The ionic salts with super oxidizing ions O$_2^+$ and N$_5^+$: Potential candidates for high-energy oxidants

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As an important component of energetic materials, high-energy oxidant is one of the key materials to improve their energy. The oxidizability of oxidant directly determines the intensity of combustion or explosion reaction. It is generally believed that when the nature of reductant is certain, the stronger the oxidizability, the more intense the reaction. Dioxygenyl cation (O$_2^+$) and pentazenium cation (N$_5^+$) are two kinds of super oxidizing ions, which oxidizability are comparable to that of fluorine. A series of high energetic ionic salts with O$_2^+$, N$_5^+$ and various anions as active components are designed, and the results show that: 1) Most ionic salts have appropriate thermodynamic stability, high density (up to 2.201 g/cm$^3$), high enthalpy of formation (up to 1863.234 kJ/mol) and excellent detonation properties (up to 10.83 km/s, 45.9 GPa); 2) The detonation velocity value of O$_2^+$ (nitrotetrazole-N-oxides) and O$_2^+$B(N$_3$)$_4$ exceed 10.0 km/s, and the detonation pressure exceed 45.0 GPa because of the O$_2^+$ salts have higher crystal density (g/cm$^3$) and oxygen balance than that of N$_5^+$salts; 3) With a higher nitrogen content than O$_2^+$, the N$_5^+$ salts have higher enthalpy of formation, which exceed 330 kJ/mol than that of O$_2^+$ salts; 4) The linear spatial structure of N$_5^+$ leads the salts to reduce their density. Encouragingly, this study proves that these super oxidizing ions have the potential to become high-energy oxidants, which could be a theoretical reference for the design of new high energetic materials.

KEYWORDS
super energetic oxidizer, O$_2^+$ and N$_5^+$ ionic salts, detonation performance, quantum chemical calculation, energetic materials

1 Introduction

An oxidant is a reactant that oxidizes or removes electrons from other reactants during a redox reaction, which is widely used in aerospace propellants, explosives, and pyrotechnics (Connelly and Geiger, 1996). The oxidants, which directly participate in combustion or explosion reactions, is one of the indispensable components for such chemical reactions. For example, dinitramide salts (Venkatachalam et al., 2004) and perchlorates (Zeng and Bernstein, 2019) are added to energetic formulas to increase the oxygen balance and density of the whole system.
In energetic materials, the functions of oxidants are: 1) Speeding up burning more intensely; 2) Causing materials that are normally not readily combustible in air to burn more readily; 3) Causing combustible materials to burn spontaneously without a source of ignition. It is generally agreed that the oxidant with strong oxidizability can significantly improve the energetic properties of mixed explosive when the nature of reductant is certain.

However, traditional oxidants (such as ammonium perchlorate, hydrazine perchlorate, nitroyl perchlorate, hydroxylamine perchlorate, etc.) often contain halogen elements, which are easy to cause harm to human body and the environment; The energy level of existing high-energy oxidants such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1,1-diamino-2,2-dinitroethylene (FOX-7), dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and hexanitrohexaazaisowurtzitane (CL-20) has reached the limit of energetic oxidants. The design and development of energetic ionic salts with super oxidation and gas products are expected to promote the innovative development of traditional energetic materials. Excitingly, the O$_2^+$ and N$_5^+$ are two super oxidizing cation systems, and their oxidizing power are comparable to that of fluorine gas. These two cations consist only of oxygen and nitrogen elements, respectively, which ensures that their reaction products are likely to be nitrogen and various gaseous non-metallic oxides.

Dioxygenyl hexafluoroplutinate containing O$_2^+$ was first synthesized by Bartlett et al. (Bartlett and Lohmann, 1962) in 1962, which started the wave of research of dioxygenyl cation. Subsequently, various O$_2^+$ salts containing fluorine anions [such as O$_2^+$MF$_6$ (M = P, As, Sb, Bi, Pt, Ru, Rh, Pd, or Au), O$_2^+$M$_2$F$_{11}$ (M = Sb, Bi, Nb, or Ta), Or O$_2^+$MF$_4$ (M = B)] were successively characterized (Grill et al., 1970; Nikitin and Rosolovskii, 1971; Goetschel and Loos, 1972; McKee and Bartlett, 1973; Christe et al., 1974; Edwards et al., 1974; Gillespie and Schrobilgen, 1974; Disalvo et al., 1975; Griffiths et al., 1975; Holloway and Schrobilgen, 1975; Rigny and Falconer, 1975). In 1973, Stein et al. (1973) used O$_2$SbF$_6$ to remove xenon and radon from the atmosphere, and oxygen was released after the reaction. It directly proved that O$_2^+$ has strong oxidizability, so that it can directly oxidize the inert gas and release oxygen. In 1976, Falconer et al. (1976) synthesized O$_2^+$PdF$_6^-$, that is, Pd (V) can be stabilized to hexafluorides by forming a complex salt with dioxygenyl cation. In 1976, Christie et al. (1976) synthesized and characterized another new O$_2^+$ salt: O$_2^+$GeF$_5^-$ which was prepared by UV photolysis of GeF$_4$-F$_2$-O$_2$ mixture in quartz at −78°C. In 1991, Fisher et al. (1991) studied the reaction between O$_2^+$ and CF$_4$/C$_2$F$_6$, and found that FCO$^+$ and F$_2$CO$^+$ would be generated after the reaction, which shows the super oxidizability of O$_2^+$. However, the above studies focus on the stability and oxidizability of dioxygenyl ions, and did not involve too much research on energetic materials. Holfter studied the reaction between O$_2^+$BF$_4^-$ and activated sodium azide in the presence of metallic aluminum in 1997 (Holfter et al., 1997). The reaction produces NaBF$_4$, N$_2$ and Al$_2$O$_3$, and releases 434 kcal/mol of heat, which fully shows that O$_2^+$BF$_4^-$ is a high energy density material.

In addition, the all-nitrogen cation N$_5^+$ is another attractive super oxidizing ion compared to the O$_2^+$. Christe et al. (1999) first reported the synthesis and characterization of N$_5^+$AsF$_6^-$ in 1999, which has a chain structure and could be a high energy density material. This study shows that N$_5^+$AsF$_6^-$ is a white solid slightly soluble in anhydrous HF, which is relatively stable at 22°C, and can be stored for several weeks without decomposition at −78°C. In 2001, Vij et al. (2001) prepared another N$_5^+$ salt: N$_5^+$Sb$_2$F$_{11}^-$, and studied the oxidation of this salt. The results

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**Scheme 1**

Fluorinated anions for stabilizing O$_2^+$ in previous works and energetic anions used in this paper to stabilize O$_2^+$ and N$_5^+$. 

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show that N5+ is a super strong single electron oxidant, which can oxidize NO, NO2, and Br2, but cannot oxidize Cl2, Xe, and O2. In 2003, Wilson et al. (2003) prepared (N5+)2SnF6, N5+SnF5−, and N5+B(CF3)− by combining N5+ and multi-electron anions. In 2004, Dixon et al. (2004) confirmed that both N5+N3− and N5+N5− were unstable structures by theoretical calculation, but pointed out that the stability prediction of individual ionic compounds could not represent the stability of such substances. In the same year, Haiges et al. (2004) also published the synthesis and characterization of N5+ high energy density materials, which include N5+[P(N3)6]−, N5+[B(N3)4]−, N5+[HF2]−·nHF, N5+[BF4]−, N5+[PF6]−, and N5+[SO3F]−.

Based on the previous researches, the super oxidation and potential energetic properties of N5+ and O2+ greatly encourage us to further study the application potential of these substances in the field of energetic materials. In this paper, N5+ and O2+ are used as the cationic components of energetic ionic salts, while the polyazole rings, BF4−, B(N3)4−, NO3−, C(NO2)3−, and N5− are used as anions to design two new types of energetic ionic salts (see Scheme 1). By means of quantum chemical calculation, we studied the physical properties (density, enthalpy of formation), stability and detonation properties of these two energetic ionic salts. We hope that this research work can deepen people’s understanding of super oxidizing ions, and provide some reference and theoretical support for the development of new energetic oxidants.

2 Calculation method

The geometries of each structure corresponding to the stationary point on the potential energy surface (PES) of the specie studied were fully optimized using density functional theory at the M06-2X/6-311+G (d, p) level with Gaussian 09 (Wong et al., 2002; Zhao and Truhlar, 2007; Frisch et al., 2016). Zero-point energies and thermal corrections to enthalpy (the correction factor is 0.97) and Gibbs free energies are computed at the same DFT level. Single-point electronic energies are afterward refined using PWPB95 (Goerigk and Grimme, 2011) functional in conjunction with a def2-QZVP (Weigend and Ahlrichs, 2005) by ORCA (Neese, 2011). The molecular van der Waals surface electrostatic potential distribution of anions and cations were obtained with Multiwfn (Lu and Chen, 2012a; b).

The crystal density (ρ) was estimated using the improved equation (Rice and Byrd, 2013) shown as follows Eq. 1.

$$\rho = \frac{M}{V_m} + \alpha \left( \frac{V_s}{A_s^2} \right) + \beta \left( \frac{V_s}{A_s^2} \right)^n + \delta$$

(1)
**FIGURE 1**
Theoretically designed energetic compounds containing $N_5^+$ ($A$–$J$) and $O_2^+$ ($A1$–$J1$) ions at M06-2X/6-311+G (d, p) theory.

**FIGURE 2**
The molecular van der Waals surface electrostatic potential distribution of anions and cations. The red region represents the higher electrostatic potential in the molecular and blue region represents the lower electrostatic potential in it.
where $M$ is the molecular mass of the compound. $V_m$ is the volume of the isolated gas molecule. The $A^+_i$ (Bohr$^2$) is the portion of a cation’s surface which has a positive electrostatic potential, and the $V^+_i$ (kcal/mol) is the average value of positive electrostatic potential; the $A^-_i$ and $V^-_i$ are the analogous quantities for an anion. These four parameters are calculated by Multiwfn (Lu and Chen, 2012a).

The volume ($V$) of ionic compounds ($M_iX_q$) (Jenkins et al., 1999; Rice et al., 2007) is estimated using the sum of the respective volumes of cations and anions by Eq. 2:

$$ V = pV_{M_i} + qV_{X_q} $$

where $V_{M_i}$ and $V_{X_q}$ are the volume of the cation $M^+$ and anion $X^-$, respectively. The $p$ and $q$ are the number of cation $M^+$ and anion $X^-$ per formula unit, respectively.

As shown in Scheme 2, based on the Born-Haber energy cycle, the enthalpy of formation (Gao et al., 2007) of ionic compounds can be predicted by Eq. 3:

$$ \Delta H_f \text{(salt, 298 K)} = \Delta H_f \text{(cation, 298 K)} + \Delta H_f \text{(anion, 298 K)} - \Delta H_L $$

(3)

where $\Delta H_L$ is the lattice energy of the salts which can be calculated by Eq. 4 put forward by Jenkins et al. (2002).

$$ \Delta H_L = U_{POT} + \left[p(n_M/2 - 2) + q(n_X/2 - 2)\right]RT $$

where $n_M$ and $n_X$ rely on the nature of the ions $M_{p+}$ and $X_{q-}$ respectively, are equal to 3 when they are monatomic ions, 5 when they are linear polyatomic ions, and 6 when they are nonlinear polyatomic ions. In addition, the lattice potential energy ($U_{POT}$) can be estimated by Eq. 5:

$$ U_{POT} = \gamma \rho M + \delta $$

(5)

where $\rho$ (g cm$^{-3}$) is the density and $M$ (g mol$^{-1}$) is the chemical formula mass of the ionic salt. For 1:1 (charge ratio) salts, the fitted coefficients $\gamma$ and $\delta$ are 1981.2 kJ mol$^{-1}$-cm and 103.8 kJ mol$^{-1}$; for 1:2 salts, they are 8375.6 kJ mol$^{-1}$-cm and -178.8 kJ mol$^{-1}$; and for 2:2, they are 6864.0 kJ mol$^{-1}$-cm and 732.0 kJ mol$^{-1}$.

The detonation velocity and pressure were predicted by empirical Kamlet-Jacobs in EXPLO5 (v6.05) program (Sučeska, 2018) by Eqs 6, 7:

$$ D = 1.01 \left[ N M^2 Q^5 \right]^{0.7} (1 + 1.30 \rho) $$

(6)

$$ P = 1.558 \rho N M^2 Q^5 $$

(7)

where $D$ is the detonation velocity (km/s), $P$ is the detonation pressure (GPa), $N$ is the moles of detonation gases per gram explosive, $M$ is the average molecular weight of these gases, $Q$ is the heat of detonation (cal/g), and $\rho$ is the loaded density of explosives (g/cm$^3$) and is replaced by the theoretical density here.

For ionic compounds ($M_{p+}X_{q-}$), the Gibbs free energy change of formation ($\Delta G_{f,exp}(salt)$, Eq. 8) can be used to describe whether it can be decomposed in thermodynamics. The reaction enthalpy change ($\Delta H_{f,exp}(salt)$, Eq. 9) of ionic salts can be obtained based on the Born-Haber cycle, (see Scheme 3), relying on the lattice energy ($\Delta H_L$) of the ionic salt, the adiabatic electron affinity ($AEA(M^{+})$) of the cation and the adiabatic ionization potential ($AIP(X^{-})$) of the anion (Dixon et al., 2004). For entropies of the

| Salts | $V$ | $V_s$ | $A^+_i$ | $V^-_i$ | $A^-_i$ | $\rho$ |
|-------|-----|-------|--------|--------|--------|-------|
| A     | 221.181 | 128.687 | 91.277 | -90.988 | 160.682 | 1.829 |
| B     | 227.326 | 128.687 | 91.277 | -89.434 | 164.537 | 1.775 |
| C     | 195.731 | 128.687 | 91.277 | -98.713 | 136.468 | 1.807 |
| D     | 150.759 | 128.687 | 91.277 | -118.677 | 94.990 | 1.626 |
| E     | 265.753 | 128.687 | 91.277 | -76.187 | 218.036 | 1.677 |
| F     | 140.178 | 128.687 | 91.277 | -124.560 | 90.170 | 1.944 |
| G     | 206.867 | 128.687 | 91.277 | -96.324 | 147.161 | 1.881 |
| H     | 171.494 | 128.687 | 91.277 | -107.599 | 117.227 | 1.806 |
| I     | 134.838 | 128.687 | 91.277 | -127.760 | 83.231 | 1.700 |
| J     | 130.518 | 128.687 | 91.277 | -129.171 | 79.263 | 1.490 |
| A1    | 178.071 | 180.048 | 43.677 | -90.988 | 160.682 | 2.030 |
| B1    | 184.216 | 180.048 | 43.677 | -89.434 | 164.537 | 1.961 |
| C1    | 152.620 | 180.048 | 43.677 | -98.713 | 136.468 | 2.014 |
| D1    | 107.649 | 180.048 | 43.677 | -107.599 | 117.227 | 2.028 |
| E1    | 222.643 | 180.048 | 43.677 | -76.187 | 218.036 | 1.834 |
| F1    | 97.066  | 180.048 | 43.677 | -124.560 | 90.170 | 2.263 |
| G1    | 163.757 | 180.048 | 43.677 | -96.324 | 147.161 | 2.102 |
| H1    | 128.384 | 180.048 | 43.677 | -107.599 | 117.227 | 2.028 |
| I1    | 91.728  | 180.048 | 43.677 | -127.760 | 83.231 | 1.917 |
| J1    | 87.408  | 180.048 | 43.677 | -129.171 | 79.263 | 1.610 |
the N5 + salts, various anions and their corresponding salts (ΔHf salt) A to J for N5 + salts and A1 to J1 for O2 + salts, as well as lattice energies (ΔU) of these salts. (unit, kJ/mol).

| Salts | ΔHf (cation) | ΔHf (anion) | ΔHf L | ΔHf J |
|-------|--------------|--------------|--------|--------|
| A     | 1496.733     | 106.228      | 505.305| 1097.656|
| B     | 1496.733     | 83.104       | 501.934| 1077.903|
| C     | 1496.733     | 238.726      | 521.344| 1214.115|
| D     | 1496.733     | 316.461      | 557.376| 1255.817|
| E     | 1496.733     | 849.433      | 482.932| 1863.234|
| F     | 1496.733     | −1724.827    | 567.272| −795.366|
| G     | 1496.733     | −90.096      | 513.820| 892.816 |
| H     | 1496.733     | −30.616      | 539.262| 926.855 |
| I     | 1496.733     | −244.451     | 573.084| 679.198 |
| J     | 1496.733     | 226.004      | 578.134| 1144.603|
| A1    | 1197.073     | 106.228      | 543.823| 759.478 |
| B1    | 1197.073     | 83.104       | 539.582| 740.595 |
| C1    | 1197.073     | 238.726      | 566.424| 869.375 |
| D1    | 1197.073     | 316.461      | 623.040| 890.494 |
| E1    | 1197.073     | 849.433      | 514.958| 1531.548|
| F1    | 1197.073     | −1724.827    | 555.300| 551.677 |
| G1    | 1197.073     | −90.096      | 555.300| 551.677 |
| H1    | 1197.073     | −30.616      | 592.801| 573.656 |
| I1    | 1197.073     | −244.451     | 648.782| 303.840 |
| J1    | 1197.073     | 226.004      | 660.504| 762.573 |

*: Gaseous enthalpy of formation of cations.
**: Gaseous enthalpy of formation of anions.
***: Lattice energy.
****: Enthalpy of formation of ionic salts.

3 Results and discussion

3.1 Configuration

Figure 1 shows two types of energetic ionic salt compounds in this paper. For N5 + salts (A to J), all the anions are located inside the V-shape of the N5 +. These spatial relative configurations are consistent with previous studies (Wang et al., 2011; Lian et al., 2012; Yu et al., 2015). The reason for this spatial distribution may be due to the electrostatic potential distribution on the surface of the N5 +. Similarly, the structures of the O2 + salts are A1 to J1. The intrinsic cause of this spatial structure distribution remains the distribution of electrostatic potential on the surface of anions and cations. As can be seen from Figure 2, the high electrostatic potential portions of N5 + and O2 + are mainly concentrated in the V-shaped inner region of the N5 + (red region) and in the direction vertical to the bond axis of the O-O bond in O2 + (red region). This high positive electrostatic potential region tends to interact with the low negative electrostatic potential in the anion, thus affecting the molecular conformations of the ionic salts in Figure 1.

3.2 Crystal density

Crystal density is a critical consideration for energetic materials. In this section, the effects of different anions on the density of O2 + and N5 + salts are investigated separately. Table 1 lists the volumes, relevant parameters and densities of the individual ionic salt. It is easy to find that the densities of these two classes of ionic salts are designed to be between 1.490 and 2.263 g cm−3.

On the whole, the density of salts formed by anion and O2 + is higher than that of ionic salts formed by anion and N5 +. Compared with O2 +, the volume of N5 + with V-shaped structure is larger than that of O2 +, which is not conducive to the formation of dense accumulation, resulting in the density in the kind of ionic salts are generally lower than these of O2 (+). Among all ionic salts, A, C, F, G, H for N5 + salts and A1 to I1 for O2 + salts with a density higher than 1.800 g cm−3. Although the densities of O2 + salts are higher than those of HMX (1.90 g cm−3) (Wang et al., 2018) and RDX (1.80 g cm−3) (Wang et al., 2018), while the densities of A1, C1, D1, F1,
TABLE 3 Predicted explosive properties, specific impulse (Isp) and oxygen balance of N5− and O2− salts.

| Salts   | Qf (kJ kg−1) | Df (km s−1) | Pf (GPa) | Isp (s) | OB (%) |
|---------|--------------|-------------|----------|---------|--------|
| A       | 7797.40      | 9694        | 40.58    | 295.46  | 0      |
| B       | 7628.79      | 9592        | 40.78    | 305.06  | −17.61 |
| C       | 7793.69      | 9765        | 40.59    | 303.91  | 8.00   |
| D       | 9026.90      | 9778        | 38.16    | 348.23  | 0      |
| E       | 8560.77      | 9331        | 35.06    | 305.98  | −9.64  |
| F       | 2487.00      | 7162        | 20.15    | 166.54  | 5.10   |
| G       | 5830.04      | 9128        | 35.67    | 270.07  | 29.08  |
| H       | 5247.90      | 8920/8859   | 32.76/32.3 | 268.18  | 63.65  |
| I       | 5103.58      | 8433/8642   | 28.02/30.3 | 265.72  | 63.65  |
| J       | 10,196.80    | 9402        | 33.83    | 367.67  | 0      |
| A1      | 8086.01      | 9985        | 46.71    | 286.96  | 16.84  |
| B1      | 9579.26      | 9983        | 47.33    | 302.66  | −4.23  |
| C1      | 7701.67      | 10,025      | 46.92    | 293.26  | 29.61  |
| D1      | 8390.83      | 9895        | 42.69    | 324.52  | 31.36  |
| E1      | 8686.17      | 10,833      | 56.63    | 349.70  | 3.79   |
| F1      | —            | —           | —        | —       | —      |
| G1      | 5219.46      | 9226        | 39.53    | 254.96  | 52.73  |
| H1      | 4198.91      | 8737        | 33.80    | 241.48  | 69.55  |
| J1      | 3288.32      | 7605        | 24.27    | 216.79  | 85.10  |
| J1      | 3989.90      | 9174        | 34.95    | 340.44  | 43.23  |

*Explosive heat.

*Detonation velocity.

*Detonation pressure and detonation velocity calculated in literature (Sun et al., 2020).

3.3 Enthalpy of formation

A high and positive enthalpy of formation is a typical feature of energetic compounds. In this section we study the enthalpy of formation of the designed ionic salts. Table 2 contains the enthalpy of formation of each anion (ΔHf (anion)), cation (ΔHf (cation)) and corresponding salt (ΔHf). It is easy to find from Table 2 that the enthalpy of formation of salts formed by anion and O2− is higher than that of ionic salt formed by anion and O2−. The O2− and N5− have very high enthalpy of formation (both >1000 kJ/mol), which maybe determine the ultra-high enthalpy of formation for these ionic salts. As deduced earlier, the enthalpy of formation of all the remaining ionic salts are positive except for F and F1. Among them, the highest enthalpy of formation is E (up to 1863.23 kJ/mol) and the lowest is H1 (up to 303.84 kJ/mol). Except for F, the enthalpy of formation of the remaining N5− salts are all much higher than that of CL-20 (365.4 kJ/mol) (Wang et al., 2018). Although the enthalpy of formation of O2− salts is not as high as that of N5− salts, most of the salts also have a fairly high enthalpy of formation (1531.55 kJ/mol for E1).

In addition, the effect of different anions on the enthalpy of formation of these two types of ionic salts is reflected in Figure 4, respectively. In Figure 4, the red closed line wraps the blue one, indicating that the enthalpy of formation of the N5− salts is greater than that of the O2− salts. Among all ionic salts, the salts formed by B(N3)4− anion have the highest enthalpy of formation, reaching 1164.36 kJ/mol for N5− salts and 1531.55 kJ/mol for O2− salts, which implies that the B(N3)4− anion can significantly increase the enthalpy of formation of the compound. However, salts formed from BF4− anions have the lowest enthalpy of formation, −795.37 kJ/mol for N5− salts and −1164.36 kJ/mol for O2− salts, respectively. The enthalpy of formation of O2− salts is not as high as that of N5− salts, most of the salts also have a fairly high enthalpy of formation (1531.55 kJ/mol for E1).

In addition, the effect of different anions on the enthalpy of formation of these two types of ionic salts is reflected in Figure 3, respectively. In Figure 3, the blue closed line wraps the red one, indicating that the density of the O2− salts is greater than that of the N5− salts. Among all ionic salts, the salts formed by BF4− anion have the highest density, reaching 1.944 g cm−3 (1.99 g cm−3 in the literature (Wang et al., 2011)) for N5− salts and 2.263 g cm−3 for O2− salts. However, salts formed from N5− have the lowest densities, 1.490 g cm−3 for N5− salts and 1.610 g cm−3 for O2− salts, respectively. The radar plot shows that the order of the effect of different anions on the ionic salts density are BF4− > C(NO2)3− > 3,5-Dinitro-1,2,4-triazole anion > 5-Nitro-tetrazole-1-N-oxide anion > N(NO2)2− > 3,5-Dinitro-4H-pyrazole anion > NO3− > B(N3)4− > N5− > N3− for N5− salts and BF4− > C(NO2)3− > 3,5-Dinitro-1,2,4-triazole anion > N5− = N(NO2)2− > 5-Nitro-tetrazole-1-N-oxide anion > 3,5-Dinitro-4H-pyrazole anion > NO3− > B(N3)4− > N5− > N3− for O2− salt.
3.4 Energetic properties

The explosive properties of energetic materials are to evaluate the energy performance of the characteristic parameters, mainly including the detonation velocity ($D$), detonation pressure ($P$), detonation heat ($Q$), etc. Table 3 contains the $D$, $P$, $Q$ and specific impulse ($I_{sp}$) for all designed ionic salts.

It is easy to find that most of the ionic salts have $D$ in excess of 8,000 m/s. Among the $\text{N}_5^+$ salts, all except $\text{F}$ (7,162 m/s), $\text{H}$ (8,920 m/s) and $\text{I}$ (8,433 m/s) have $D$ exceeding 9000 m/s, owing to their high density. Similarly, among the $\text{O}_2^+$ salts, the $D$ exceeded 9000 m/s for all salts except $\text{H}_1$ (8,737 m/s), $\text{I}_1$ (7,605 m/s) and $\text{F}_1$. Excitingly, the $D$ of $\text{C}_1$ (10,025 m/s) and $\text{E}_1$ (10,833 m/s) exceeded 10,000 m/s, which fully demonstrates the potential of $\text{O}_2^+$ as active ingredients of ultra-high energy oxidants. The introduction of $\text{O}_2^+$ into the system significantly increases the crystal density and oxygen balance, which fundamentally determines the high detonation velocity properties of this category of salts.

The $P$ is another important index of energetic materials. Compared with the $P$ of CL-20, the $P$ of $\text{A}_1$, $\text{B}_1$, $\text{C}_1$, and $\text{E}_1$ are all higher than that of CL-20 in $\text{O}_2^+$ salts, reaching 46.71, 47.73, 46.92, 56.63 GPa, respectively. In the case of $\text{N}_5^+$ salts, although the highest $P$ value is not as high as $\text{E}_1$ in $\text{O}_2^+$ salts, the $P$ of some $\text{N}_5^+$ salts ($\text{A}$, $\text{B}$, $\text{C}$) also reaches more than 40 GPa.

Oxygen balance is an important reference indicator for screening energetic materials. As can be seen in Table 3, the oxygen balance of the $\text{O}_2^+$ salts are higher than these of the $\text{N}_5^+$ salts for salts composed of the same anion, which directly indicates that the way to improve the oxygen balance is to introduce $\text{O}_2^+$ into the system. Energetic ionic salts can be used not only as energetic materials, but also as propellants. The value of $I_{sp}$ can be used to compare the performance of different rocket propellants. Among the $\text{N}_5^+$ salts, the $I_{sp}$ is higher than 260 s for all ionic salts except $\text{F}$ (166.54 s). Five $\text{N}_5^+$ salts

![Figure 5](image-url)
have $I_{sp}$ value exceeding 300 s, with the highest value of J reaching 367.67 s. In contrast, among the O$_2^+$ salts, there are four ionic salts with $I_{sp}$ exceeding 300 s, namely B1 (302.66 s), D1 (324.52 s), E1 (349.70 s), and J1 (340.44 s). The ultra-high $I_{sp}$ value further illustrate the promise of these super-oxidizing ionic salts to drive further development of conventional propellants.

In addition, Figure 5 shows the effect of different anions on the detonation velocity A, detonation pressure B, detonation heat C and specific impulse D. Based on the degree of overlap of the two curves (the blue and the red) in the radar plots, we can clearly find the effect of different anions on the detonation parameters of the ionic salts.

Among these ten anion structures, it is not possible to calculate the detonation parameters of the O$_2^+$ salts composed of BF$_4^-$ by the Kamlet–Jacobs formula. The reason for this phenomenon may be due to the ultra-low enthalpy of formation of this ionic salts (−1164.355 kJ/mol for F1). As a comparison, the ionic salt formed by BF$_4^-$ and N$_5^+$ has a calculated detonation parameter, which indicates that the N$_5^+$ enhances the energy of this system more than the O$_2^+$ (enthalpy of formation of F is −795.37 kJ/mol). It is obvious from the radar plot (Figures 5C,D) that the N$_3^-$ has a greater influence on the heat of explosion and specific impulse than other anions. The effects of 3,5-Dinitro-1,2,4-triazole anion, 3,5-Dinitro-4H-pyrazole anion, 5-Nitro-tetrazole-1-N-oxide anion and N$_5^-$ on the detonation velocity are similar in both N$_5^+$ and O$_2^+$ salts.

### TABLE 4 Values of $H_{50}$ for N$_5^+$ and O$_2^+$ salts.

| Salts     | $\sigma^2$ (kcal/mol)$^2$ | $\nu$   | $H_{50}$ (cm) |
|-----------|---------------------------|---------|---------------|
| A         | 147.31                    | 0.1599  | 34.23         |
| B         | 109.04                    | 0.1875  | 41.15         |
| C         | 152.62                    | 0.1856  | 40.40         |
| D         | 225.06                    | 0.2464  | 54.61         |
| E         | 202.13                    | 0.1528  | 32.17         |
| F         | 239.91                    | 0.2222  | 48.69         |
| G         | 222.65                    | 0.1896  | 40.93         |
| H         | 202.54                    | 0.1926  | 41.77         |
| I         | 141.78                    | 0.2443  | 54.63         |
| J         | 97.87                     | 0.2193  | 48.89         |
| A1        | 96.35                     | 0.0929  | 18.37         |
| B1        | 144.31                    | 0.1239  | 25.55         |
| C1        | 86.65                     | 0.1415  | 30.17         |
| D1        | 70.77                     | 0.2277  | 51.10         |
| E1        | 60.76                     | 0.2268  | 50.93         |
| F1        | 88.54                     | 0.1619  | 35.10         |
| G1        | 69.70                     | 0.0997  | 20.18         |
| H1        | 67.51                     | 0.0792  | 15.26         |
| J1        | 58.23                     | 0.0707  | 13.27         |
| J1        | 60.25                     | 0.1221  | 25.66         |
| N$_5$AsF$_6$ | 288.82                | 0.1664  | 34.91         |
| N$_5$SbF$_6$ | 294.90               | 0.1559  | 32.32         |
TABLE 5 Calculated adiabatic ionization potential (AIP), adiabatic electron affinity (AEA), lattice energy (ΔH_L), reaction enthalpy change (ΔH_rxn), entropy change (ΔS_rxn) and Gibbs free energy change of formation (ΔG_rxn) for N5+ salts and O2− salts.

| Salts | AIP | AEA | ΔH_rxn | ΔS_rxn | ΔG_rxn |
|-------|-----|-----|--------|--------|--------|
| A     | 525.295 | −1017.967 | 505.305 | 13.262 | −435.673 | 143.093 |
| B     | 500.468 | −1017.967 | 501.934 | −15.566 | −427.389 | 111.796 |
| C     | 394.085 | −1017.967 | 521.344 | −102.539 | −414.667 | 21.032 |
| D     | 200.414 | −1017.967 | 557.376 | −260.177 | −348.683 | −156.270 |
| E     | 310.204 | −1017.967 | 482.932 | −224.832 | −360.604 | −117.372 |
| F     | 682.290 | −1017.967 | 567.272 | 231.514 | −382.040 | 345.362 |
| G     | 448.287 | −1017.967 | 513.820 | −55.860 | −455.085 | 79.756 |
| H     | 429.914 | −1017.967 | 539.262 | −48.791 | −405.680 | 72.101 |
| I     | 387.624 | −1017.967 | 573.084 | −57.259 | −361.632 | 50.507 |
| J     | 253.111 | −1017.967 | 587.134 | −186.721 | −332.297 | −87.697 |
| A1    | 525.925 | −966.911 | 543.823 | 102.857 | −391.005 | 219.356 |
| B1    | 500.468 | −966.911 | 539.262 | 73.139 | −382.720 | 187.189 |
| C1    | 394.085 | −966.911 | 566.424 | −6.403 | −369.998 | 103.856 |
| D1    | 200.414 | −966.911 | 623.040 | −143.457 | −304.015 | −52.861 |
| E1    | 310.204 | −966.911 | 514.958 | −141.749 | −315.936 | −47.600 |
| F1    | 682.290 | −966.911 | 636.601 | 351.899 | −337.371 | 425.435 |
| G1    | 448.287 | −966.911 | 555.300 | 36.676 | −410.416 | 158.980 |
| H1    | 429.914 | −966.911 | 592.801 | 55.804 | −361.012 | 163.385 |
| I1    | 387.624 | −966.911 | 648.782 | 69.495 | −316.964 | 163.950 |
| J1    | 253.111 | −966.911 | 660.504 | 53.296 | −287.627 | 32.418 |

1Adiabatic ionization potential.
2Adiabatic electron affinity.
3Lattice energy.
4Enthalpy change of reaction.
5Entropy change of reaction.
6Gibbs free energy change of formation.

Figure 7
The radar plots of the effect of different anions on the Gibbs free energy change of the formation of the N5+ and O2− salts.

3.5 Impact sensitivity
Impact sensitivity (H50) is used to describe the degree of difficulty of explosion of energetic materials under impact stimulation, which indicates the stability of compounds to a certain extent. The higher the value of H50, the more stable the compound is to shock stimulation. Table 4 lists the positive variance (σ2), balance of charges (υ) and H50 of each ionic salt. The computational results show that the H50 of these ionic salts are between 13.27 cm (I1) and 54.63 cm (I). Since the sensitivity of energetic materials is affected by many factors, the impact sensitivity here can only be used as a reference. Forcibly analyzing this part of the content is very likely to get meaningless or even wrong conclusions.

3.6 Stability
The newly designed high-energy oxidizing ionic salts need to have not only excellent detonation performance, but also sufficient stability. As an allotrope of N5+, the N5+ was successfully synthesized by researchers in 2017 (Xu et al., 2017; Zhang et al., 2017). It is believed that the N5+ is stable at atmospheric pressure because of its ability to form coordination interactions with metal cations and to form hydrogen bonds with water molecules. Subsequently, a series of ionic salts formed by N5+ and organic nitrogen-rich cations (Yang et al., 2018; Xu et al., 2019) were designed and synthesized, which further broadened the study of N5+ ions.

Based on this stabilization mechanism, we hypothesize that the N5+ is also capable of stabilizing with certain nonmetallic anions through electrostatic interactions or other van der Waals interactions. Therefore, we first analyzed the various interactions (see Figure 6) existing within the ionic salts by interaction region indicator (IRI) (Lu and Chen, 2021) analyses, and then calculated the Gibbs free energies change of formation of the ionic salts as ways of which to illustrate the stability of the designed energetic ionic salts.
In Figure 6, for $N_3^-$ salts, the presence of dark blue portions of N9-N15 in A, N3-N6 in B and N4-N14 in C, respectively, can be found in the IRI isosurface map, implying that all these bonds are relatively strong covalent chemical bonds. In D, E, and H, the presence of dark blue regions at the space outside the ionic fragment, which implies the presence of strong interactions in these parts. However, there is no dark blue region in F, G and J, which is similar to that in D, E and H, suggesting that the binding degree of cation and anion in these three compounds is relatively weak. However, for $O_2^+$ salts in Supplementary Figure S1), except D1, there is no obvious covalent interaction between anions and cations in other salts. The results show that in F1, BF4$^-_3$ seems to dissociate, forming F$^-$ and BF3 groups, and there is a strong interaction between O2$^+$ and F$^-$ in F1. In other ionic compounds, O2$^+$ seems to form a strong van der Waals interaction with anions (green IRI isosurface rather than dark blue isosurface), and a strong interaction (blue IRI isosurface) appears to be formed between O2$^+$ and N3$^-$ in D1. In short, multiple interactions within ionic compounds contribute to the stability of their own structures.

In addition, Table 5 lists the Gibbs free energy change of the formation of each ionic salt. It is easy to find that except for a few ionic salts (D, E, and J in $N_3^-$ salts and D1, E1 in $O_2^+$ salts), the Gibbs free energy changes of the formation of other ionic salts are positive, indicating that these ionic salt structures can exist stably in thermodynamics. Figure 7 represents the effect of different anions on the Gibbs free energy of ionic salt generation. Relative to the other anions, the BF4$^-_3$ has the highest Gibbs free energy change of the formation of each ionic salt (345.36 kJ/mol for F and 452.44 kJ/mol for F1). In contrast, ionic salts containing N3$^-$ have the lowest Gibbs free energy change of the formation (-156.27 kJ/mol for D and -52.861 kJ/mol for D1). The negative Gibbs free energy change of the formation indicate that both D and D1 cannot exist stably, which is consistent with the conclusions of Christe’s study (Dixon et al., 2004). Also, our findings indicate that the free energy change of the ionic salt J formed from the N3$^-$ and $N_3^-$ is also negative, implying that this ionic salt also cannot exist stably, which is once again consistent with the conclusion of Christe’s study. However, the Gibbs free energy change of the formation of J1, an ionic salt formed from N9$^-$ and O2$^+$, becomes positive, implying that this compound can be thermodynamically stable. Finally, the order of the influence of other anions on the Gibbs free energy change of ionic salt are: BF4$^-_3$ > 3,5-Dinitro-1,2,4-triazole anion > 3,5-Dinitro-4H-pyrazole anion > C(NO2)$_2$ > N(NO2)$_2$ > NO$_2$ > 5-Nitro-tetrazole-1-N-oxide anion > N$_3^-$ > B(N3)$_4$ > N$_3^-$ for $N_3^-$ ionic salts or BF4$^-_3$ > 3,5-Dinitro-1,2,4-triazole anion > 3,5-Dinitro-4H-pyrazole anion > NO$_2$ > N(NO2)$_2$ > C(NO2)$_2$ > 5-Nitro-tetrazole-1-N-oxide anion > N$_3^-$ > B(N3)$_4$ > N$_3^-$ for $O_2^+$ ionic salts.

4 Conclusion

The combination of high-energy oxidants N9$^-$ and O2$^+$ with high nitrogen organic anions is a new design idea proposed with the help of quantum chemical calculations. This idea can not only ensure the overall high energy level of ionic salt, but also consider the thermodynamic stability. Most ionic salts have good detonation velocity and pressure because of their high density and enthalpy of formation, suggesting these ionic salts have potential as candidates for high-energy oxidants. The introduction of O2$^+$ into the system is an important means to improve the ionic salt oxygen balance. Considering the energy properties (enthalpy of formation, detonation velocity, detonation pressure, detonation heat, specific impulse) and stability (formation of Gibbs free energy) of these designed ionic salts, we believe that A, B, C, G, H for $N_3^-$ salts and A1, B1, C1, G1, H1 for $O_2^+$ salts are expected to be further studied and experimentally developed.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

XY: Investigation, data curation, visualization, theoretical calculation, writing-original draft. NL, YL, and SP: Writing-review and editing, funding acquisition, conceptualization.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.1005816/full#supplementary-material
Wilson, W. W., Vij, A., Vij, V., Bernhardt, E., and Christe, K. O. (2003). Polynitrogen chemistry: Preparation and characterization of \((N_5)_2SnF_6, N_5SnF_5,\) and \(N_5B(CF_3)_4\). *Chem. Eur. J.* 9 (12), 2840–2844. doi:10.1002/chem.200304973

Wong, M. W., Gill, P. M. W., Nobes, R. H., and Radom, L. (2002). A second-row analogue of the 8-311G(d) basis set: calculated heats of formation for second-row hydrides. *J. Phys. Chem.* 96 (17), 4875–4880. doi:10.1021/j100328a015

Xu, Y., Tian, L., Li, D., Wang, P., and Lu, M. (2019). A series of energetic cyclo-pentazolate salts: Rapid synthesis, characterization, and promising performance. *J. Mat. Chem. A Mat.* 7 (20), 12468–12479. doi:10.1039/c9ta01077g

Xu, Y., Wang, Q., Shen, C., Lin, Q., Wang, P., and Lu, M. (2017). A series of energetic metal pentazolate hydrates. *Nature* 549 (7670), 78–81. doi:10.1038/nature23662

Yang, C., Zhang, C., Zheng, Z., Jiang, C., Lin, J., Du, Y., et al. (2018). Synthesis and characterization of cyclo-pentazolate salts of \(NH_4^+, NH_2OH^+, N_2H_5^+, C(NH_2)_3^+,\) and \(N(CH_3)_4^+\). *J. Am. Chem. Soc.* 140 (48), 16488–16494. doi:10.1021/jacs.8b03106

Yu, Y., Li, Y. C., Chen, J. F., Sun, C. H., Li, J. S., Fan, G. J., et al. (2015). Towards understanding the stability of the \(N_5^+\)-containing salts: The role of counterions. *RSC Adv.* 5 (127), 104841–104845. doi:10.1039/c5ra16304h

Zeng, Z., and Bernstein, E. R. (2019). Ammonium perchlorate and ammonium dihydrogen phosphate as energetic materials: Comparison to ammonium nitrate. *J. Phys. Chem. C* 123 (19), 12149–12153. doi:10.1021/acs.jpcc.9b02410

Zhang, C., Sun, C., Hu, B., Yu, C., and Lu, M. (2017). Synthesis and characterization of the pentazolate anion cyclo-\(N_5\) in \((N_5)_6(H_3O)_3(NH_4)_4Cl\). *Science* 355 (6323), 374–376. doi:10.1126/science.aah3840

Zhao, Y., and Truhlar, D. G. (2007). The \(\text{M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four \(M06-\alpha\) class functionals and 12 other functionals.} \text{Theor. Chem. Acc.} 120 (1-3), 215–241. doi:10.1007/s00214-007-0310-x