis study to explore the decomposition kinetics is recommended. The decomposed material can then be analyzed by x-ray diffraction to detect the presence or absence of metaboric acid, and determine if the kinetic bottleneck has been avoided. Calorimetry should also be obtained to determine heat of formation and combustion.

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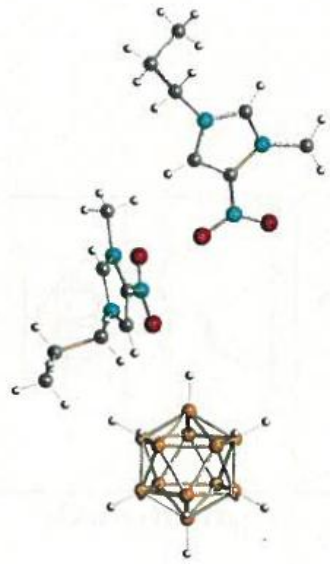
APPENDIX A
FTIR AND MELTING POINT DATA

Table A-1
FTIR and melting point data of the dodecaborate and methylnitroimidazolium salts and their metathesized products

Molecular Formula	$K_2B_{12}H_{12}$	$C_7H_{12}N_4O_5$	$C_{14}H_{36}B_{12}N_6O_4$	$C_7H_{12}N_3O_2I$	$C_{14}H_{36}B_{12}N_6O_4$
Molecular Weight (g/mol)	220.02	232.19	482.21	297.09	482.21
TGA					
Melting point (°C)	>800	114±0.5	203.7±0.7	174.2±0.4	215.3±0.4
FTIR					
B-H	2487, 1075, 715	NA	2467, 1058	NA	2467, 1056, 713
NO_2	NA	1522, 1403	1530, 1399	1521, 1400	1520, 1394, 713

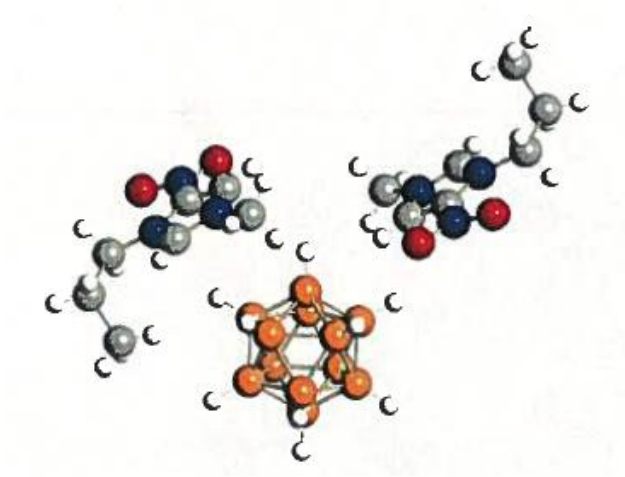
Reaction was successful with an increased melting point coupled with the appearance of B-H stretching in the product FTIR spectra.

APPENDIX B
SINGLE CRYSTAL X-RAY ANALYSIS



MP5NI(DDB)						
	Synthesized from MP5NI Iodide Salt			Synthesized from MP5NI Nitrate Salt		
Chemical formula	$C_{14}H_{36}B_{12}N_6O_4$			$C_{14}H_{36}B_{12}N_6O_4$		
Formula weight	482.21			482.21		
Space group	P 2_1/c			P 1 21/c 1		
Unt Cell dimensions						
a (Å)	8.8651(2)	α (°)	90	8.8649(19)	α (°)	90
b (Å)	18.1099(4) Å	β (°)	94.2820(10)	18.096(4)	β (°)	94.324(4)
c (Å)	16.2541(3) Å	γ (°)	90	16.288(4)	γ (°)	90
V (Å)	2602.25(10) $Å^3$			2605.5(10) $Å^3$		
$\rho_{calc.}$ /g cm^{-3}	1.231			1.229		
Wavelength	1.54178 Å			0.71073 Å		
Z	4			4		
Temperature (K)	100(2)			100(2)		
Crystal size	0.05 x 0.12 x 0.23 mm			0.48 x 0.17 x 0.03 mm3		
Crystal habit	clear light colourless plate			clear light colourless plate		
Crystal system	monoclinic			monoclinic		
Theta range for data collection	3.66 to 72.03°			1.68 to 26.52°.		
Index ranges	-10<=h<=9, -22<=k<=22, -19<=l<=19			-10<=h<=9, -22<=k<=22, -19<=l<=19		
Reflections collected	37939			23566		
Independent reflections	5007 [R(int) = 0.0261]			5352 [R_{int} = 0.0417]		
F(000)	1016			1016		
Goodness-of-fit on F2	1.055			1.049		
Largest diff. peak and hole	0.575 and -0.307 $eÅ^{-3}$			0.315 and -0.239 $e.Å^{-3}$		
Absorption coefficient	0.620 mm^{-1}			0.078 mm^{-1}		
Max. and min. transmission	0.9697 and 0.8705			0.7454 and 0.6269		
Data / restraints / parameters	5007 / 0 / 324			5352 / 0 / 329		
Refinement method	Full-matrix least-squares on F2			Full-matrix least-squares on F2		

Figure B-1
Single crystal x-ray of **I** and **Ia** obtained from the University of Missouri and D. Parrish at NRL synthesized from the iodide and nitrate salt, respectively. Analysis shows two positively charged (1-methyl-3-propyl-5-nitro)imidazolium cations ionically bound to one dodecaborate anion.



	MP4NI(DDB)		
Chemical formula	$C_{14}H_{36}B_{12}N_6O_4$		
Formula weight	482.21		
Space group	P 1 21/c 1		
Unt Cell dimensions			
a (Å)	8.50210(10)	α (°)	90
b (Å)	19.2046(3)	β (°)	114.3000(10)
c (Å)	8.55620(10)	γ (°)	90
V (Å)	1273.28(3)		
$\rho_{calc.}$ /Mg cm^{-3}	1.258		
Wavelength (Å)	1.54178 Å		
Z	2		
Temperature (K)	100(2)		
Crystal size	0.04 x 0.05 x 0.15 mm		
Crystal system	monoclinic		
Theta range for data collection	4.60 to 72.14°		
Index ranges	-10<=h<=10, -23<=k<=23, -10<=l<=10		
Reflections collected	18924		
Independent reflections	2505 [R(int) = 0.0225]		
F(000)	508		
Goodness-of-fit on F2	1.045		
Largest diff. peak and hole	0.247 and -0.287 eÅ^{-3}		
Absorption coefficient	0.634 mm^{-1}		
Max. and min. transmission	0.9751 and 0.9109		
Data / restraints / parameters	2505 / 0 / 165		
Refinement method	Full-matrix least-squares on F2		

Figure B-2
Single crystal x-ray of II obtained from the University of Missouri. Analysis shows two positively charged (1-methyl-3-propyl-4-nitro)imidazolium cations ionically bound to one dodecaborate anion.

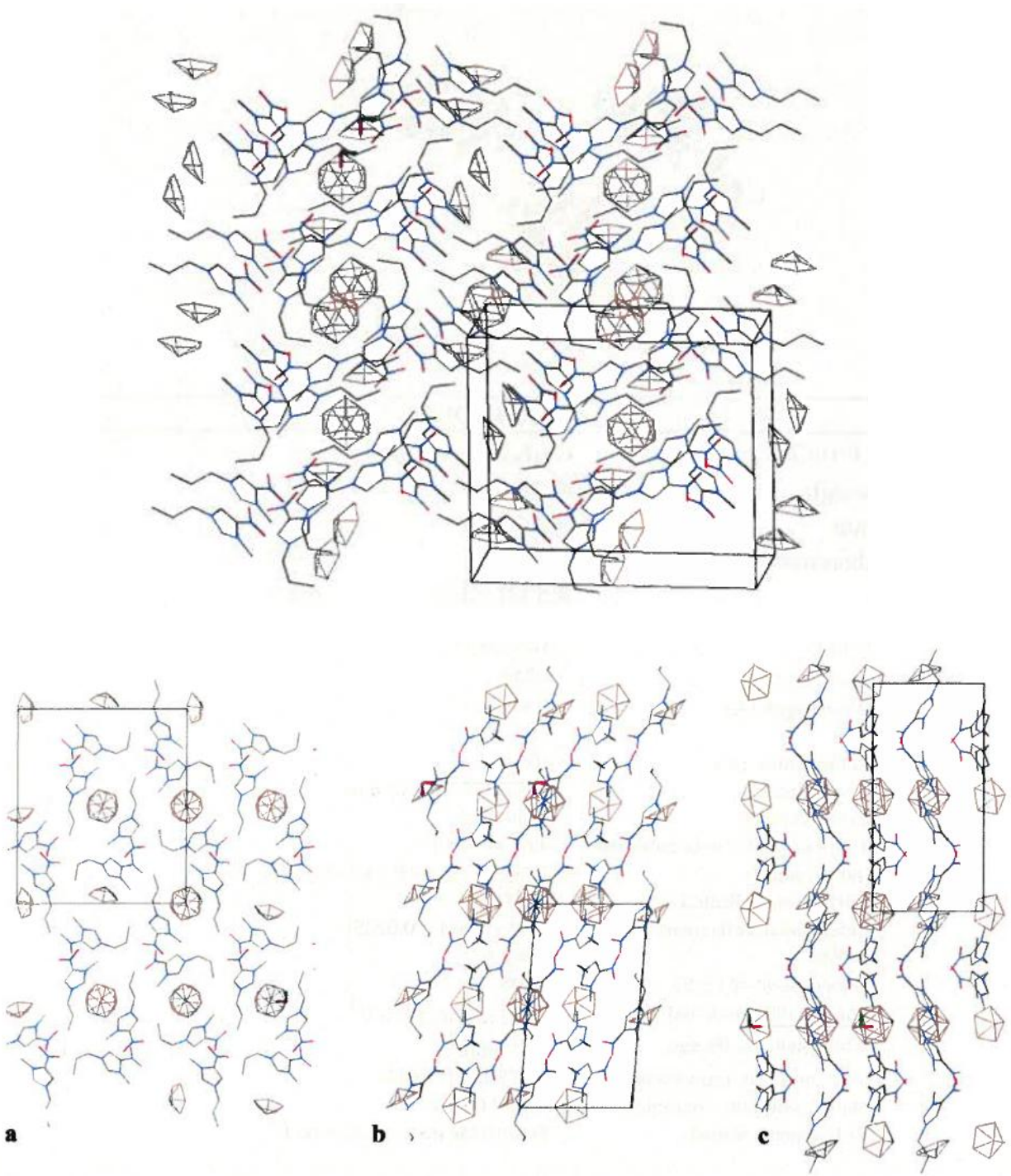


Figure B-3
1-x, 1-y, 1-z space grouping of MP5NI(DDB) showing the crystal packing of the material. a) stick diagram showing the view along the a-axis b) stick diagram showing view along the b-axis c) stick diagram showing view along the c-axis

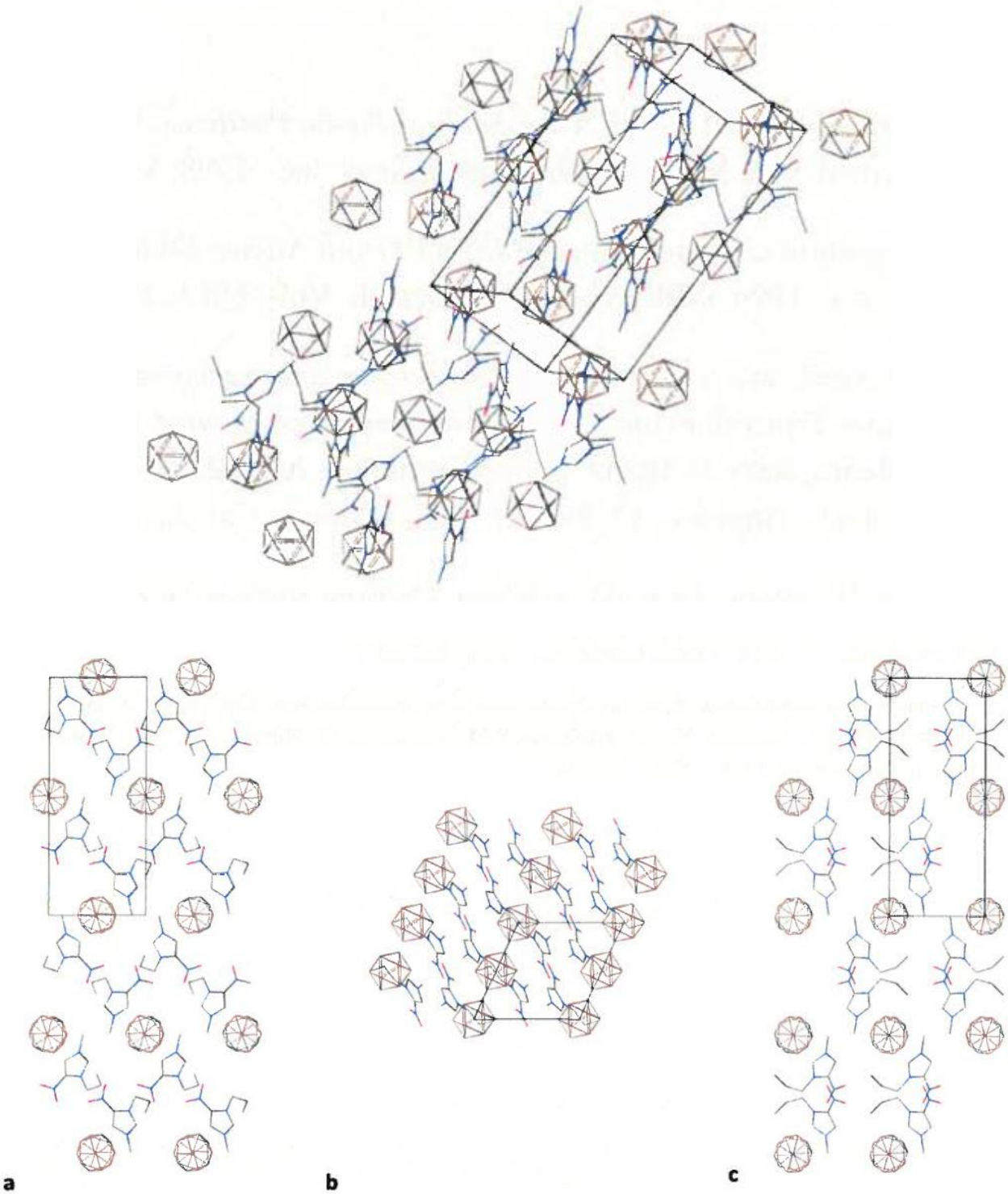


Figure B-4
1-z. 1-y. 1-z space grouping of MP4NI(DDB) showing the crystal packing of the material. a) stick diagram showing the view along the a-axis b) stick diagram showing view along the b-axis c) stick diagram showing view along the c-axis

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