Nitrogen-Rich 5-(1-Methylhydrazinyl)tetrazole and its Copper and Silver Complexes

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ⓢ *Supporting Information*

ABSTRACT: Nitrogen-rich 5-(1-methylhydrazinyl)tetrazole (**1**, MHT) was synthesized by using a straightforward method. White plate crystals of **1** were isolated in acetonitrile and crystallized in the monoclinic system $P2_1/c$ (# 14) (a = 3.8713(18) Å, b = 12.770(6) Å, c = 9.974(5) Å, α = 90°, β = 93.397(6)°, γ = 90°, V = 492.3(4) Å^3, Z = 4). The reactions of Cu(II) and Ag(I) ions in aqueous solution with **1** were investigated and found to form two complexes under mild conditions. The crystal structures of **2** and **3** are discussed with respect to the coordination mode of the MHT anion. Thermal stabilities were determined from differential scanning calorimetry (DSC) combined with thermogravimetric analysis (TGA) tests. Impact sensitivity was determined by BAM standards showing that these MHT salts are insensitive to impact (>40 J) confirmed by UN standards. The energies of combustion of **1**−**3** were determined using oxygen bomb calorimetry values and were used to obtain the corresponding enthalpies of formation. Combined with these data above, the neutral MHT is an attractive nitrogen-rich ligand for metallic energetic materials. Its copper and silver coordinated complexes are of interest as potential "green" metal energetic materials with high thermal stability as well as low sensitivity to impact and a high molar enthalpy of formation.
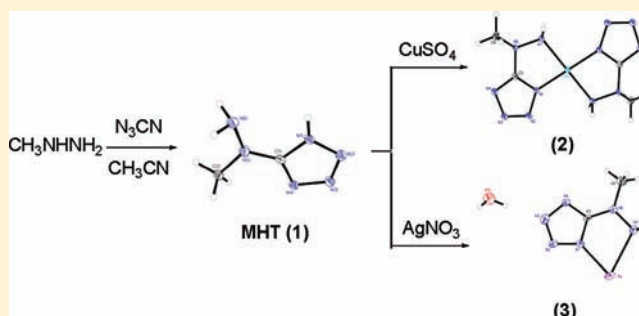
■ INTRODUCTION

Recently, nitrogen-rich tetrazoles have attracted considerable interest in applications as energetic materials,[1] ligands in coordination chemistry,[2] intermediates in organic synthesis,[3] and drugs in pharmaceuticals.[4] Nitrogen-rich tetrazoles (for example, 5-aminotetrazole,[5] 5-nitrotetrazole,[6] 5-azidotetrazole,[7] 5-cyanotetrazole,[8] 1,5-diaminotetrazole,[9] 5,5′-bistetrazole,[10] 5,5′-azobistetrazole,[11] 5,5′-bistetrazolylamine,[12] etc.) and many of their ionic derivatives combine several advantages such as smokeless combustion, positive heats of formation, excellent propulsion power, and good specific impulse when they serve as propellants or pyrotechnics. They are considered to be potential green replacements vis-á-vis traditional energetic materials including 2,4,6-trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).[13] Thus, preparation of new nitrogen-rich compounds is important for improving the performance of energetic materials and developing new metallic coordination compounds. However, compared with their numerous energetic salt derivatives, the types of nitrogen-rich tetrazole frameworks are still very limited. In addition, some tetrazoles that contain −NO$_2$ and −N$_3$ groups are too sensitive to heat, shock, and friction for useful application.[6,7] Therefore, novel nitrogen-rich tetrazoles that would possess a much lower sensitivity and a higher heat of formation are interesting.

Moreover, "green" metal complexes based on nitrogen-rich tetrazole derivatives are also to be expected.[14]

Herein, we report the straightforward synthesis of 5-(1-methylhydrazinyl)tetrazole (**1**) under mild metal-free conditions. We also report the synthesis of its copper and silver complexes. Their structures were studied in detail to illustrate the coordination ability of the 5-(1-methylhydrazinyl)-tetrazolate anion to metals. The assessments of their physiochemical properties along with their energetic performance characteristics were studied. Their thermal stabilities were investigated using DSC concomitantly with TGA. The standard enthalpy of formation was obtained by determining combustion energies by oxygen bomb calorimetry. Furthermore, to assess the energetic properties, the impact sensitivity was also determined by the BAM standards.

■ RESULTS AND DISCUSSION

Synthesis. 5-(1-Methylhydrazinyl)tetrazole (MHT, **1**) was prepared by the reaction of methylhydrazine and cyanogen azide in an acetonitrile solution. The synthesis of MHT is described in Scheme 1. The metathesis reaction of cyanogen bromide and sodium azide in acetonitrile resulted in cyanogen

**Scheme 1. Synthesis of 5-(1-Methylhydrazinyl)Tetrazole (1)**
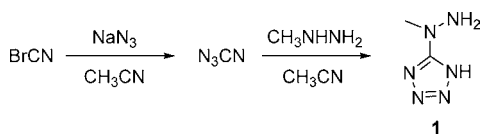
azide.[15] Byproduct sodium bromide was removed as a precipitate, and anhydrous cyanogen azide in acetonitrile solution was obtained. The mixture of cyanogen azide in acetonitrile solution and methyl hydrazine was stirred for 4 h at 0 °C. After the acetonitrile solution was concentrated, **1** was obtained as a white powder. X-ray-quality crystals were obtained from a concentrated acetonitrile solution within three days. This synthetic route is straightforward and metal- and catalyst-free.

Compound **1** was characterized by NMR, IR spectral, and elemental and single crystal analysis. The NMR data were collected in d_6-DMSO by using a 300 MHz nuclear magnetic resonance spectrometer. In the ^{13}C NMR spectrum, the signal at 161.88 ppm is assigned to the tetrazole ring. In the IR spectrum, three characteristic bands of the amino group were observed at 3314, 3211, and 1597 cm^{-1}, which are attributed to the asymmetric and symmetric N−H stretching modes and the asymmetric bending mode, respectively. Moreover, three different band regions of the N−CH$_3$ modes centered at 2938, 2779, and 1412 cm^{-1} can also be distinguished.

As a nitrogen-rich tetrazole, **1** is a potential ligand to coordinate with metals. In order to obtain "green" metal energetic complexes, copper and silver complexes of **1** were synthesized. The copper complex **2** was synthesized by the reaction of stoichiometric amounts of copper sulfate pentahydrate with **1** in water (Scheme 2). Dark blue needles, suitable

Scheme 2. Syntheses of Copper and Silver Salts of 5-(1-Methylhydrazinyl)Tetrazolate: 2, Copper Di-5-(1-methylhydrazinyl)tetrazolate; 3, Silver 5-(1-Methylhydrazinyl)tetrazolate Monohydrate
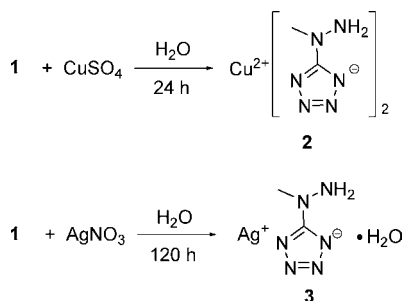
for X-ray structure determination, of compound **2** crystallized from a clear green solution after one day. Using an analogous route, silver complex **3** was obtained as colorless plates. Complexes **2** and **3** were characterized by IR and elemental analysis.

X-Ray Crystallography. Compound **1** has good solubility in polar solvents, including water, alcohol, acetonitrile, and DMSO. Slow recrystallization from acetonitrile gave colorless plates suitable for X-ray diffraction. The structure of **1** is shown in Figure 1. Crystallographic and structural refinement data for compound **1** are listed in Table 1, and selected bond lengths and angles are included in Table 2, torsion angles in Table 3. Compound **1** crystallizes in the monoclinic space group $P2_1/c$

(# 14) with four molecular moieties in each unit cell (Figure 1), a density of 1.540 g cm^{-3}, and a unit cell volume of 492.3(4) Å^3 (Table 1). No coordinated water molecules are found. In the MHT molecule, the interatomic distances of N1−C5, N4−C5, and C5−N6 bonds are 1.3440(16), 1.3363(16), and 1.3450(17) Å, respectively. These C−N bonds (Table 2) are much shorter than the classical C−N single bond but significantly longer than a C=N double bond, suggesting that some multiple bond character is present. An analogous trend is observed for the N−N bonds such as N1−N2 (1.3592(15) Å), N2−N3 (1.2881(16) Å), and N3−N4 (1.3683(15) Å) bonds. The N1−C5−N4 angle in the tetrazole ring is 108.93(11)°, close to that in the structure of neutral 5-aminotetrazole (107.9(1)°). Further, the torsion angles show that the tetrazole ring in MHT is coplanar. A delocalized 6π-aromatic system is in agreement with the structure found in 5-aminotetrazole.[5] In addition, this delocalization is not associated with the amino group or methyl group attached to the N(5) atom, based on the evident structural features: (a) the N6−N7 (1.4167(15) Å) and N6−C8 (1.4514(16) Å) bonds are close to the length of a N−N single bond and C−N single bond, respectively; (b) neither the methyl nor the amino group is in the plane of the tetrazole ring, based on their corresponding angles and torsion angles (reference bond lengths: C−N, 1.47 Å; N=N, 1.24 Å; and N−N, 1.47 Å).[16]

The packing structure of **1** as built up by hydrogen bonding is given in Figure 1b, viewed along the *a* axis. The whole molecular charge delocalization is accomplished by extensive hydrogen bonding in the extended structure, which may lead to the enhanced decrease of C−N bond lengths in MHT. Each MHT moiety forms moderate hydrogen bonds with two molecules *via* the hydrogen directly linked to the tetrazole ring (N1−H1⋯N4#1, 2.8496(19) Å; #1 = *x*, −*y* + 3/2, *z* − 1/2 symmetry transformation; Table 4). The sheets are also cross-linked by weak hydrogen bonds from the terminal amino group N7 to the neighboring MHT molecules (N7−H7⋯N3#2, 3.1739(19) Å; #2 = −*x* + 1, *y* + 1/2, −*z* + 3/2 symmetry transformation). The combination of this extensive hydrogen bonding in the extended structure forms a three-dimensional supramolecular network.

On the basis of our previous studies, the structure of **1** is surprising since, in our hands, in every other case where CNN$_3$ has been reacted with primary or secondary or methoxy amines or substituted hydrazines, the amino substituent is at the C5 position of the product tetrazole ring. That is, we would have predicted that the product would be 1-methylamino-5-amino-tetrazole rather than 5-(1-methylhydrazinyl)tetrazole, **1**. These earlier observations are strongly supported by X-ray crystal structure determinations.

Compound **2** is a simple copper salt of **1** which exists as dark blue needles. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (# 14) by analysis of systematic absences, with two molecular moieties in each unit cell (Figure 2), a density of 2.031 g cm^{-3}, and a unit cell volume of 473.75(3) Å^3 (Table 1). The MHT anion displays delocalization of the negative charge because of bond homogenization. In the molecules of **2**, each Cu(II) ion is six coordinate, with an octahedral geometry. No water molecules occupy the cavities. In this structure, the MHT anion ligand is bidentate at the N1 and N7 positions while monodentate at the N4 position. The basal equatorial plane is formed by the atoms N1 and N7 from two bidentate MHT ligands. A different coordination ability with the Cu(II) ion is
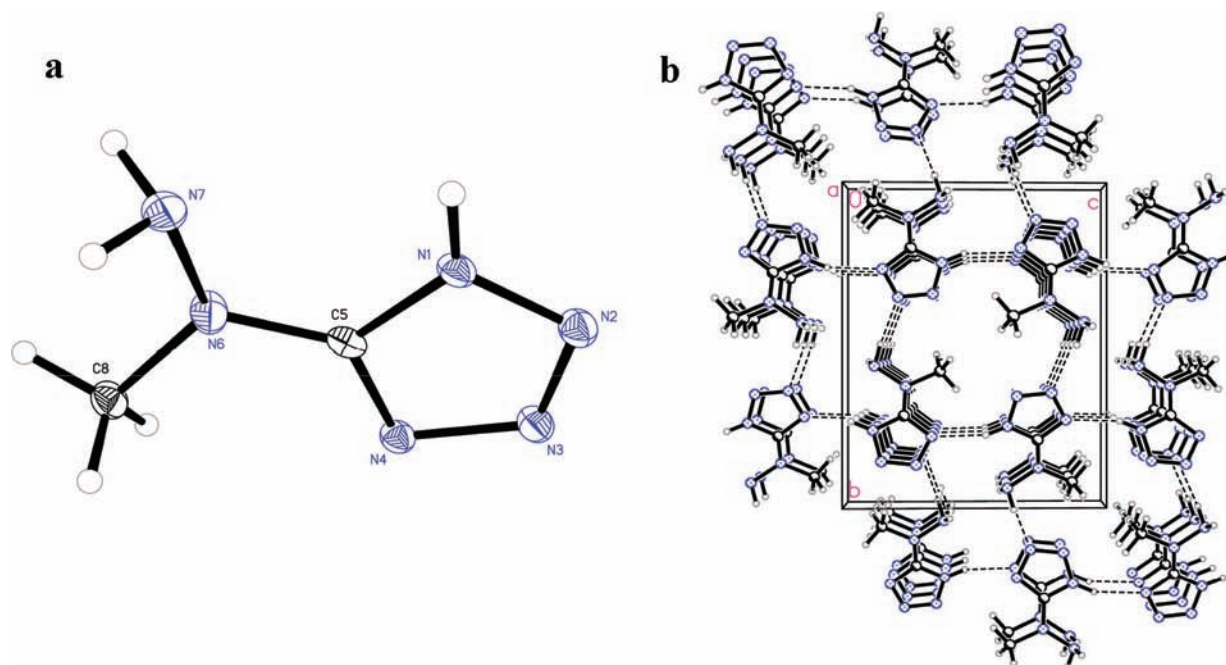
Figure 1. (a) Molecular structure of **1** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are shown as open spheres of arbitrary radius and are unlabeled for clarity. (b) Packing diagram of **1** viewed down the *a* axis.

Table 1. Crystal Data and Structure Refinement for Compounds 1−3

	1	2	3
formula	$C_2H_6N_6$	$C_4H_{10}CuN_{12}$	$C_2H_7AgN_6O$
FW (g mol^{-1})	114.13	289.78	239.01
size (mm^3)	0.60 × 0.12 × 0.04	0.38 × 0.19 × 0.18	0.37 × 0.26 × 0.02
cryst. syst.	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	3.8713(18)	6.2643(2)	6.1635(6)
b (Å)	12.770(6)	9.6889(3)	15.8852(15)
c (Å)	9.974(5)	7.8137(3)	6.7800(7)
α (deg)	90	90	90
β (deg)	93.397(6)	92.6330(10)	104.003(4)
γ (deg)	90	90	90
V (Å^3)	492.3(4)	473.75(3)	644.09(11)
Z	4	2	4
ρ (g cm^{-3})	1.540	2.031	2.465
T (K)	93(2)	90(2)	173(2)
μ (mm^{-1})	0.117	2.308	24.671
F(000)	240	294	464
$\lambda_{MoK\alpha}$ (Å)	0.71073	0.71073	1.54178
reflns	4942	7000	2906
R_{int}	0.0297	0.0141	0.0469
params	80	88	99
S on F^2	1.089	1.136	1.094
R_1 $(I > 2\sigma(I))^a$	0.0399	0.0204	0.0382
wR_2 $(I > 2\sigma(I))^b$	0.1027	0.0611	0.1057
R_1 (all data)^a	0.0444	0.0207	0.0383
wR_2 (all data)^b	0.1059	0.0613	0.1058
$\Delta\rho_{min\ and\ max}$ (e Å^{-3})	0.391 and −0.285	0.356 and −0.416	0.835 and −1.397
CCDC	816158	816156	816157

$^a R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$. $^b wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

found from the observed lengths of the Cu−N bonds (Cu−N1#1, 1.944(1) Å; Cu−N7#1, 2.055(1) Å).

The N1 position provides stronger coordination ability than N7 because of the negative charge on the tetrazolate ring. In addition, a rather longer distance (0.586−0.697 Å) of the axial Cu−N4 (2.641 Å) bonds is observed in contrast to that of the basically equatorial Cu−N bonds (symmetry code: #1 −x + 2, −y + 1, −z; #2 x − 1, −y + 3/2, z − 1/2; #3 x, −y + 3/2, z − 1/2; #4 x − 1, y, z). Single-crystal X-ray analysis of **2** shows that it is a three-dimensional coordination inorganic−organic hybrid with MHT anions as bridging ligands.

The packing structure of **2** is built up by hydrogen bonding (Figure 2b). The entire molecule charge delocalization is accomplished by extensive hydrogen bonding in the extended structure, which may lead to the enhanced decrease of C−N bond lengths in **2**. Each MHT molecule forms hydrogen bonds cross-linked with three neighboring MHT molecules. The hydrogen bonding scheme starts from the terminal amino group N7 directly linked to the tetrazole ring (N7−H7A···N3#2, 3.2050(17) Å; N7−H7B···N2#4, 3.0545(17) Å; #1 −x + 2, −y + 1, −z; #2 x − 1, −y + 3/2, z − 1/2; #4 x − 1, y, z symmetry transformation). The donor−acceptor distances are presented, with an essentially nonlinear DHA angle (N7−H7A···N3#2, 138.2(18)°; N7−H7B···N2#4, 145.1(19)°). The third type of weak hydrogen bonds are also starting from N7 but linked to N6 of the neighboring MHT molecule (N7−H7A···N6#3, 3.3472(18) Å; #1 −x + 2, −y + 1, −z; #3 x, −y + 3/2, z − 1/2 symmetry transformation). A three-dimensional supramolecular network is formed by the combination of this extensive hydrogen bonding in the extended structure.

Complex **3** is the simple silver salt of MHT as colorless plates with crystallized water. Complex **3** also crystallizes in the monoclinic space group $P2_1/c$ (Figure 3a), with four molecular moieties in each unit cell, a density of 2.465 g cm^{-3}, and a unit cell volume of 644.09(11) Å^3 (Table 1). A delocalized MHT

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Crystals for 1−3

bond lengths (Å)	1	2	3	bond angles (deg)	1	2	3
N1−N2	1.3592(15)	1.3594(16)	1.364(5)	C5−N1−N2	107.92(10)	105.55(11)	105.9(4)
N2−N3	1.2881(16)	1.3053(18)	1.301(6)	C5−N4−N3	104.91(10)	103.47(12)	106.6(4)
N3−N4	1.3683(15)	1.3722(17)	1.354(6)	C5−N6−N7	115.72(10)	110.10(10)	116.4(4)
N6−N7	1.4167(15)	1.4522(16)	1.416(5)	C5−N6−C8	120.77(10)	116.53(11)	123.1(4)
N1−C5	1.3440(16)	1.3307(18)	1.350(6)	N7−N6−C8	120.31(10)	113.62(11)	118.6(4)
N4−C5	1.3363(16)	1.3286(18)	1.334(6)	N3−N2−N1	106.76(10)	108.04(11)	108.9(4)
C5−N6	1.3450(17)	1.3912(17)	1.339(7)	N2−N3−N4	111.48(10)	110.60(11)	109.3(4)
N6−C8	1.4514(16)	1.4652(18)	1.453(6)	N4−C5−N6	126.02(11)	126.18(12)	127.3(4)
N7−H7A	0.917(13)	0.87(2)	0.88(5)	N4−C5−N1	108.93(11)	112.33(12)	109.3(4)
N7−H7B	0.934(14)	0.85(2)	0.88(5)	N1−C5−N6	124.99(11)	121.36(12)	123.3(4)
Cu−N1		1.9438(12)		N1−Cu−N7		80.97(5)	
Cu−N7		2.0546(12)		N1#−Cu−N7		99.03(5)	
Cu−N4#1		2.641(12)		N1#1−Cu−N1		180.0	
Ag−N1			2.138(4)	N1−Ag−N7			70.75(13)
Ag−N7			2.528(4)	N4#1−Ag−N7			120.06(14)
Ag−N4#1			2.132(4)	N4#1−Ag−N1			169.06(15)

Table 3. Torsion Angles for 1−3 (deg)

torsion angles	deg	torsion angles	deg	torsion angles	deg
		1			
C5−N1−N2−N3	−0.39(13)	N3−N4−C5−N6	176.44(12)	N1−C5−N6−N7	−13.96(18)
N1−N2−N3−N4	−0.14(13)	N2−N1−C5−N4	0.79(13)	N4−C5−N6−C8	9.4(2)
N2−N3−N4−C5	0.61(13)	N2−N1−C5−N6	−176.53(11)	N1−C5−N6−C8	−173.78(11)
N3−N4−C5−N1	−0.84(13)	N4−C5−N6−N7	169.19(11)		
		2			
N1#1−Cu1−N1−N2	−108(14)	N2−N3−N4−C5	−0.40(15)	N4−C5−N6−C8	45.83(19)
N7−Cu−N1−C5	−5.37(10)	N3−N4−C5−N1	0.75(15)	N1−C5−N6−C8	−138.47(13)
N7#1−Cu−N1−C(5)	174.63(10)	N3−N4−C5−N6	176.78(13)	C5−N6−N7−Cu	2.17(13)
N1#1−Cu−N1−N2	81(14)	N2−N1−C5−N4	−0.81(15)	C8−N6−N7−Cu	134.94(10)
N7−Cu−N1−N2)	−176.52(15)	Cu−N1−C5−N4	−174.84(9)	N1#1−Cu−N7−N6	−178.40(9)
N7#1−Cu−N1−N2	3.48 (15)	N2−N1−C5−N6	−177.06(12)	N1−Cu−N7−N6	1.60(9)
C5−N1−N2−N3	0.52(15)	Cu−N1−C5−N6	8.91(16)	N7#1−Cu−N7−N6	84(15)
Cu−N1−N2−N3	172.18(11)	N4−C5−N6−N7	177.10(13)		
N1−N2−N3−N4	−0.07(15)	N1−C5−N6−N7	−7.21(17)		
		3			
N4#1−Ag−N4−C5	167.1(6)	N3−N4−C5−N6	177.8(4)	N1−C5−N6−N7	−8.3(7)
N7−Ag−N1−C5	−4.5(3)	Ag#2−N4−C5−N6	9.0(8)	N4−C5−N6−C8	10.2(8)
N4#1−Ag−N1−N2	−3.8(9)	N3−N4−C5−N1	−0.1(5)	N1−C5−N6−C8	−172.2(4)
N7−Ag−N1−N2	−175.4(4)	Ag#2−N4−C5−N1	−168.9(3)	C5−N6−N7−Ag	3.6(5)
C5−N1−N2−N3	−0.1(5)	N2−N1−C5−N4	0.1(5)	C8−N6−N7−Ag	168.3(3)
Ag−N1−N2−N3	171.8(3)	Ag−N1−C5−N4	−173.0(3)	N4#1−Ag−N7−N6	−177.8(3)
N1−N2−N3−N4	0.0(5)	N2−N1−C5−N6	−177.9(4)	N1−Ag−N7−N6	0.4(3)
N2−N3−N4−C5	0.1(5)	Ag−N1−C5−N6	9.0(6)		
N2−N3−N4−Ag#2	171.7(3)	N4−C5−N6−N7	174.1(4)		

anion is also found. In the molecules of **3**, each Ag(I) ion is three coordinate, with a planar geometry. One water molecule is found, which is not coordinated to the centered Ag(I) ion. In this structure, the MHT anion ligand is also found to be bidentate at the N1 and N7 positions while monodentate at the N4 position. The distances of Ag−N bonds are in the range of 2.132(4)−2.528(4) Å. The Ag−N bonds between the centered Ag(I) ion to the N atoms in the tetrazole ring have similar lengths (Ag−N1, 2.138(4) Å; Ag−N4#1, 2.132(4) Å). However, a different coordination ability of the Ag(I) ion to the N atom of the terminal amino group is found (Ag−N7, 2.528(4) Å). The N7 position provides weaker coordinating ability than N1 and N4 in the tetrazole ring. In addition, the length of the Ag−N7 bond is much longer (0.473 Å) than the length of the Cu−N7 bond in complex **2** (Cu−N7#1, 2.055(1) Å).

In contrast to **2**, the arrangement of the molecules in the crystal structure of **3** is different. Complex **3** forms an infinite one-dimensional coordination array polymer built from centro-asymmetric mononuclear [Ag(MHT)(H$_2$O)] units that are linked by MHT bridges. There is one water molecule in the crystal without any coordinated water molecules. The two adjacent MHT ligands are in opposite orientations. The fundamental units linked by MHT bridges form well-isolated linear-like structure ribbons (Figure 3b). These infinite linear ribbons are connected through hydrogen bonds with the water molecules.

The hydrogen bonded network in **3** can be described as a three-dimensional system (Figure 3b). Each MHT molecule forms hydrogen bonds cross-linked with four neighboring water molecules. The hydrogen bonding scheme starts from the

Table 4. Hydrogen Bonds for 1−3 (Å and deg)

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
		1^a		
N1−H1···N4#1	0.88	2.02	2.8496(19)	157.3
N7−H7A···N3#2	0.917(13)	2.264(14)	3.1739(19)	171.4(14)
		2^b		
N7−H7A···N3#2	0.87(2)	2.51(2)	3.2050(17)	138.2(18)
N7−H7A···N6#3	0.87(2)	2.62(2)	3.3472(18)	141.8(18)
N7−H7B···N2#4	0.85(2)	2.32(2)	3.0545(17)	145.1(19)
		3^c		
N7−H7A···O1S#3	0.8800(11)	2.186(16)	3.035(5)	162(5)
N7−H7B···O1S#1	0.8800(11)	2.54(5)	3.034(5)	116(4)
O1S−H1SA···N2#4	0.8500(11)	2.34(4)	3.013(5)	136(5)
O1S−H1SB···N3	0.8500(11)	2.086(9)	2.932(6)	173(6)

^{a}Symmetry transformations used to generate equivalent atoms. For **1**: #1 x, $−y + 3/2$, $z − 1/2$; #2 $−x + 1$, $y + 1/2$, $−z + 3/2$. ^{b}For **2**: #1 $−x + 2$, $−y + 1$, $−z$; #2 $x − 1$, $−y + 3/2$, $z − 1/2$; #3 x, $−y + 3/2$, $z − 1/2$; #4 $x − 1$, y, z. ^{c}For **3**: #1 $x + 1$, $−y + 1/2$, $z + 1/2$; #2 $x − 1$, $−y + 1/2$, $z − 1/2$; #3 $−x$, $y + 1/2$, $−z − 1/2$; #4 $−x$, $−y$, $−z$.
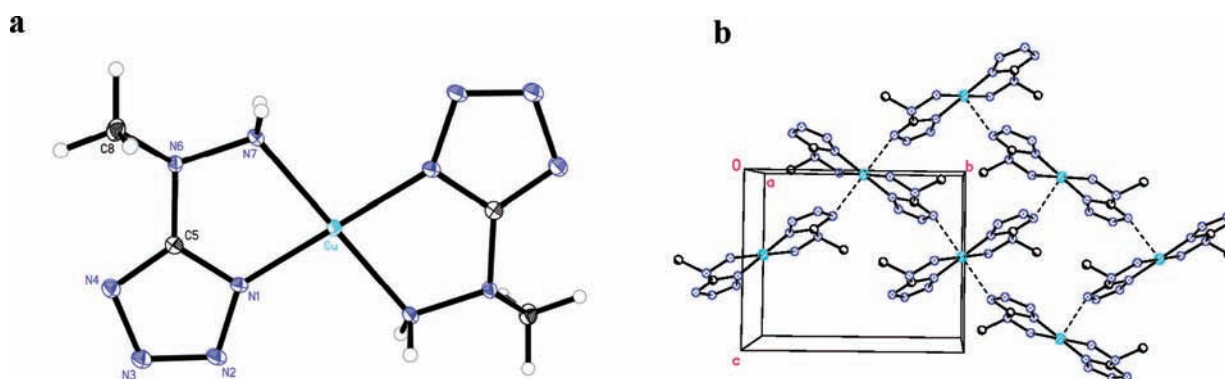
Figure 2. (a) Molecular structure of **2** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are shown as open spheres of arbitrary radius and are unlabeled for clarity. (b) Packing diagram of **2** viewed down the *a* axis.
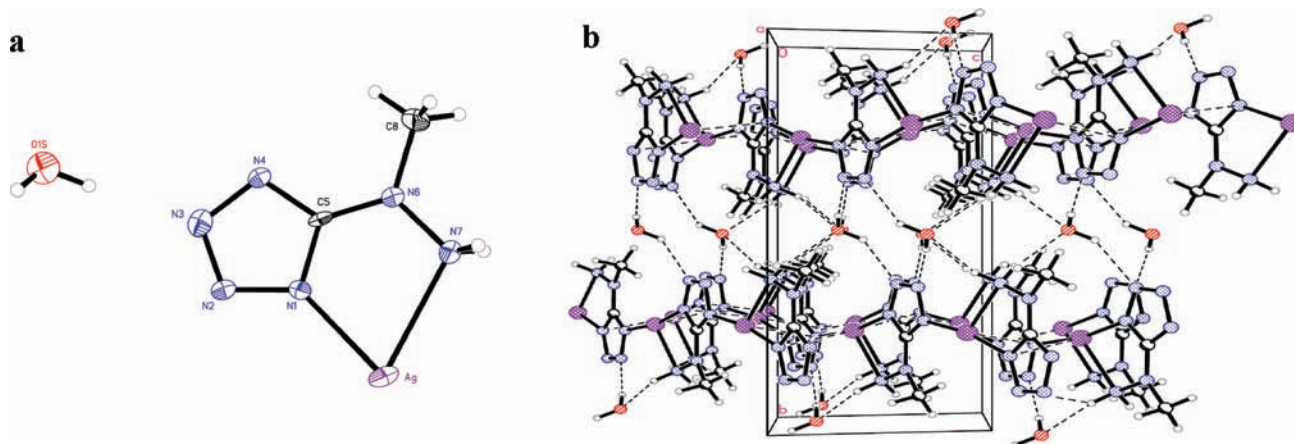
Figure 3. (a) Molecular structure of **3** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are shown as open spheres of arbitrary radius and are unlabeled for clarity. (b) Packing diagram of **3** viewed down the *a* axis.

terminal amino group N7 directly linked to water (N7−H7A···O1S#3, 3.035(5) Å; N7−H7B···O1S#1, 3.034(5) Å; #1 $x + 1$, $−y + 1/2$, $z + 1/2$ #3 $−x$, $y + 1/2$, $−z − 1/2$ symmetry transformation). The other two hydrogen bonds start from the O atom in the water molecule linked to N atoms in the tetrazole ring of the neighboring MHT molecule (O1S−H1SA···N2#4, 3.013(5) Å; O1S−H1SB···N3, 2.932(6) Å; #1 $x + 1$, $−y +1/2$, $z + 1/2$; #4 $−x$, $−y$, $−z$ symmetry transformation). A three-dimensional supramolecular network

is formed by the combination of this extensive hydrogen bonding in the extended structure. The N−H···O hydrogen bonding gives a rather short distance in contrast to the N−H···N type in complex **2**.

Physicochemical Properties. The physicochemical properties of **1−3** are summarized in Table 5. The densities of **1−3** are 1.54, 2.03, and 2.47 g cm^{-3}, respectively. The nitrogen content of **1** is relatively high, 73.65%, which is nearly the same as that of a typical energetic nitrogen-rich tetrazole compound,

Table 5. Physicochemical Properties of Compounds 1–3

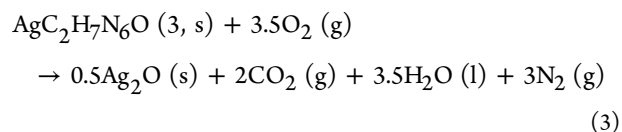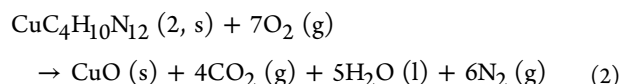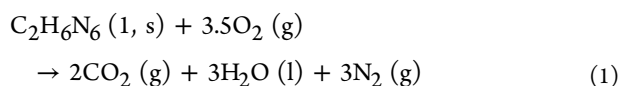|	1	2	3
T_m (°C)[a]			110 ($-H_2O$)
T_d (°C)[b]	193	212	200
N (%)[c]	73.65	58.01	35.17
ρ (g cm^{-3})[d]	1.540	2.031	2.465
$-\Delta_c U$ (cal g^{-1})[e]	4052	2691	1544
$-\Delta_c H$ (kJ mol^{-1})[f]	1930	3253	1539
$\Delta_f H$ (kJ mol^{-1})[g]	286	93	−263
$\Delta_f H$ (kJ g^{-1})[g]	2.50	0.32	−1.10
IS (J)[h]	>40	>40	>40

[a]Melting point. [b]Decomposition temperature. [c]Nitrogen content. [d]Density, 25 °C. [e]Experimental (constant-volume) energy of combustion. [f]Experimental molar enthalpy of combustion. [g]Molar enthalpy of formation. [h]Impact sensitivity.

bis(tetrazolyl)amine (H$_2$Bta·H$_2$O, 73.67%). The copper salt of this nitrogen-rich ligand possesses the nitrogen content of 58.01%.

The thermal behavior of the crystals has been investigated using differential scanning calorimetry (DSC). Melting points are not observed for compounds **1** and **2** based on their DSC plots. Compound **1** is thermally stable to 193 °C in ambient nitrogen. The decomposition of **2** occurs with an onset peak at 212 °C. For compound **3**, an endothermic peak is observed at 110 °C, corresponding to the release of the water of crystallization. The water molecules are dispersed among the molecules based on weak hydrogen bonding and are easily removed upon heating. In addition, a decomposition exothermic peak at 200 °C is found for the silver complex. The considerable thermal stabilities of **2** and **3** are substantially greater than the neutral molecule (**1**). The copper complex has relatively higher thermal stability than the silver derivative. The thermal stabilities of **2** and **3** are higher than the criterion of 200 °C for "green" metal energetic materials.[14] Therefore, these metal complexes with the MHT ligand are sufficiently thermally stable to be "green" metal energetic materials.

Impact sensitivity was determined for **1**–**3** by the drop hammer test (BAM method).[17] The data collected for impact sensitivity testing are summarized in Table 5. Compounds **1**–**3** are insensitive toward impact (>40 J). The delocalization in **1** can result in relatively insensitive compounds. On the basis of the UN classification standard of sensitivities,[18] **1**–**3** can be defined as impact-insensitive energetic materials.

Enthalpy of Formation. The constant-volume energies of combustion ($\Delta_c U$) of these complexes were determined experimentally using oxygen bomb calorimetry and are summarized in Table 5. The enthalpy of combustion, $\Delta_c H°$, was calculated from $\Delta_c U$, and a correction for the change in gas volume during combustion was included: $\Delta_c H_m = \Delta_c U_m + \Delta n R T$, where Δn is the difference in the number of moles of gases between the products and the reactants. The standard enthalpies of formation of **1**–**3**, $\Delta_f H°$, were back-calculated from the heats of combustion on the basis of combustion eqs 1–3, Hess's Law as applied in thermochemical eqs 4–6, and known stande, CO$_2$ (−393.51 kJ mol^{-1}) and H$_2$O (−285.83 kJ mol^{-1}).[19]

$$C_2H_6N_6 \text{ (1, s)} + 3.5O_2 \text{ (g)}$$
$$\rightarrow 2CO_2 \text{ (g)} + 3H_2O \text{ (l)} + 3N_2 \text{ (g)} \qquad (1)$$

$$CuC_4H_{10}N_{12} \text{ (2, s)} + 7O_2 \text{ (g)}$$
$$\rightarrow CuO \text{ (s)} + 4CO_2 \text{ (g)} + 5H_2O \text{ (l)} + 6N_2 \text{ (g)} \qquad (2)$$

$$AgC_2H_7N_6O \text{ (3, s)} + 3.5O_2 \text{ (g)}$$
$$\rightarrow 0.5Ag_2O \text{ (s)} + 2CO_2 \text{ (g)} + 3.5H_2O \text{ (l)} + 3N_2 \text{ (g)} \qquad (3)$$

$$\Delta_f H°\text{(1, s)} = 2\Delta_f H°(CO_2, g) + 3\Delta_f H°(H_2O, l) - \Delta_c H°(1, s) \qquad (4)$$

$$\Delta_f H°\text{(2, s)} = \Delta_f H°(CuO, s) + 4\Delta_f H°(CO_2, g) + 5\Delta_f H°(H_2O, l) - \Delta_c H°(2, s) \qquad (5)$$

$$\Delta_f H°\text{(3, s)} = 0.5\Delta_f H°(Ag_2O, s) + 2\Delta_f H°(CO_2, g) + 3.5\Delta_f H°(H_2O, l) - \Delta_c H°(3, s) \qquad (6)$$

The standard enthalpy of formation of a compound is governed by their molecular structure. The N−N, N−C, and N−O bonds in a molecule always give high heats of formation. The heterocycles with higher nitrogen content exhibit a higher enthalpy of formation. In the case of **1**, the enthalpy of combustion was determined experimentally from three independent measurements to be −1930 kJ mol^{-1}, which is derived from its combustion energy value (−4052 kJ mol^{-1}). With the experimentally determined enthalpy of combustion and the known enthalpies of formation of CO$_2$ (−393.51 kJ mol^{-1}) and H$_2$O (−285.83 kJ mol^{-1}). The enthalpy of formation of **1**, $\Delta_f H°$ (**1**, s), was calculated to be +286 kJ mol^{-1}. The value of **1** is higher than those of imidazole (+58 kJ mol^{-1}), 1,2,4-triazole (+109 kJ mol^{-1}), and tetrazole (+237 kJ mol^{-1}).[12b] The data are also higher than the common energetic compound TNT (−67 J kJ mol^{-1}) and RDX (+75 kJ mol^{-1}).[20]

The compounds of metal combined with the nitrogen-rich molecule MHT exhibit high enthalpies of formation. An analogous method was used to obtain the standard enthalpy of formation for complexes **2** and **3**. The complexes **2** and **3** show high enthalpies of formation, +93 and −263 kJ mol^{-1}, respectively. Complex **2** has a relative high energy, for its structure owing to many N−N and N−C bonds. The enthalpy of formation of copper complex **2** is higher than that of silver complex **3**, because of the two nitrogen-rich MHT ligands coordinated to the center copper ion. Complex **3** should have a relatively thermodynamically stable structure.

■ **CONCLUSION**

The synthesis of compound **1**, MHT, provides a new approach to obtain a novel nitrogen-rich tetrazole framework. Copper and silver complexes of MHT were synthesized and characterized. These metal coordination complexes along with the neutral MHT have been studied by single-crystal X-ray analysis. The crystal structure of neutral **1** was discussed with a delocalized 6π-aromatic system. Its metal complexes **2** and **3** were also checked for their structures with respect to the coordination mode of the MHT anion. Their physiochemical properties were determined. Furthermore, they are all impact-insensitive energetic materials. These metal MHT salts may be potential "green" energetic materials useful as gas generators or additives in solid rockets as low-smoke propellant ingredients,

since they show promising properties with respect to stability, sensitivity, and energetic aspects.

■ EXPERIMENTAL SECTION

Caution! Pure cyanogen azide is extremely dangerous and should always be dissolved in a solvent to give a dilute solution.[8] We have not experienced any problems in handling these compounds. Although they are impact-insensitive, they should be handled in small amounts with extreme care using appropriate standard safety precautions (leather gloves and working behind a safety shield).

General Methods. All chemicals were pure analytical grade materials obtained commercially and used as received. IR spectra were recorded using KBr pellets with a Biorad Model 3000 FTS spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively, by using d_6-DMSO as a locking solvent. Chemical shifts are reported in parts per million relative to tetramethylsilane, $Si(CH_3)_4$. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Impact sensitivity tests were carried out using a BAM fallhammer method.

X-Ray Crystallography. The crystals were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals of **1** and **2** were irradiated using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An MSC X-Stream low-temperature device was used to keep the crystals at a constant 93(2) K during data collection. The crystals of **3** were irradiated using a rotating anode Cu Kα source ($\lambda = 1.54178$ Å) with incident beam Helios optics. A Bruker Kryo-Flex low-temperature device was used to keep the crystals at a constant −100 °C during data collection. Data collection was performed, and the unit cell was initially refined using APEX2 [v2.1−0].[21] Data reduction was performed using SAINT [v7.34A][22] and XPREP [v2005/2].[23] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].[24] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[25] The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC Q10 calorimeter equipped with an Autocool accessory and calibrated using indium, which was gently flooded with N_2 at flow rate of 20 mL min^{-1}. Samples were sealed in aluminum pans in nitrogen gas. Measurements were carried out by heating from 40 to 400 °C at 10 °C min^{-1}. The reference sample was an empty Al container with air.

Decomposition Temperatures. Decomposition temperatures, T_{dec}, were determined by a thermogravimetric analyzer of TA TGA Q50. Thermogravimetric analysis (TGA) measurements were accomplished by heating samples at 10 °C min^{-1} from 25 to 500 °C in a dynamic nitrogen atmosphere at flow rate of 70 mL min^{-1}. T_{dec} values were obtained from onset analysis by evaluating the intersection of the baseline before decomposition and the tangent to the mass loss versus the temperature.

Bomb Calorimetry. For the calorimetric measurements, a Parr 1425 semimicro bomb calorimeter (static jacket) equipped with a Parr 1672 calorimetric thermometer for the combustion of samples was used. The samples were placed in a platinum pan and burned in a 3.2 MPa atmosphere of pure oxygen. Small pellets of benzoic acid were added to ignite the samples, and the values were deducted from the final data. A printer was furnished with the 1425 calorimeter to produce a record of the activity in the calorimeter. Typical experimental results of the constant-volume combustion energy ($\Delta_c U$) of the salts are summarized in Table 5. The standard molar enthalpy of combustion ($\Delta_c H_{298}°$) was derived from $\Delta_c H_{298}° = \Delta_c U + \Delta n RT$ ($\Delta n = \sum n_i$ (products, g) − $\sum n_i$ (reactants, g); $\sum n_i$ is the total molar amount of gases in the products or reactants). The enthalpy of

formation, $\Delta_f H_{298}°$, for each of the corresponding compounds was calculated at 298.15 K using designed Hess thermochemical cycles.

5-(1-Methylhydrazinyl)tetrazole (1). Sodium azide (5.0 g, 77 mmol) was added to a 30 mL dry acetonitrile solution of cyanogen bromide (2.0 g, 19 mmol) at 0 °C. The reaction mixture was stirred for 4 h at 0 °C. After the reaction, the white precipitate was filtered with general filtration method under atmospheric pressure. The resulting cyanogen azide solution was then added to a 20 mL acetonitrile solution of methylhydrazine (230 mg, 5 mmol). The mixture was stirred for 4 h at 0 °C. The resulting acetonitrile solution was concentrated and dried to yield the desired product **1** as a white powder. Yield: white solid 417 mg (73%).

^{1}H NMR (d_6-DMSO): 5.01 (s, 1H, −NH), 3.37 (s, 2H, −NH$_2$), 3.14 (s, 3H, −CH$_3$). ^{13}C NMR (d_6-DMSO): 161.88, 42.45. IR (KBr): 3314, 3211, 2938, 2779, 2650, 1674, 1597, 1460, 1412, 1280, 1180, 1112, 1028, 907, 733, 679 cm^{-1}. Anal. Calcd for $C_2H_6N_6$ (MW 114.11): C, 21.05; H, 5.30; N, 73.65. Found: C, 21.05; H, 5.38; N, 73.27.

Copper Di-5-(1-methylhydrazinyl)tetrazolate (2). Copper sulfate pentahydrate (25 mg, 0.1 mmol) was dissolved in water (5 mL). Then, an aqueous solution of **1** (23 mg, 0.2 mmol, 10 mL) was slowly added to form a clear green solution. Dark blue needles of **2** suitable for X-ray structural determination crystallized from the solution after 1 day. Yield: 27 mg (93%).

IR (KBr): 3232, 3159, 3132, 2922, 1608, 1545, 1441, 1410, 1333, 1266, 1227, 1163, 1113, 991, 932, 758, 649, 570 cm^{-1}. Anal. Calcd for $C_4H_{10}CuN_{12}$ (MW 289.75): C, 16.58; H, 3.48; N, 58.01. Found: C, 16.49; H, 3.54; N, 57.80.

Silver 5-(1-Methylhydrazinyl)Tetrazolate Hydrate (3). Silver nitrate (34 mg, 0.2 mmol) was dissolved in water (20 mL). An aqueous solution of **1** (23 mg, 0.2 mmol, 20 mL) was slowly dropped into the solution. The mixture was heated to boiling to form a clear colorless solution. Then, the solution was slowly cooled. After five days, colorless plates of **3** suitable for X-ray analysis were obtained. Yield: 44 mg (92%).

IR (KBr): 3434, 3313, 2924, 2873, 1621, 1522, 1445, 1398, 1372, 1335, 1248, 1217, 1126, 1074, 1016, 908, 825, 748, 631, 540 cm^{-1}. Anal. Calcd for $C_2H_{7.5}AgN_6O_{1.25}$ (MW 243.49): C, 9.87; H, 3.10; N, 34.52. Found: C, 9.76; H, 2.77; N, 34.22.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

X-ray crystallographic data for **1−3** in CIF format and DSC curves of **1−3**. 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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