Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# Synthesis and crystal structure of bis(2-aminobenzimidazolium) *catena*-[metavanadate(V)]

**Kholida Jabborova,[a]* Jamshid Ashurov,[b] Akmaljon Tojiboev[c] and Shahlo Daminova[d,e]**

[a]Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, 100170, M. Ulugbek Str 77a, Tashkent, Uzbekistan, [b]Institute of Bioorganic Chemistry, Academy of Sciences of Uzbekistan, 100125, M. Ulugbek Str 83, Tashkent, Uzbekistan, [c]University of Geological Sciences, Olimlar Street, 64, Mirzo Ulugbek district, Tashkent, Uzbekistan, [d]National University of Uzbekistan named after Mirzo Ulugbek, University Street 4, Tashkent 100174, Uzbekistan, and [e]Uzbekistan–Japan Innovation Center of Youth, University Street 2B, Tashkent, 100095, Uzbekistan. *Correspondence e-mail: jabborova0707@gmail.com

Received 8 May 2024
Accepted 10 June 2024

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** crystal structure; 2-aminobenzimidazole; hybrid vanadate; hydrogen bonding.

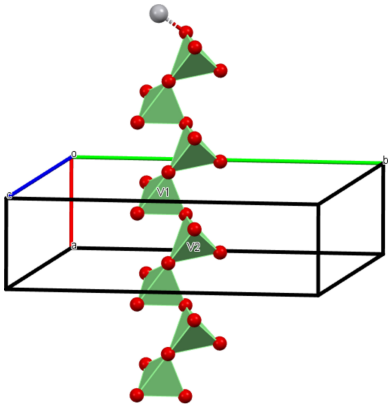
**CCDC reference:** 2291372

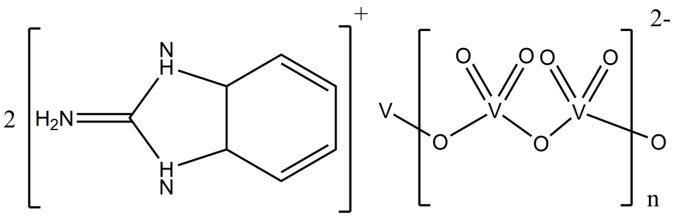
**Supporting information:** this article has supporting information at journals.iucr.org/e

The structure of polymeric *catena*-poly[2-aminobenzimidazolium [[dioxidovanadium(V)]-$\mu$-oxido]], $\{(C_7H_8N_3)_2[V_2O_6]\}_n$, has monoclinic symmetry. The title compound is of interest with respect to anticancer activity. In the crystal structure, infinite linear zigzag vanadate $(V_2O_6)^{2-}$ chains, constructed from corner-sharing $VO_4$ tetrahedra and that run parallel to the *a* axis, are present. Two different protonated 2-aminobenzimidazole molecules are located between the $(V_2O_6)^{2-}$ chains and form classical N—H···O hydrogen bonds with the vanadate oxygen atoms, which contribute to the cohesion of the structure.

## 1. Chemical context

In recent years, vanadate compounds have attracted attention in various fields due to their various compositions and interesting structures (Smith *et al.*, 2012; Wutkowski *et al.*, 2009; Wang *et al.*, 2007). This is partly due to the ability of vanadium to adopt tetrahedral [$VO_4$], square-pyramidal [$VO_5$], trigonal–bipyramidal [$VO_5$] or octahedral [$VO_6$] coordination environments together with possible stable oxidation states of +III, +IV and +V. Interestingly, all major vanadate compounds known to date containing cage-, shell-, belt-, barrel-, or basket-shaped entities are structurally related to the layer structure of vanadium pentoxide (Ishaque Khan *et al.*, 2000). These compounds have many practical pharmacological applications, ranging from anticancer agents to antifungal agents and, more recently, as insulin mimetics (Singh *et al.*, 2014; Abakumova *et al.*, 2012; Amin *et al.*, 2000) where they interact with several points in the cell-signaling pathway associated with the hormone insulin (Amin *et al.*, 2000; Srivastava & Mehdi, 2005). Studies have also indicated that vanadate compounds interact directly with glucose transporters located on the cell surface (Hiromura *et al.*, 2007; Makinen & Brady, 2002). Furthermore, vanadium has been found to have important interactions in DNA repair systems, making it a useful target for many oncological/pharmacological studies (Abakumova *et al.*, 2012; Kostova, 2009). Given the structural dependence on functions and application, a deeper study of the molecular and crystal structures of such complexes is warranted. In this context, we describe the synthesis and structural features of the polymeric title compound $\{(C_7H_8N_3)_2\ (V_2O_6)\}_n$.





## 2. Structural commentary

The asymmetric unit comprises two 2-aminobenzimidazolium cations (denoted *A* and *B*) and two V and six O atoms of the polymeric metavanadate anion (Fig. 1). The cationic molecules are almost planar (root-mean-square deviation for *A* = 0.0127 Å and for *B* = 0.0064 Å), and their N—C bond-length distributions are similar to those in related compounds (Aliabadi *et al.*, 2021; Ruzieva *et al.*, 2022). The linear zigzag metavanadate $(V_2O_6)^{2-}$ chain runs parallel to the *a* axis and is constructed from corner-sharing $VO_4$ tetrahedra (Fig. 2). Typical for such chains, the bridging O atoms (O3 and O4) have considerably longer V—O bonds than the terminal O atoms (O1 and O2 for the $V1O_4$ tetrahedron and O5 and O6 for the $V2O_4$ tetrahedron; Table 1). The corresponding V—O and V═O bond lengths are similar to those reported for related hybrid metavanadate compounds (Smith *et al.*, 2012; Wutkowski *et al.*, 2009; Wang *et al.*, 2007; Tyrselova *et al.*, 1996).

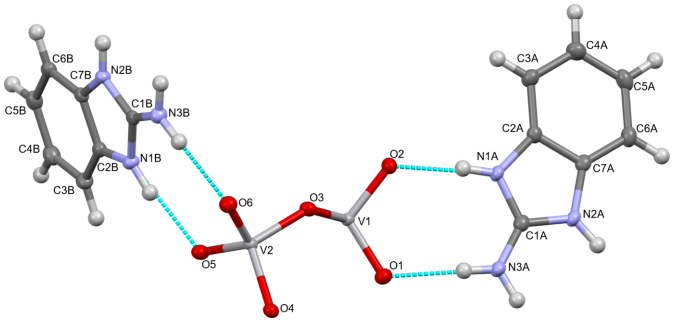


**Figure 1**
The asymmetric unit of the title compound with the labeling scheme and displacement ellipsoids drawn at the 50% probability level. Dotted lines indicate N—H···O hydrogen-bonding interactions.

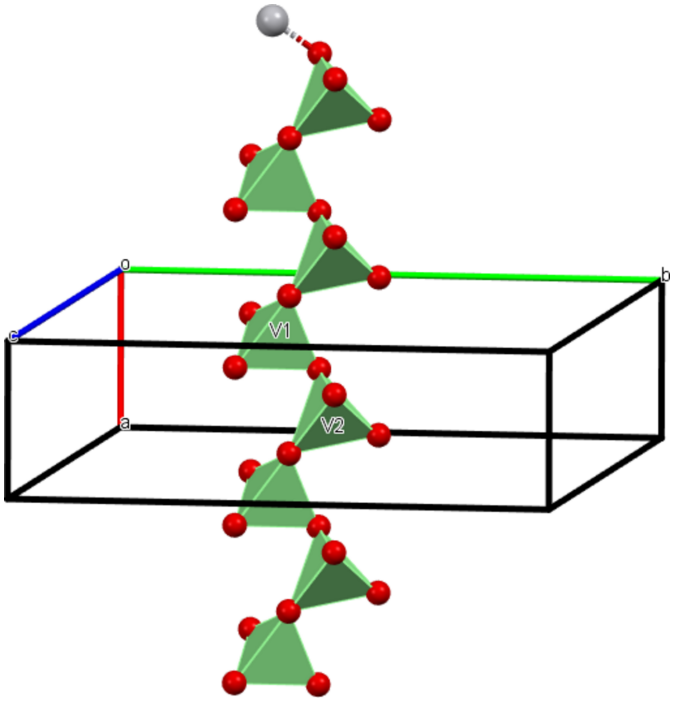


**Figure 2**
The metavanadate chain with the two different tetrahedra in polyhedral representation.

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| V1—O1 | 1.6300 (14) | V2—O6 | 1.6317 (14) |
| V1—O2 | 1.6534 (14) | V2—O5 | 1.6521 (14) |
| V1—O3 | 1.8061 (15) | V2—O3 | 1.8049 (14) |
| V1—O4$^{i}$ | 1.8280 (14) | V2—O4 | 1.8118 (14) |

Symmetry code: (i) $x+1, y, z$.

## 3. Supramolecular features

The crystal packing exhibits an intricate network of classical intermolecular N—H···O hydrogen bonds between the NH and $NH_2$ groups of the cations and all oxygen atoms of the metavanadate chain (Fig. 3, Table 2). Additional short

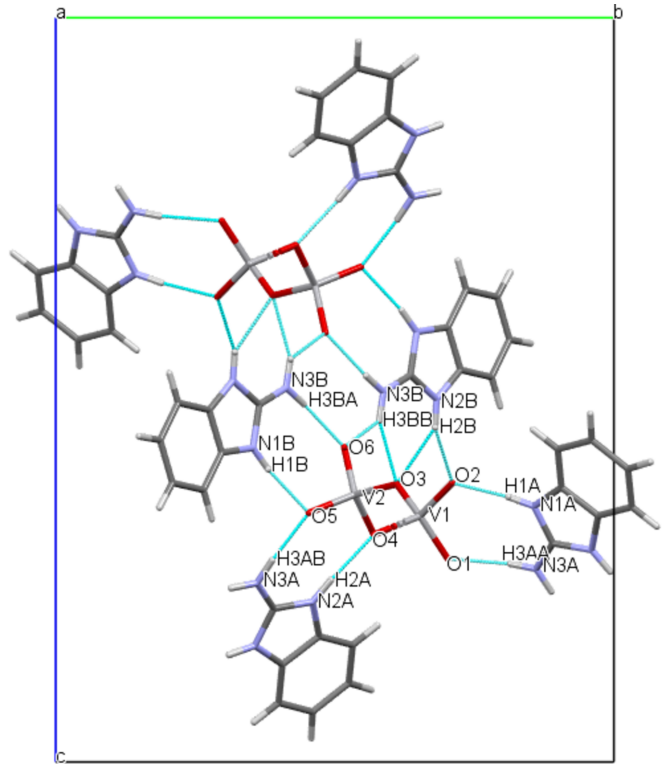


**Figure 3**
View of the crystal structure of the title compound along the *a* axis, showing N—H···O hydrogen bonds drawn as blue dotted lines.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3$B$—H3$BA$···O6 | 0.88 | 1.97 | 2.830 | 169 (2) |
| N1$A$—H1$A$···O2 | 0.87 | 1.85 | 2.722 | 174 (2) |
| N1$B$—H1$B$···O5 | 0.88 | 1.91 | 2.774 | 171 (2) |
| N3$A$—H3$AA$···O1 | 0.87 | 1.97 | 2.837 | 169 (2) |
| N2$A$—H2$A$···O4$^{ii}$ | 0.87 | 1.93 | 2.798 | 177 (2) |
| N2$B$—H2$B$···O2$^{iii}$ | 0.87 | 2.44 | 3.123 | 137 (2) |
| N2$B$—H2$B$···O3$^{iv}$ | 0.87 | 2.26 | 2.960 | 138 (2) |
| N3$B$—H3$BB$···O3$^{iv}$ | 0.87 | 2.18 | 2.938 | 145 (2) |
| N3$B$—H3$BB$···O6$^{v}$ | 0.87 | 2.41 | 2.887 | 115 (2) |
| N3$A$—H3$AB$···O5$^{ii}$ | 0.88 | 1.90 | 2.779 | 175 (2) |

Symmetry codes: (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $-x-1, -y+1, -z+1$.

contacts (Fig. 4) between the vanadate O6 atom and the centroid of the N1$B$/C1$B$/N2$B$/C7$B$/C2$B$ ring (V2—O6···$Cg4$($-1+x, y, z$) = 3.8768 (16) Å) consolidate the tri-periodic network structure.

## 4. Database survey

A search in the Cambridge Structural Database (CSD, version 5.43, update of November 2022; Groom *et al.*, 2016) revealed four hybrid compounds with protonated 2-aminobenzimidazole moieties, two with gallium (WURVAJ, WURVEN; Aliabadi *et al.*, 2021) and two with lanthanum (JARVOQ, WEGRAF; Ruzieva *et al.*, 2022). A search for the metavanadate moiety with linear zigzag chains similar to that in the title structure gave the following hits: CEHQEN and CEHQIR, for which dipole moments were calculated using iterative Hirshfeld partial atomic charges (Smith *et al.*, 2012); $(H_3NCH_2CH_2NH_3)(V_2O_6)$ (FUDLOF02; Ishaque Khan *et al.*, 2000); 1,6-hexanediammonium metavanadate (KOYJAJ; Tyršelová & Pavelčík, 1992); 3-aza-1,5-pentamethylenediammonium metavanadate (KUGGUO; Roman *et al.*, 1992); $[Cu(H_2O)(C_5H_{14}N_2)_2](VO_3)_2$ (POYNAT; Wutkowski *et al.*, 2009); *catena*-poly[*N*,*N*′-bis(2-ammonioethyl)oxamide [dioxidovanadate-$\mu$-oxido-dioxidovanadate-$\mu$-oxido]] (TIGBUH; Wang *et al.*, 2007); *catena*-poly[2,2′,2″-nitrilotris(ethanaminium) [tri-$\mu$-oxido-tris[dioxidovanadate(V)]] monohydrate] (VIPRET; Chang *et al.*, 2013); {piperazinediium poly[trioxovanadate], $\{(C_4H_{12}N_2)(VO_3)_2\}$ (ZITSEA; Tyrselova *et al.*, 1996); *catena*[bis[tris(2-ammonioethyl)amine]hexakis($\mu_2$-oxo)dodecaoxohexavanadium trihydrate] (IMATOG; Li *et al.*, 2009); *catena*-[pentakis(cyclohexylammonium) pentakis($\mu_2$-oxo)decaoxopentavanadium(V)] (NACFON; Wang *et al.*, 2004).

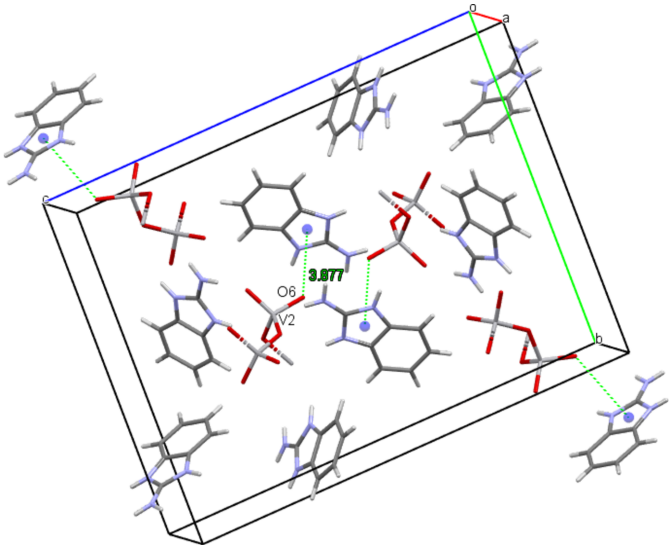



**Figure 4**
V2—O6···$Cg4$ interactions in the crystal structure of the title compound.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $(C_7H_8N_3)_2[V_2O_6]$ |
| $M_r$ | 466.21 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 100 |
| $a, b, c$ (Å) | 4.8817 (1), 16.8263 (2), 22.4354 (2) |
| $\beta$ (°) | 90.675 (1) |
| $V$ (Å$^3$) | 1842.74 (5) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 8.93 |
| Crystal size (mm) | 0.28 × 0.24 × 0.18 |
| Data collection | |
| Diffractometer | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2020) |
| $T_{min}$, $T_{max}$ | 0.349, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 17440, 3540, 3413 |
| $R_{int}$ | 0.037 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.615 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.030, 0.084, 1.07 |
| No. of reflections | 3540 |
| No. of parameters | 286 |
| No. of restraints | 8 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.38, −0.44 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

## 5. Synthesis and crystallization

All reagents for synthesis and analysis were commercially available and purchased from Sigma Aldrich and used as received without further purification. Chemically pure vanadyl acetylacetonate, 2-aminobenzimidazole, and 96% vol ethanol were used. Vanadyl acetylacetonate (0.0265 g, 1 mmol) dissolved in 5 ml of EtOH and 2-aminobenzimidazole (0.0133 g, 1 mmol) dissolved in 5 ml of EtOH were mixed with constant stirring until the color of the solution turned to green. The stirring was continued for three hours. The resulting green solution was then allowed to cool to room temperature and green crystals were grown over seven days *via* slow evaporation of the mother liquor. Selected IR bands (KBr pellet,

$cm^{-1}$): 3447 (N—H), 1647 (C═N), 868 (V═O), 898 (V—O), 943 (O═V═O), 655 (V—O—V).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms bound to C atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.95 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C). H atoms bound to N atoms were discernible in difference-Fourier maps and were refined with N—H bond length restraints of 0.86 (2) Å.

## Acknowledgements

The authors acknowledge support from the MIRAI FUND (JICA) and technical equipment support provided by the Institute of Bioorganic Chemistry of Academy Sciences of Uzbekistan.

## References

Abakumova, O. Y., Podobed, O. V., Belayeva, N. F. & Tochilkin, A. I. (2012). *Biochem. Moscow Suppl. Ser. B*, **6**, 164–170.
Aliabadi, A., Hakimi, M., Hosseinabadi, F., Motieiyan, E., Rodrigues, V. H. N., Ghadermazi, M., Marabello, D. & Abdolmaleki, S. (2021). *J. Mol. Struct.* **1223**, 129005.
Amin, S. S., Cryer, K., Zhang, B., Dutta, S. K., Eaton, S. S., Anderson, O. P., Miller, S. M., Reul, B. A., Brichard, S. M. & Crans, D. C. (2000). *Inorg. Chem.* **39**, 406–416.
Chang, K. B., Smith, M. D., Zeller, M. & Norquist, A. J. (2013). *Acta Cryst.* E**69**, m570–m571.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Hiromura, M., Nakayama, A., Adachi, Y., Doi, M. & Sakurai, H. (2007). *J. Biol. Inorg. Chem.* **12**, 1275–1287.
Ishaque Khan, M., Hope, T., Cevik, S., Zheng, Ch. & Powell, D. (2000). *J. Cluster Sci.* **11**, 433–447.
Kostova, I. (2009). *Anticancer Agents Med. Chem.* **9**, 827–842.
Li, J., Xing, Y. H., Ge, M. F., Wang, C. G., Li, Z. P. & Niu, S. Y. (2009). *J. Struct. Chem.* **50**, 532–538.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Makinen, M. W. & Brady, M. J. (2002). *J. Biol. Chem.* **277**, 12215–12220.
Rigaku OD (2020). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Roman, P., Macias, R., Luque, A. & Gutiérrez-Zorrilla, J. M. (1992). *Mater. Res. Bull.* **27**, 573–580.
Ruzieva, B., Kunafiev, R., Kadirova, Z. & Daminova, S. (2022). *Acta Cryst.* E**78**, 647–651.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Singh, R., Neerupama, G. K., Sharma, P. & Sachar, R. (2014). *Chem. Sci. Trans.* **3**, 1099–1109.
Smith, M. D., Blau, M. S., Chang, B. K., Tran, T. T., Zeller, M., Halasyamani, P. Sh., Schrier, J. & Norquist, A. J. (2012). *J. Solid State Chem.* **195**, 86–93.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Srivastava, A. K. & Mehdi, M. Z. (2005). *Diabet. Med.* **22**, 2–13.
Tyrselová, J., Kuchta, L. & Pavelcík, F. (1996). *Acta Cryst.* C**52**, 17–19.
Tyršelová, J. & Pavelčík, F. (1992). *Acta Cryst.* C**48**, 1207–1209.
Wang, G.-M., Li, J.-H., Han, J. & Liu, H.-L. (2007). *Acta Cryst.* E**63**, m2189.
Wang, J. P., Zhao, J. W., Niu, J. Y. & Bo, Y. (2004). *Jiegou Huaxue*, **23**, 655.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wutkowski, A., Näther, C. & Bensch, W. (2009). *Z. Anorg. Allg. Chem.* **635**, 753–758.

# supporting information

*Acta Cryst.* (2024). E**80**, 751-754 [https://doi.org/10.1107/S2056989024005528]

## Synthesis and crystal structure of bis(2-aminobenzimidazolium) *catena*-[metavanadate(V)]

**Kholida Jabborova, Jamshid Ashurov, Akmaljon Tojiboev and Shahlo Daminova**

### Computing details

***catena*-Poly[2-aminobenzimidazolium [[dioxidovanadium(V)]-*μ*-oxido]]**

*Crystal data*

$(C_7H_8N_3)_2[V_2O_6]$
$M_r$ = 466.21
Monoclinic, $P2_1/c$
$a$ = 4.8817 (1) Å
$b$ = 16.8263 (2) Å
$c$ = 22.4354 (2) Å
$\beta$ = 90.675 (1)°
$V$ = 1842.74 (5) Å$^3$
$Z$ = 4
$F(000)$ = 944
$D_x$ = 1.680 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54184 Å
Cell parameters from 11386 reflections
$\theta$ = 3.3–71.2°
$\mu$ = 8.93 mm$^{-1}$
$T$ = 100 K
Block, green
0.28 × 0.24 × 0.18 mm

*Data collection*

XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer
Detector resolution: 10.0000 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2020)
$T_{min}$ = 0.349, $T_{max}$ = 1.000
17440 measured reflections
3540 independent reflections
3413 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 71.5°, $\theta_{min}$ = 3.3°
$h$ = −5→5
$k$ = −20→20
$l$ = −27→27

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.084
$S$ = 1.07
3540 reflections
286 parameters
8 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 1.0444P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.44 e Å$^{-3}$
Extinction correction: SHELXL (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00059 (12)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| V2 | −0.28372 (6) | 0.46447 (2) | 0.35937 (2) | 0.01360 (11) |
| V1 | 0.24874 (6) | 0.34781 (2) | 0.33048 (2) | 0.01340 (11) |
| O4 | −0.5361 (3) | 0.42994 (8) | 0.30547 (6) | 0.0165 (3) |
| O6 | −0.4298 (3) | 0.48306 (8) | 0.42291 (6) | 0.0194 (3) |
| O3 | −0.0282 (3) | 0.38899 (8) | 0.37331 (6) | 0.0175 (3) |
| O2 | 0.4310 (3) | 0.28954 (8) | 0.37509 (6) | 0.0182 (3) |
| O5 | −0.1386 (3) | 0.54667 (8) | 0.33474 (6) | 0.0194 (3) |
| O1 | 0.1365 (3) | 0.29770 (8) | 0.27302 (6) | 0.0213 (3) |
| N2B | 0.1986 (3) | 0.68245 (10) | 0.51241 (7) | 0.0161 (3) |
| N1B | 0.0739 (3) | 0.64665 (10) | 0.42202 (7) | 0.0165 (3) |
| N1A | 0.6212 (4) | 0.14345 (10) | 0.34384 (7) | 0.0175 (3) |
| N3B | −0.1562 (4) | 0.58715 (10) | 0.50284 (7) | 0.0190 (3) |
| N3A | 0.3272 (4) | 0.13954 (10) | 0.25959 (8) | 0.0209 (4) |
| N2A | 0.6531 (4) | 0.03991 (10) | 0.28485 (7) | 0.0176 (3) |
| C2A | 0.8201 (4) | 0.09402 (11) | 0.36893 (9) | 0.0170 (4) |
| C1B | 0.0284 (4) | 0.63523 (11) | 0.48039 (8) | 0.0154 (4) |
| C1A | 0.5216 (4) | 0.10926 (12) | 0.29382 (9) | 0.0176 (4) |
| C2B | 0.2814 (4) | 0.70255 (11) | 0.41573 (8) | 0.0158 (4) |
| C7B | 0.3623 (4) | 0.72532 (11) | 0.47309 (8) | 0.0155 (4) |
| C7A | 0.8420 (4) | 0.02816 (12) | 0.33111 (9) | 0.0171 (4) |
| C3B | 0.4005 (4) | 0.73529 (12) | 0.36553 (9) | 0.0201 (4) |
| H3B | 0.343148 | 0.720517 | 0.326468 | 0.024* |
| C6B | 0.5667 (4) | 0.78067 (12) | 0.48278 (9) | 0.0181 (4) |
| H6B | 0.621111 | 0.796047 | 0.521905 | 0.022* |
| C3A | 0.9760 (4) | 0.10065 (12) | 0.42048 (9) | 0.0212 (4) |
| H3A | 0.957695 | 0.144818 | 0.446506 | 0.025* |
| C5B | 0.6896 (4) | 0.81295 (12) | 0.43252 (9) | 0.0210 (4) |
| H5B | 0.832215 | 0.850884 | 0.437509 | 0.025* |
| C4B | 0.6082 (4) | 0.79089 (12) | 0.37508 (9) | 0.0221 (4) |
| H4B | 0.695992 | 0.814193 | 0.341798 | 0.027* |
| C4A | 1.1607 (5) | 0.03984 (13) | 0.43252 (10) | 0.0248 (5) |
| H4A | 1.271173 | 0.042284 | 0.467625 | 0.030* |
| C6A | 1.0281 (4) | −0.03202 (12) | 0.34269 (10) | 0.0213 (4) |
| H6A | 1.045994 | −0.076194 | 0.316655 | 0.026* |
| C5A | 1.1874 (4) | −0.02505 (13) | 0.39392 (10) | 0.0242 (4) |
| H5A | 1.317900 | −0.065244 | 0.403102 | 0.029* |
| H3BA | −0.259 (4) | 0.5555 (12) | 0.4812 (9) | 0.023 (6)* |
| H2B | 0.217 (5) | 0.6788 (16) | 0.5508 (5) | 0.026 (7)* |
| H3AA | 0.251 (5) | 0.1857 (9) | 0.2664 (12) | 0.031 (7)* |

| | | | | |
|---|---|---|---|---|
| H2A | 0.619 (5) | 0.0069 (13) | 0.2558 (9) | 0.029 (7)* |
| H3BB | −0.160 (5) | 0.5797 (17) | 0.5413 (5) | 0.034 (7)* |
| H3AB | 0.263 (5) | 0.1129 (14) | 0.2288 (8) | 0.027 (7)* |
| H1B | −0.004 (5) | 0.6193 (15) | 0.3933 (9) | 0.036 (7)* |
| H1A | 0.566 (5) | 0.1897 (9) | 0.3563 (12) | 0.035 (7)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| V2 | 0.01470 (19) | 0.01364 (18) | 0.01242 (17) | −0.00046 (11) | −0.00200 (12) | 0.00155 (11) |
| V1 | 0.01604 (19) | 0.01193 (17) | 0.01219 (17) | −0.00065 (11) | −0.00225 (12) | 0.00014 (11) |
| O4 | 0.0192 (7) | 0.0153 (7) | 0.0150 (6) | −0.0008 (5) | −0.0029 (5) | 0.0023 (5) |
| O6 | 0.0199 (7) | 0.0207 (7) | 0.0174 (7) | −0.0005 (5) | 0.0004 (5) | 0.0001 (5) |
| O3 | 0.0172 (7) | 0.0192 (7) | 0.0160 (6) | 0.0011 (5) | −0.0027 (5) | 0.0011 (5) |
| O2 | 0.0226 (7) | 0.0155 (7) | 0.0166 (6) | 0.0018 (5) | −0.0009 (5) | 0.0001 (5) |
| O5 | 0.0227 (7) | 0.0195 (7) | 0.0159 (7) | −0.0033 (5) | −0.0033 (5) | 0.0026 (5) |
| O1 | 0.0268 (8) | 0.0190 (7) | 0.0181 (7) | −0.0018 (6) | −0.0043 (6) | −0.0015 (5) |
| N2B | 0.0208 (8) | 0.0151 (8) | 0.0124 (7) | −0.0007 (6) | −0.0026 (6) | 0.0011 (6) |
| N1B | 0.0185 (8) | 0.0177 (8) | 0.0133 (8) | −0.0022 (6) | −0.0008 (6) | −0.0012 (6) |
| N1A | 0.0224 (9) | 0.0134 (8) | 0.0165 (8) | 0.0013 (6) | −0.0017 (7) | −0.0042 (6) |
| N3B | 0.0218 (9) | 0.0186 (8) | 0.0165 (8) | −0.0027 (7) | 0.0006 (7) | 0.0002 (7) |
| N3A | 0.0291 (10) | 0.0164 (8) | 0.0171 (8) | 0.0017 (7) | −0.0044 (7) | −0.0037 (7) |
| N2A | 0.0225 (9) | 0.0141 (8) | 0.0162 (8) | −0.0013 (6) | −0.0004 (7) | −0.0035 (6) |
| C2A | 0.0166 (9) | 0.0150 (9) | 0.0195 (9) | −0.0016 (7) | 0.0008 (7) | 0.0005 (7) |
| C1B | 0.0174 (9) | 0.0133 (9) | 0.0155 (9) | 0.0042 (7) | −0.0017 (7) | −0.0001 (7) |
| C1A | 0.0206 (10) | 0.0164 (9) | 0.0159 (9) | −0.0030 (7) | 0.0022 (7) | −0.0001 (7) |
| C2B | 0.0166 (9) | 0.0141 (9) | 0.0168 (9) | 0.0016 (7) | −0.0008 (7) | −0.0005 (7) |
| C7B | 0.0165 (9) | 0.0147 (9) | 0.0152 (9) | 0.0028 (7) | 0.0001 (7) | 0.0011 (7) |
| C7A | 0.0184 (10) | 0.0168 (9) | 0.0161 (9) | −0.0024 (7) | 0.0038 (7) | −0.0006 (7) |
| C3B | 0.0258 (11) | 0.0198 (10) | 0.0148 (9) | 0.0014 (8) | 0.0022 (8) | 0.0003 (7) |
| C6B | 0.0181 (10) | 0.0168 (9) | 0.0194 (10) | 0.0015 (7) | −0.0039 (7) | −0.0003 (7) |
| C3A | 0.0212 (10) | 0.0203 (10) | 0.0220 (10) | −0.0012 (8) | −0.0013 (8) | −0.0035 (8) |
| C5B | 0.0171 (10) | 0.0178 (10) | 0.0282 (10) | −0.0004 (8) | −0.0006 (8) | 0.0020 (8) |
| C4B | 0.0242 (11) | 0.0203 (10) | 0.0221 (10) | 0.0015 (8) | 0.0060 (8) | 0.0043 (8) |
| C4A | 0.0223 (11) | 0.0260 (11) | 0.0261 (11) | −0.0008 (8) | −0.0047 (9) | 0.0012 (8) |
| C6A | 0.0220 (10) | 0.0164 (10) | 0.0256 (10) | 0.0000 (7) | 0.0043 (8) | −0.0007 (8) |
| C5A | 0.0202 (10) | 0.0199 (10) | 0.0326 (12) | 0.0027 (8) | 0.0008 (9) | 0.0053 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| V1—O1 | 1.6300 (14) | N2A—C1A | 1.348 (3) |
| V1—O2 | 1.6534 (14) | N2A—C7A | 1.394 (3) |
| V1—O3 | 1.8061 (15) | N2A—H2A | 0.871 (10) |
| V1—O4$^{i}$ | 1.8280 (14) | C2A—C3A | 1.381 (3) |
| V2—O6 | 1.6317 (14) | C2A—C7A | 1.401 (3) |
| V2—O5 | 1.6521 (14) | C2B—C3B | 1.387 (3) |
| V2—O3 | 1.8049 (14) | C2B—C7B | 1.395 (3) |
| V2—O4 | 1.8118 (14) | C7B—C6B | 1.380 (3) |

| | | | |
|---|---|---|---|
| V2—V1$^{ii}$ | 3.0736 (4) | C7A—C6A | 1.383 (3) |
| N2B—C1B | 1.351 (3) | C3B—C4B | 1.394 (3) |
| N2B—C7B | 1.398 (2) | C3B—H3B | 0.9500 |
| N2B—H2B | 0.866 (10) | C6B—C5B | 1.394 (3) |
| N1B—C1B | 1.345 (3) | C6B—H6B | 0.9500 |
| N1B—C2B | 1.391 (3) | C3A—C4A | 1.388 (3) |
| N1B—H1B | 0.873 (10) | C3A—H3A | 0.9500 |
| N1A—C1A | 1.347 (3) | C5B—C4B | 1.394 (3) |
| N1A—C2A | 1.393 (3) | C5B—H5B | 0.9500 |
| N1A—H1A | 0.871 (10) | C4B—H4B | 0.9500 |
| N3B—C1B | 1.315 (3) | C4A—C5A | 1.401 (3) |
| N3B—H3BA | 0.874 (10) | C4A—H4A | 0.9500 |
| N3B—H3BB | 0.873 (10) | C6A—C5A | 1.385 (3) |
| N3A—C1A | 1.316 (3) | C6A—H6A | 0.9500 |
| N3A—H3AA | 0.875 (10) | C5A—H5A | 0.9500 |
| N3A—H3AB | 0.877 (10) | | |

| | | | |
|---|---|---|---|
| O6—V2—O5 | 108.98 (7) | N1B—C1B—N2B | 109.04 (17) |
| O6—V2—O3 | 106.96 (7) | N3A—C1A—N1A | 124.85 (18) |
| O5—V2—O3 | 110.42 (7) | N3A—C1A—N2A | 126.10 (18) |
| O6—V2—O4 | 110.11 (7) | N1A—C1A—N2A | 109.05 (17) |
| O5—V2—O4 | 109.64 (7) | C3B—C2B—N1B | 131.57 (18) |
| O3—V2—O4 | 110.68 (6) | C3B—C2B—C7B | 121.52 (18) |
| O1—V1—O2 | 110.21 (7) | N1B—C2B—C7B | 106.90 (16) |
| O1—V1—O3 | 111.87 (7) | C6B—C7B—C2B | 121.79 (18) |
| O2—V1—O3 | 107.84 (6) | C6B—C7B—N2B | 131.79 (18) |
| O1—V1—O4$^{i}$ | 109.71 (7) | C2B—C7B—N2B | 106.42 (16) |
| O2—V1—O4$^{i}$ | 109.10 (7) | C6A—C7A—N2A | 132.15 (18) |
| O3—V1—O4$^{i}$ | 108.04 (6) | C6A—C7A—C2A | 121.32 (19) |
| V2—O4—V1$^{ii}$ | 115.22 (7) | N2A—C7A—C2A | 106.53 (17) |
| V2—O3—V1 | 134.26 (8) | C2B—C3B—C4B | 116.91 (19) |
| C1B—N2B—C7B | 108.71 (16) | C2B—C3B—H3B | 121.5 |
| C1B—N2B—H2B | 122.9 (18) | C4B—C3B—H3B | 121.5 |
| C7B—N2B—H2B | 127.5 (18) | C7B—C6B—C5B | 116.93 (18) |
| C1B—N1B—C2B | 108.93 (16) | C7B—C6B—H6B | 121.5 |
| C1B—N1B—H1B | 124.6 (19) | C5B—C6B—H6B | 121.5 |
| C2B—N1B—H1B | 126.2 (19) | C2A—C3A—C4A | 116.97 (19) |
| C1A—N1A—C2A | 108.96 (16) | C2A—C3A—H3A | 121.5 |
| C1A—N1A—H1A | 122.5 (19) | C4A—C3A—H3A | 121.5 |
| C2A—N1A—H1A | 128.5 (19) | C6B—C5B—C4B | 121.54 (19) |
| C1B—N3B—H3BA | 123.6 (16) | C6B—C5B—H5B | 119.2 |
| C1B—N3B—H3BB | 119.4 (19) | C4B—C5B—H5B | 119.2 |
| H3BA—N3B—H3BB | 116 (3) | C3B—C4B—C5B | 121.30 (18) |
| C1A—N3A—H3AA | 123.1 (18) | C3B—C4B—H4B | 119.4 |
| C1A—N3A—H3AB | 120.6 (18) | C5B—C4B—H4B | 119.4 |
| H3AA—N3A—H3AB | 116 (2) | C3A—C4A—C5A | 121.3 (2) |
| C1A—N2A—C7A | 108.88 (16) | C3A—C4A—H4A | 119.4 |
| C1A—N2A—H2A | 125.2 (18) | C5A—C4A—H4A | 119.4 |

| | | | |
|---|---|---|---|
| C7A—N2A—H2A | 125.9 (18) | C7A—C6A—C5A | 117.07 (19) |
| C3A—C2A—N1A | 131.68 (18) | C7A—C6A—H6A | 121.5 |
| C3A—C2A—C7A | 121.74 (19) | C5A—C6A—H6A | 121.5 |
| N1A—C2A—C7A | 106.57 (17) | C6A—C5A—C4A | 121.6 (2) |
| N3B—C1B—N1B | 125.63 (18) | C6A—C5A—H5A | 119.2 |
| N3B—C1B—N2B | 125.31 (18) | C4A—C5A—H5A | 119.2 |

| | | | |
|---|---|---|---|
| O6—V2—O4—V1$^{ii}$ | −51.54 (10) | C3B—C2B—C7B—N2B | 178.79 (18) |
| O5—V2—O4—V1$^{ii}$ | −171.43 (7) | N1B—C2B—C7B—N2B | −0.4 (2) |
| O3—V2—O4—V1$^{ii}$ | 66.52 (9) | C1B—N2B—C7B—C6B | −179.8 (2) |
| O6—V2—O3—V1 | −168.95 (10) | C1B—N2B—C7B—C2B | 0.6 (2) |
| O5—V2—O3—V1 | −50.50 (13) | C1A—N2A—C7A—C6A | −179.1 (2) |
| O4—V2—O3—V1 | 71.09 (12) | C1A—N2A—C7A—C2A | −0.1 (2) |
| V1$^{ii}$—V2—O3—V1 | 100.81 (10) | C3A—C2A—C7A—C6A | −2.3 (3) |
| O1—V1—O3—V2 | −67.14 (13) | N1A—C2A—C7A—C6A | 178.54 (17) |
| O2—V1—O3—V2 | 171.52 (10) | C3A—C2A—C7A—N2A | 178.57 (17) |
| O4$^{i}$—V1—O3—V2 | 53.72 (12) | N1A—C2A—C7A—N2A | −0.6 (2) |
| V2$^{i}$—V1—O3—V2 | 86.44 (11) | N1B—C2B—C3B—C4B | −179.92 (19) |
| C1A—N1A—C2A—C3A | −177.9 (2) | C7B—C2B—C3B—C4B | 1.2 (3) |
| C1A—N1A—C2A—C7A | 1.1 (2) | C2B—C7B—C6B—C5B | −0.1 (3) |
| C2B—N1B—C1B—N3B | 179.08 (18) | N2B—C7B—C6B—C5B | −179.57 (19) |
| C2B—N1B—C1B—N2B | 0.5 (2) | N1A—C2A—C3A—C4A | −179.6 (2) |
| C7B—N2B—C1B—N3B | −179.32 (18) | C7A—C2A—C3A—C4A | 1.5 (3) |
| C7B—N2B—C1B—N1B | −0.7 (2) | C7B—C6B—C5B—C4B | 0.6 (3) |
| C2A—N1A—C1A—N3A | 178.88 (18) | C2B—C3B—C4B—C5B | −0.7 (3) |
| C2A—N1A—C1A—N2A | −1.2 (2) | C6B—C5B—C4B—C3B | −0.2 (3) |
| C7A—N2A—C1A—N3A | −179.26 (19) | C2A—C3A—C4A—C5A | 0.2 (3) |
| C7A—N2A—C1A—N1A | 0.8 (2) | N2A—C7A—C6A—C5A | −179.8 (2) |
| C1B—N1B—C2B—C3B | −179.1 (2) | C2A—C7A—C6A—C5A | 1.3 (3) |
| C1B—N1B—C2B—C7B | 0.0 (2) | C7A—C6A—C5A—C4A | 0.3 (3) |
| C3B—C2B—C7B—C6B | −0.8 (3) | C3A—C4A—C5A—C6A | −1.0 (3) |
| N1B—C2B—C7B—C6B | −179.98 (17) | | |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*−1, *y*, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3*B*—H3*BA*···O6 | 0.88 | 1.97 | 2.830 | 169 (2) |
| N1*A*—H1*A*···O2 | 0.87 | 1.85 | 2.722 | 174 (2) |
| N1*B*—H1*B*···O5 | 0.88 | 1.91 | 2.774 | 171 (2) |
| N3*A*—H3*AA*···O1 | 0.87 | 1.97 | 2.837 | 169 (2) |
| N2*A*—H2*A*···O4$^{iii}$ | 0.87 | 1.93 | 2.798 | 177 (2) |
| N2*B*—H2*B*···O2$^{iv}$ | 0.87 | 2.44 | 3.123 | 137 (2) |
| N2*B*—H2*B*···O3$^{v}$ | 0.87 | 2.26 | 2.960 | 138 (2) |
| N3*B*—H3*BB*···O3$^{v}$ | 0.87 | 2.18 | 2.938 | 145 (2) |

| | | | | |
|---|---|---|---|---|
| N3*B*—H3*BB*···O6$^{vi}$ | 0.87 | 2.41 | 2.887 | 115 (2) |
| N3*A*—H3*AB*···O5$^{iii}$ | 0.88 | 1.90 | 2.779 | 175 (2) |

Symmetry codes: (iii) −*x*, *y*−1/2, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*, −*y*+1, −*z*+1; (vi) −*x*−1, −*y*+1, −*z*+1.