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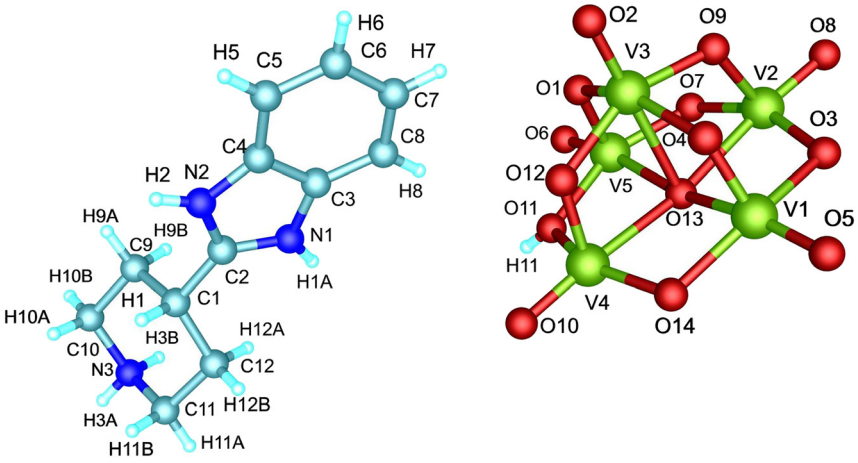
The crystal structure of bis(2-(piperidin-1-ium-4-yl)-1Hbenzo[d]imidazol-3-ium) dihydrogen decavanadate, $C_{24}H_{36}N_6O_{28}V_{10}$



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Abstract

$C_{24}H_{36}N_6O_{28}V_{10}$, monoclinic, $P2_1/c$ (no. 14), a = 10.4869(6) Å, b = 11.5123(7) Å, c = 17.4627(9) Å, β = 108.459(3)°, V = 1999.8(2) Å^3, Z = 2, $R_{gt}(F)$ = 0.0209, $wR_{ref}(F^2)$ = 0.0582, T = 296 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.23 × 0.22 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.33 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II,
θ_{max}, completeness:	25.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9980, 3600, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3286
$N(param)_{refined}$:	311
Programs:	Bruker,[1] Olex2,[2] SHELX[3,4]

1 Source of materials

The title compound was prepared by hydrothermal methods in a mixture of 2-(piperidin-1-ium-4-yl)-*1H*benzo[d]imidazol-3-ium dichloride dihydrate, (0.62 g, 2 mmol), $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ (1.173 g, 1 mmol) and H_2O (10 mL). The mixture was stirred for 1 h in air and then transferred to a Teflon-lined stainless steel autoclave (20 mL) and kept at 373 K for 2 h. After the autoclave had cooled to room temperature over 6 h, orange block crystals were filtered off, washed with distilled water, and air-dried to give a yield of 70 % based on V.

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All H-atoms from C atoms and N atoms were positioned with idealized geometry and refined isotropically (U_{iso}(H) = 1.2 U_{eq}(C) or 1.2 U_{eq}(N) for all H atoms) using a riding model with C–H = 0.93–0.97 Å and N–H = 0.86–0.90 Å.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2373 (2)	0.98257 (18)	0.64079 (12)	0.0199 (4)
H1	0.263063	1.063125	0.656335	0.024*
C2	0.2843 (2)	0.95465 (18)	0.57115 (13)	0.0194 (4)
C3	0.3646 (2)	0.86481 (19)	0.48322 (13)	0.0199 (4)
C4	0.3330 (2)	0.97885 (19)	0.45744 (13)	0.0193 (4)
C5	0.3534 (2)	1.0205 (2)	0.38728 (13)	0.0240 (5)
H5	0.331533	1.096321	0.369575	0.029*
C6	0.4070 (2)	0.9446 (2)	0.34590 (13)	0.0259 (5)
H6	0.420153	0.968827	0.298158	0.031*
C7	0.4429 (2)	0.8307 (2)	0.37326 (14)	0.0265 (5)
H7	0.481361	0.782333	0.343961	0.032*
C8	0.4226 (2)	0.7890 (2)	0.44239 (14)	0.0251 (5)
H8	0.446674	0.713716	0.460696	0.030*
C9	0.0832 (2)	0.9765 (2)	0.61482 (13)	0.0270 (5)
H9A	0.045412	1.030844	0.571058	0.032*
H9B	0.053883	0.899024	0.595146	0.032*
C10	0.0323 (2)	1.0051 (2)	0.68442 (14)	0.0292 (5)
H10A	0.051819	1.085750	0.699868	0.035*
H10B	−0.064431	0.994647	0.667844	0.035*
C11	0.2462 (3)	0.9392 (2)	0.78194 (14)	0.0320 (6)
H11A	0.284167	0.888437	0.827837	0.038*
H11B	0.271810	1.018390	0.799060	0.038*
C12	0.3015 (2)	0.9068 (2)	0.71469 (13)	0.0247 (5)
H12A	0.282645	0.825642	0.700651	0.030*
H12B	0.398195	0.917458	0.732621	0.030*
N1	0.33117 (18)	0.85341 (15)	0.55419 (11)	0.0213 (4)
H1A	0.339542	0.791044	0.582473	0.026*
N2	0.28333 (18)	1.03039 (15)	0.51395 (11)	0.0200 (4)
H2	0.255872	1.101044	0.512092	0.024*
N3	0.0970 (2)	0.92901 (17)	0.75433 (12)	0.0302 (5)
H3A	0.066252	0.947766	0.795345	0.036*
H3B	0.073982	0.854746	0.740575	0.036*
O1	0.63256 (14)	0.59421 (13)	0.35088 (9)	0.0214 (3)
O2	0.73942 (17)	0.75834 (14)	0.27888 (9)	0.0296 (4)
O3	1.06539 (13)	0.46613 (12)	0.39161 (8)	0.0146 (3)
O4	0.98921 (14)	0.69078 (12)	0.38479 (8)	0.0189 (3)
O5	1.23587 (14)	0.62714 (12)	0.48346 (9)	0.0188 (3)
O6	0.50827 (15)	0.43224 (15)	0.41383 (10)	0.0282 (4)
O7	0.71201 (14)	0.37255 (12)	0.35978 (9)	0.0188 (3)
O8	0.89631 (15)	0.31388 (13)	0.28668 (9)	0.0223 (3)
O9	0.82871 (14)	0.53766 (12)	0.29354 (8)	0.0190 (3)
O10	0.83716 (16)	0.76169 (13)	0.60115 (9)	0.0254 (3)
O11	0.68318 (15)	0.58854 (13)	0.51012 (10)	0.0216 (3)
O12	0.79857 (14)	0.75138 (12)	0.44448 (8)	0.0194 (3)
O13	0.87623 (13)	0.53098 (11)	0.45235 (8)	0.0146 (3)
O14	1.03994 (14)	0.68448 (11)	0.54707 (8)	0.0149 (3)
V1	1.07214 (3)	0.59862 (3)	0.46004 (2)	0.01400 (9)
V2	0.88052 (3)	0.40645 (3)	0.35176 (2)	0.01579 (9)
V3	0.79001 (4)	0.66266 (3)	0.34769 (2)	0.01906 (10)
V4	0.85241 (4)	0.67133 (3)	0.53516 (2)	0.01662 (9)
V5	0.65692 (3)	0.47615 (3)	0.42060 (2)	0.01832 (10)
H11	0.641 (3)	0.583 (2)	0.5372 (16)	0.031 (8)*

The H-atom positions of dihydrogen decavanadate were fixed as found (O–H = 0.85 Å, with U_{iso}(H) = 1.5 U_{eq}(O)), which is also consistent with empirical bond length/bond number calculation.

3 Comment

The synthesis and structure of decavanadate-based inorganic-organic hybrid crystalline compounds have sparked extensive research in coordination chemistry.[5–15] Among them, dihydrogen decavanadate anion, $[H_2V_{10}O_{28}]^{4-}$ receives growing interest for studying the most probable protonation sites and understanding the key factors determining the crystal packing mode by hydrogen bonding.[11–15] As is known to all, benzimidazole derivatives have exhibited much better biological activity in clinical applications and may form hydrogen bonds with oxygen atoms of $[H_2V_{10}O_{28}]^{4-}$. To the best of our knowledge, there are no examples based on the assembly of 2-(piperidin-1-ium-4-yl)-*1H*-benzo[d]imidazol-3-ium and $[H_2V_{10}O_{28}]^{4-}$. For above considerations, we design and synthesize a new compound with molecular formula: $(C_{12}H_{17}N_3)_2[H_2V_{10}O_{28}]$.

As shown in figure, the asymmetrical unit is made of 2-(piperidin-1-ium-4-yl)-*1H*-benzo[d]imidazol-3-ium and half of one dihydrogendecavanadate anion, $[H_2V_{10}O_{28}]^{4-}$. Compared to previous $[H_2V_{10}O_{28}]^{4-}$, all the bond lengths and angles of the $[H_2V_{10}O_{28}]^{4-}$ anion in title compound are comparable to above analogues.[11–14]

The 2-(piperidin-1-ium-4-yl)-*1H*-benzo[d]imidazol-3-ium of the title compound adopts an entirely different conformation with previous report,[16] in which two nitrogen atoms are protonated for balancing charge and stabilizing the crystal structure by hydrogen bonds. There are extensive hydrogen bonds between the protonation of organic amine and $[H_2V_{10}O_{28}]^{4-}$ cluster. The typical hydrogen bonds are N1···O5 = 2.921 Å, N2···O12 = 2.824 Å and N3···O3 = 2.797 Å, which ultimately leads to a three-dimensional supermolecular structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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