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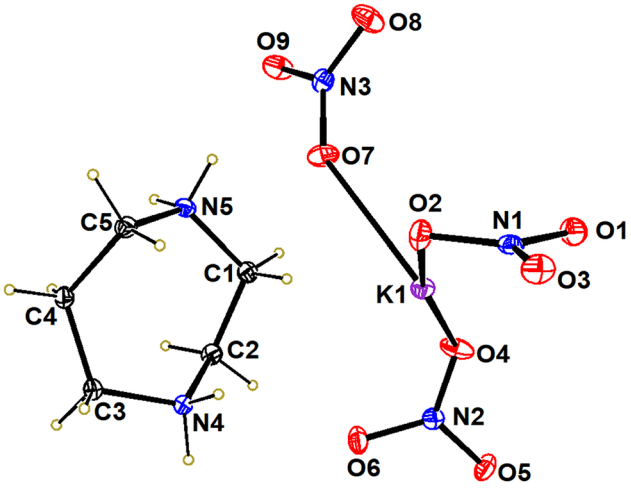
The crystal structure of 1,4-diazepane-1,4-diium potassium trinitrate, $C_5H_{14}KN_5O_9$



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Abstract

$C_5H_{14}KN_5O_9$, monoclinic, $P2_1/c$, a = 9.3820(3) Å, b = 9.3372(3) Å, c = 14.1593(5) Å, β = 98.916°, V = 1225.39 Å^3, Z = 4, $R_{gt}(F)$ = 0.0249, $wR_{ref}(F^2)$ = 0.0640, T = 100 K.

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The figure shows the thermal ellipsoid plot of asymmetric unit of a crystal structure with an ellipsoid ratio of 50 %.

1 Source of materials

1.002 g Homopiperazine (10 mmol), 1.011 g KNO_3 (10 mmol), and 1.983 g nitric acid (20 mmol) solids were dissolved into the 40 ml H_2O and stirred continuously at 50 °C for 30 min. The above mixture solution was slowly evaporated at room temperature for 2 weeks to get colorless and clear crystals.

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Table 1: Data collection and handling.

Crystal:	Block
Size:	0.20 × 0.17 × 0.15 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.49 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy R, φ and ω scans
θ_{max}, completeness:	25.0°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7141, 2152, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1,984
$N(param)_{refined}$:	181
Programs:	Rigaku[1], SHELX[3]

2 Experimental details

A summary of the crystal parameters, data acquisition, and refinement procedures can be found in Table 1 and the list of the atoms including atomic coordinates and displacement parameters can be found in Table 2. The multi-scan absorption correction was carried out by the SADABS[1] software. The initial structure determination was conducted via the Intrinsic Phasing technique within the OLEX2[2] interface by ShelXT.[3] Subsequent refinement was performed using the ShelXL.[4] Hydrogen atoms were positioned on the basis of riding model while their equivalent temperature factors (U_{eq}) set to 1.2 or 1.5 times those of respective parent atoms. These hydrogen atoms were then refined to convergence alongside the isotropic and anisotropic non-hydrogen atoms.

3 Comment

Molecular perovskite high-energetic materials are synthesized by simple and green methods without organic solvents, heavy metals, toxic organic components, or any explosive precursors.[5–7] They have a good oxygen balance, high crystal density, good stability, high packing coefficient, excellent environmental tolerance and low mechanical sensitivity, which shows great potential in the field of energetic materials.[8–11] Perovskite materials have excellent structural tunability. By regulating the A, B, and X sites of their structure, the photoelectric, catalytic, energy, and electromagnetic properties of the material can be controlled.[11] In this work, we regulated the A-site of perovskite structure to obtain better oxygen balance characteristics of high-energetic materials. The structure of the synthesized sample has a different A-site

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
K1	0.75066 (3)	0.76843 (3)	0.71592 (2)	0.01114 (11)
O1	1.06577 (11)	0.84480 (11)	0.79407 (7)	0.0137 (2)
O2	0.91516 (11)	1.01687 (11)	0.74704 (7)	0.0145 (2)
O3	1.09278 (11)	1.05463 (11)	0.86241 (7)	0.0149 (2)
O4	0.62558 (12)	0.50245 (12)	0.71879 (8)	0.0182 (3)
O5	0.52965 (11)	0.37818 (12)	0.82235 (7)	0.0161 (2)
O6	0.40946 (11)	0.55150 (12)	0.74667 (8)	0.0178 (3)
O7	0.66752 (12)	0.78384 (12)	0.52272 (7)	0.0182 (3)
O8	0.82679 (11)	0.77248 (12)	0.42626 (8)	0.0197 (3)
O9	0.60395 (11)	0.72022 (12)	0.37493 (8)	0.0180 (3)
N1	1.02530 (13)	0.97248 (13)	0.80123 (9)	0.0103 (3)
N2	0.52172 (13)	0.47851 (13)	0.76220 (9)	0.0110 (3)
N3	0.70080 (13)	0.75982 (13)	0.44227 (9)	0.0111 (3)
N4	0.20570 (13)	0.72462 (13)	0.62830 (9)	0.0101 (3)
H4A	0.298045	0.747168	0.653762	0.012*
H4B	0.160077	0.695140	0.677098	0.012*
N5	0.32914 (13)	0.71445 (13)	0.43029 (9)	0.0108 (3)
H5A	0.254849	0.688982	0.384147	0.013*
H5B	0.411584	0.710281	0.403971	0.013*
C1	0.33965 (15)	0.60694 (16)	0.50904 (10)	0.0119 (3)
H1A	0.426192	0.628677	0.556321	0.014*
H1B	0.353545	0.510945	0.482206	0.014*
C2	0.20934 (16)	0.60190 (15)	0.56038 (10)	0.0111 (3)
H2A	0.120475	0.603556	0.512483	0.013*
H2B	0.210519	0.510804	0.596269	0.013*
C3	0.13251 (16)	0.85772 (15)	0.58571 (10)	0.0122 (3)
H3A	0.167891	0.940234	0.626641	0.015*
H3B	0.027611	0.848746	0.586690	0.015*
C4	0.15577 (15)	0.88981 (16)	0.48338 (10)	0.0114 (3)
H4C	0.088019	0.829531	0.439799	0.014*
H4D	0.128505	0.990888	0.469315	0.014*
C5	0.30638 (16)	0.86704 (15)	0.45881 (11)	0.0117 (3)
H5C	0.320836	0.931585	0.405640	0.014*
H5D	0.378858	0.892078	0.514890	0.014*

compared to the literature, while the B and X sites are the same.[12]

The molecular perovskite energetic materials take 1,4-diazepane-1,4-diium as the A-site, potassium ions as the B-site, and nitrate as the X-site, respectively. The 1,4-diazepane-1,4-diium consists of a seven-membered ring with five carbon atoms and two nitrogen atoms. In the 1,4-diazepane-1,4-diium cation, the bond lengths of C1–C2, C4–C5 and C4–C3 are 1.517, 1.522 and 1.528 Å, respectively. Meanwhile, the three nitrate groups serve as the bridges, forming a framework of perovskite with K ions.

References

1. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* **2015**, *48* (1), 3–10.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341.
3. Sheldrick, G. M. SHELXT Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A Found. Adv.* **2015**, *71* (Pt 1), 3–8.
4. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *71* (1), 3–8.
5. Feng, Y.; Zhang, J.; Cao, W.; Zhang, J.; Shreeve, J. M. A Promising Perovskite Primary Explosive. *Nat. Commun.* **2023**, *14* (1), 7765.
6. Chen, S. L.; Yang, Z. R.; Wang, B. J.; Shang, Y.; Sun, L. Y.; Zhou, H. L.; Zhang, W. X.; Chen, X. M. Molecular Perovskite High-Energetic Materials. *Sci. China Mater.* **2018**, 1123–1128. https://doi.org/10.1007/s40843-017-9219-9.
7. Xu, J.; Zheng, S.; Huang, S.; Tian, Y.; Liu, Y.; Zhang, H.; Sun, J. Host-Guest Energetic Materials Constructed by Incorporating Oxidizing Gas Molecules into an Organic Lattice Cavity Toward Achieving Highly-Energetic and Low-Sensitivity Performance. *Chem. Commun*. **2019**, *55* (7), 909–9012.
8. Shang, Y.; Huang, R. K.; Chen, S. L.; He, C. T.; Yu, Z. H.; Ye, Z. M.; Zhang, W. X.; Chen, X. M. Metal-Free Molecular Perovskite High-Energetic Materials. *Cryst. Growth Des*. **2020**, *20* (3), 1013–1018.
9. Zhou, J.; Ding, L.; Zhao, F.; Wang, B.; Zhang, J. Thermal Studies of Novel Molecular Perovskite Energetic Material $(C_6H_{14}N_2)NH_4(ClO_4)_3$. *Chin. Chem. Lett*. **2019**, *31* (2), 554–558.
10. Shang, Y.; Chen, S. L.; Yu, Z. H.; Huang, R. K.; Ye, Z. M.; Zhang, W. X.; Chen, X. M. Silver(I)-Based Molecular Perovskite Energetic Compounds with Exceptional Thermal Stability and Energetic Performance. *Inorg. Chem.* **2022**, *61*, 4143–4149.
11. Chen, S. L.; Shang, Y.; He, C. T.; Sun, L. Y.; Ye, Z. M.; Zhang, W. X.; Chen, X. M. Optimizing the Oxygen Balance by Changing the A-Site Cations in Molecular Perovskite High Energetic Materials. *CrystEngComm* **2018**, *20* (46), 7458–7463.
12. Chen, S.; Shang, Y.; Jiang, J.; Huang, M.; Ren, J. T.; Guo, T.; Yu, C. X.; Zhang, W. X.; Chen, X. M. A New Nitrate-Based Energetic Molecular Perovskite as a Modern Edition of Black Powder. *Energ. Mater. Front.* **2022**, *3* (3), 122–127.