Synthesis and Crystal Structure of the Energetic Compound [BAP(NO_3)(ClO_4)]

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Abstract. A novel azido amine compound of [BAP(NO_3) (ClO_4)] (BAP= *N*, *N*'-1,4-bis(2-azidoethyl)- piperazine) was synthesized for the first time. The structure of [BAP(NO_3) (ClO_4)] was characterized by elemental analysis and FT-IR spectroscopy. Single crystals of [BAP(NO_3) (ClO_4)] were obtained through slow evaporation of a saturated water solution. The crystal structure was determined by X-ray single crystal diffraction and the crystallographic data showed that the compound crystallizes in the triclinic space group *P*-1 with crystal parameters of a=6.4899(2) Å, b=11.2349(2) Å, c=12.1047(2) Å, α=105.524(2) °, β=91.065(2) °, γ=103.056(2) °, V=825.47(4) Å^3, Z=2.

1. Introduction

Amine azides are low molecular weight organic amine compouds containing at least one tertiary nitrogen and one azide functional group. These compounds have superior properties such as high enthalpy of formation, high density, clean combustion products, high burning rate and low toxicity [1-3]. So they are widely used as jet fuels, dual component pyrophoric liquid propellant, gel propellant, aerospace high energy density propellant fuel component, and expected to replace hydrazines[4-5]. Various amine azides have been synthesized and evaluated as potentional hypergolic fuel compounds, such as dimethylaminoethylazide (DMAZ), pyrollidinylethylazide (PYAZ) and bis (ethyl azide) methylamine (BAZ). DMAZ having the structure $(CH_3)_2NCH_2CH_2N_3$ appears to be one of the better candidates for hydrazine compouds. But DMAZ systems cannot meet higher performance standards set by monomethylhydrazine systems.

In order to obtain a higher energy density fuel, an amine azide containing piperazine ring was synthesized and obtained its crystal in the paper.

2. Experimental

2.1. Reagents and instruments

All analytical grade chemicals and solvents werepurchased commercially and used without further purification. Elemental analyses were performed on a Carlo Erba 1106 full-automatic trace element analyzer. The FTIR spectra were recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000-400 cm^{-1}.

2.2. Synthesis of [BAP(NO3)(ClO4)]

Synthesis of [BAP(NO_3) (ClO_4)]: *N*, *N*'-1,4-bis(2-azidoethyl)-piperazine nitrate(10 mmol) was dissolved in distilled water (20 mL), and charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 50°C. Perchloric acid (10 mmol) was added to the piperazine nitrate aqueous solution with continuous stirring. The mixture was stirred at 50°C for 3h. Then solvent was removed by rotary evaporation. Colorless crystals were collected. Anal. Calcd. $C_8H_{18}ClN_9O_7$ weight (%): C, 24.81; H, 4.65; N, 32.56. Found: C, 24.93; H, 4.23; N, 32.84. IR (cm^{-1}): 2945, 2108, 1632, 1520, 1370, 1280, 1074, 912.

2.3. Synthesis of [BAP(NO3)(ClO4)]

The crystallographic data collection of [BAP(NO_3) (ClO_4)] was carried out on a Bruker Smart1000 CCD diffractometer by using Mo-K_α radiation (λ=0.71073 Å) with φ and ω scan modes. A total of 8686 reflections (4048 unique) were measured in the range of 2.954°< θ <28.311°, and used for the determination and refinement of the crystal structure ($-5 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 14$). The structure was solved by direct methods using the SHELXS-97 program, and refined by using the full-matrix least-squares method on F^2 with the SHELXL-97 program. The detailed crystallographic data are listed in table 1.

Table 1. Crystal data and structure refinement for[BAP(NO_3)(ClO_4)].

Item	Value
empirical formula	$C_8H_{18}ClN_9O_7$
formula weight	387.76
crystal size (mm)	0.12×0.12×0.06
crystal system	triclinic
space group	*P*-1
a/Å	6.4899(2)
b/Å	11.2349(3)
c/Å	12.1047(4)
β/°	91.065(2)
V/Å^3	825.47(4)
Z	2
Dc/g·cm^{-3}	1.560
F(000)	404
λ/Å	0.71073
θ/°	2.954-28.311
measured reflections	8686
unique data (R_{int})	4048
R_1, $wR_2[I>2\sigma(I)]$	0.0590, 0.1463
R_1, wR_2(all data)	0.0858, 0.1616
h/*k*/*l*	–5-8/–14-14/–16-14
S	0.996

[a] $w = 1/[\sigma^2(F_o^2)+(0.0368P)^2+0.6860P]$, [b] $P = (F_o^2+2F_c^2)/3$.

3. Organization of the Text Result and discussion

[BAP(NO_3) (ClO_4)] crystallizes in the monoclinic system with space group *P*-1. The molecular structure of the title compoud is shown in Fig.1. The calculated density at 276 K is 1.560 g·cm^{-3}. The lengths of C-N bonds (1.491(3) Å-1.504(3) Å;C(2)-N(1), 1.504(3) Å; C(3)-N(1), 1.491(3) Å; C(4)-N(1), 1.494(3) Å) in piperazine ring are longer than the others C-N bonds of C-N_3(C(1)-N(2), 1.461(3) Å). Intermolecular hydrogen bonds between nitrate groups, perchlorate groups and C-H groups are found in all crystals resulting in a 3D supramolecular structure as shown in Fig.2.

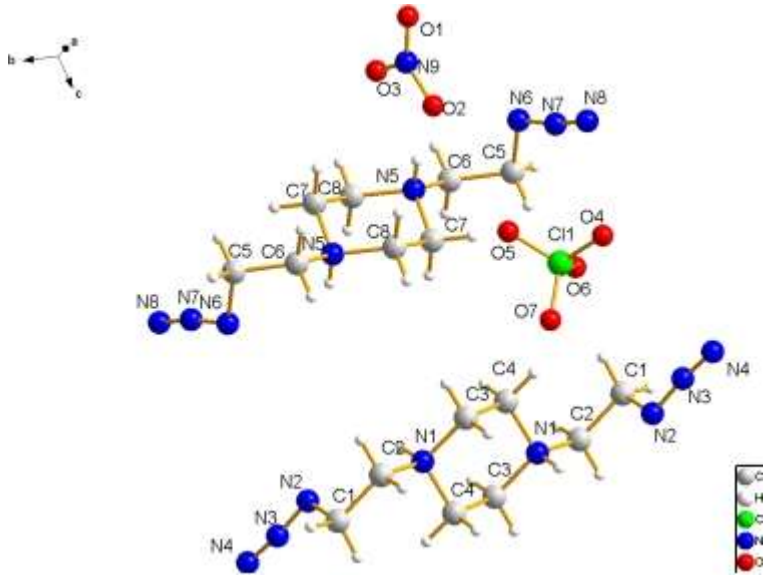

Figure 1. Atomic labeling diagmm of [BAP(NO_3)(ClO_4)].

Table 2. Selected bond lengths (Å) and bond angles (°) for [BAP(NO_3)(ClO_4)].

bond		bond		bond	
C(1)-N(2)	1.461(4)	C(3)-N(1)	1.491(3)	Cl(1)-O(4)	1.415(2)
C(1)-C(2)	1.507(4)	C(3)-C(4)	1.508(4)	Cl(1)-O(6)	1.421(3)
C(1)-H(1A)	0.9700	C(3)-H(3A)	0.9700	Cl(1)-O(7)	1.428(3)
C(1)-H(1B)	0.9700	C(3)-H(3B)	0.9700	N(2)-N(3)	1.228(4)
C(2)-N(1)	1.504(3)	C(4)-H(4A)	0.9700	N(3)-N(4)	1.126(4)
C(2)-H(2A)	0.9700	C(4)-H(4B)	0.9700	N(9)-O(1)	1.186(3)
C(2)-H(2B)	0.9700	Cl(1)-O(5)	1.412(3)	N(9)-O(2)	1.257(3)
Angle		Angle		Angle	
N(2)-C(1)-C(2)	107.4(2)	N(1)-C(2)-C(1)	113.0(2)	N(1)-C(3)-H(3A)	109.4
N(2)-C(1)-H(1A)	110.2	N(1)-C(2)-H(2A)	109.0	C(4)-C(3)-H(3A)	109.4
C(2)-C(1)-H(1A)	110.2	C(1)-C(2)-H(2A)	109.0	C(4)-C(3)-H(3B	109.4
N(2)-C(1)-H(1B)	110.2	N(1)-C(2)-H(2B)	109.0	H(3A)-C(3)-H(3B)	109.4
C(2)-C(1)-H(1B)	110.2	C(1)-C(2)-H(2B)	109.0	O(5)-Cl(1)-O(4)	108.70(17)
O(6)-N(8)-C(5)	120.83(19)	H(2A)-C(2)-H(2B)	107.8	O(1)-N(9)-O(2	123.6(3)
H(1A)-C(1)-H(1B)	108.5	N(2)-C(3)-H(3)	111.11(19)	O(1)-N(9)-O(3)	121.9(3)

4. Conclusion

A novel azido amine compound of [BAP(NO_3) (ClO_4)] (BAP= *N*, *N*'-1,4-bis(2-azidoethyl)- piperazine) was synthesized and obtained its crystal in the paper.

Acknowledgments

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