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Preparation and crystal structure of a non-symmetrical vanadium(II) dimer: tri- μ_2 -bromido-(hydrogen-tris(3-isopropyl-4-bromopyrazol-1-yl)borato- $\kappa^3 N, N', N''$)-tris(tetrahydrofuran- κO)divanadium(II) – tetrahydrofuran (1/1), $C_{34}H_{57}BBr_6N_6O_4V_2$

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The molecular complex is shown in the figure (a solvent molecule THF is omitted for clarity). 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:	Blue-purple block
Size:	0.50 × 0.40 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.70 mm ⁻¹
Diffractometer, scan mode:	Siemens P4, ω
$\theta_{\max}$, completeness:	27.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26077, 7061, 0.105
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6504
$N(\text{param})_{\text{refined}}$:	479
Programs:	Bruker [1, 2], SHELX [3–6], Diamond [7]

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Abstract

$C_{34}H_{57}BBr_6N_6O_4V_2$, orthorhombic, $Pna2_1$ (no. 33), $a = 17.198(2)$ Å, $b = 12.9497(11)$ Å, $c = 20.496(2)$ Å, $V = 4564.8(9)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0441$, $wR_{\text{ref}}(F^2) = 0.1093$, $T = 183(2)$ K.

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Source of material

Synthesis was carried out by reaction of 0.21 g (0.36 mmol) *trans*-[VBr₂(THT)₄] (THT = tetrahydrothiophene) [8] with the potassium salt of hydrogen-tris(3-isopropyl-4-bromopyrazol-1-yl)borate (0.11 g, 0.18 mmol) [9] in 15 mL of rigorously anhydrous and deoxygenated tetrahydrofuran. The reaction was stirred overnight at room temperature under N₂ to develop an intense blue-purple solution from which KBr precipitated. Salts were removed by filtration and previously dried Celite aided in salt removal. Concentration and cooling to 0 °C under N₂ led to quality blue-purple crystals of the title complex within 48 h.

Experimental details

The carbon-bound hydrogen atoms were placed using a riding model (AFIX 13/23/33/43) implemented in the SHELXL system using the standard parameters for the constrained $U_{\text{iso}}(\text{H})$ values [5].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.86460(6)	0.16724(7)	0.44095(5)	0.0387(2)
Br2	0.63321(6)	0.42389(8)	0.81703(6)	0.0419(3)
Br3	0.82244(8)	0.90157(8)	0.51603(6)	0.0485(3)
Br4	0.99507(4)	0.34002(6)	0.71747(4)	0.02219(18)
Br5	1.07067(4)	0.53126(7)	0.60144(4)	0.02406(18)
Br6	0.97152(4)	0.62195(6)	0.75027(4)	0.02303(18)
V1	0.93188(7)	0.49787(10)	0.65309(7)	0.0177(3)
V2	1.08962(7)	0.49834(10)	0.72741(7)	0.0188(3)
O1	1.1077(4)	0.4606(5)	0.8296(3)	0.0268(13)
O2	1.1921(3)	0.4101(5)	0.7066(3)	0.0281(14)
O3	1.1674(3)	0.6253(5)	0.7385(3)	0.0295(14)
O4	1.3732(10)	0.6166(16)	0.8491(11)	0.138(7)
N1	0.8193(4)	0.4152(5)	0.5518(4)	0.0223(14)
N2	0.8944(4)	0.3983(5)	0.5733(4)	0.0217(14)
N3	0.7559(4)	0.4778(5)	0.6547(4)	0.0237(15)
N4	0.8179(4)	0.4707(5)	0.6966(4)	0.0201(14)
N5	0.8069(4)	0.6058(6)	0.5735(4)	0.0258(16)
N6	0.8791(4)	0.6271(5)	0.5993(4)	0.0223(14)
C1	0.7999(5)	0.3454(7)	0.5058(5)	0.0258(18)
H1B	0.752995	0.341886	0.483390	0.031*
C2	0.8621(5)	0.2807(7)	0.4981(4)	0.0267(18)
C3	0.9208(5)	0.3159(7)	0.5399(4)	0.0229(17)
C4	1.0040(5)	0.2789(7)	0.5479(5)	0.0257(18)
H4	1.027935	0.320149	0.582617	0.031*
C5	1.0501(6)	0.2978(10)	0.4856(6)	0.043(3)
H5C	1.102514	0.274126	0.491340	0.065*
H5B	1.026357	0.260962	0.450142	0.065*
H5A	1.050379	0.370382	0.475920	0.065*
C6	1.0073(6)	0.1653(8)	0.5691(6)	0.040(2)
H6C	1.060526	0.144395	0.573737	0.059*
H6B	0.980903	0.157340	0.610061	0.059*
H6A	0.982394	0.123171	0.536695	0.059*
C7	0.6899(5)	0.4623(7)	0.6871(5)	0.0259(19)
H7	0.640310	0.462990	0.669042	0.031*
C8	0.7074(4)	0.4451(7)	0.7518(5)	0.0263(18)
C9	0.7888(4)	0.4518(6)	0.7573(4)	0.0207(16)
C10	0.8380(5)	0.4366(7)	0.8169(4)	0.0244(17)
H10	0.892281	0.444606	0.803257	0.029*
C11	0.8227(6)	0.5175(8)	0.8690(5)	0.035(2)
H11C	0.855530	0.504525	0.905996	0.053*
H11B	0.833840	0.584855	0.851746	0.053*
H11A	0.769233	0.514311	0.882155	0.053*
C12	0.8297(6)	0.3282(8)	0.8444(6)	0.040(2)
H12C	0.861970	0.321306	0.882395	0.059*
H12B	0.776472	0.316045	0.856083	0.059*
H12A	0.845582	0.278807	0.812109	0.059*
C13	0.7806(6)	0.6910(7)	0.5432(5)	0.031(2)
H13	0.733301	0.696073	0.521497	0.038*
C14	0.8326(6)	0.7676(7)	0.5491(5)	0.0301(19)
C15	0.8950(5)	0.7245(6)	0.5851(4)	0.0252(18)
C16	0.9706(5)	0.7758(7)	0.6057(5)	0.0278(18)
H16	1.000305	0.724176	0.630177	0.033*
C17	0.9577(6)	0.8683(8)	0.6517(6)	0.039(2)
H17C	1.007066	0.897825	0.663190	0.059*
H17B	0.926508	0.919364	0.630089	0.059*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H17A	0.931623	0.845371	0.690473	0.059*
C18	1.0206(6)	0.8076(9)	0.5472(6)	0.042(2)
H18C	1.067608	0.839521	0.562507	0.062*
H18B	1.033379	0.747583	0.521874	0.062*
H18A	0.992326	0.855650	0.520604	0.062*
C19	1.0664(8)	0.5041(9)	0.8853(5)	0.048(3)
H19B	1.017725	0.534375	0.870979	0.058*
H19A	1.097532	0.558098	0.905236	0.058*
C20	1.0512(10)	0.4228(9)	0.9328(7)	0.061(4)
H20B	0.997296	0.424086	0.946835	0.073*
H20A	1.084426	0.430280	0.970761	0.073*
C21	1.0693(8)	0.3239(9)	0.8965(6)	0.051(3)
H21B	1.023503	0.297042	0.874770	0.061*
H21A	1.089818	0.271644	0.925722	0.061*
C22	1.1303(7)	0.3586(8)	0.8475(6)	0.041(2)
H22B	1.181677	0.358657	0.867101	0.049*
H22A	1.130777	0.313535	0.809737	0.049*
C23	1.1981(6)	0.3279(9)	0.6597(7)	0.053(3)
H23B	1.179797	0.350626	0.617324	0.063*
H23A	1.167452	0.268935	0.673407	0.063*
C24	1.2825(7)	0.3003(12)	0.6567(9)	0.067(4)
H24B	1.291877	0.235273	0.678849	0.080*
H24A	1.299394	0.293918	0.611770	0.080*
C25	1.3238(7)	0.3830(10)	0.6889(8)	0.057(4)
H25B	1.338493	0.436034	0.657802	0.069*
H25A	1.370253	0.357206	0.710104	0.069*
C26	1.2674(7)	0.4249(13)	0.7382(9)	0.075(5)
H26B	1.270321	0.386770	0.778819	0.090*
H26A	1.277113	0.497393	0.746773	0.090*
C27	1.2014(10)	0.6824(13)	0.6860(7)	0.074(5)
H27B	1.161297	0.710110	0.657615	0.089*
H27A	1.235443	0.638621	0.660366	0.089*
C28	1.2461(8)	0.7673(9)	0.7171(8)	0.058(3)
H28B	1.298554	0.745412	0.727663	0.069*
H28A	1.248466	0.827501	0.689050	0.069*
C29	1.2015(13)	0.7884(12)	0.7758(9)	0.095(7)
H29B	1.160342	0.837495	0.766638	0.114*
H29A	1.234833	0.816806	0.809473	0.114*
C30	1.1686(6)	0.6888(8)	0.7968(6)	0.038(2)
H30B	1.200835	0.657448	0.830265	0.046*
H30A	1.116523	0.697920	0.813976	0.046*
C31	1.4475(8)	0.5571(15)	0.8389(10)	0.082(5)
H31B	1.451921	0.534908	0.793847	0.098*
H31A	1.492179	0.599568	0.849561	0.098*
H1A	0.717340	0.499680	0.558940	0.098*
C32	1.4434(10)	0.4703(19)	0.8812(11)	0.109(8)
H32B	1.484163	0.473586	0.913844	0.131*
H32A	1.449281	0.406697	0.856673	0.131*
C33	1.3662(10)	0.4742(17)	0.9125(10)	0.094(6)
H33B	1.336337	0.413363	0.900907	0.113*
H33A	1.371970	0.475624	0.959613	0.113*
C34	1.3283(8)	0.5613(15)	0.8919(9)	0.085(6)
H34B	1.315660	0.604038	0.929265	0.102*
H34A	1.279979	0.541848	0.870741	0.102*
B1	0.7678(5)	0.4994(8)	0.5810(5)	0.025(2)

The absolute structure determination succeeded as the derived Flack parameter is found to be near zero [−0.03(2) from 1598 selected quotients] using Parsons's method [5]. The classical calculation of the Flack parameter showed a slightly better result 0.00(1) using all unique reflections [5, 6].

Comment

The asymmetric unit consists of a dinuclear vanadium(II) complex (see the Figure) and one uncoordinated THF solvent molecule. The dinuclear $\{V^{II}(\mu_2-Br)_3V^{II}\}^+$ core of the title complex is capped by a hydrogen-tris(3-isopropyl-4-bromopyrazol-1-yl)borate ligand on one side and terminally coordinated by tetrahydrofuran molecules on the other. Inspection down the $V \cdots V$ axis show pyrazolyl rings bisect the bromides of the $\{V^{II}(\mu_2-Br)_3V^{II}\}^+$ core, with boron sitting unperturbed on the $V \cdots V$ axis, i.e., the angle made by $B(1)-V(1)-V(2)$ is 178.3° . A space-filling plot illustrated that steric bulk presented by the three isopropyl groups that point toward the $\{V^{II}(\mu_2-Br)_3V^{II}\}^+$ core prohibited coordination of a second hydrogen-tris(3-isopropyl-4-bromopyrazol-1-yl)borate ligand.

While a Cambridge Structural Database [10] search shows several examples of dinuclear tri- μ_2 -chlorido vanadium(II) complexes [11–19], dinuclear tri- μ_2 -bromido transition metal complexes are rare with only one other structurally characterized example reported to the best of our knowledge [20]. The distances between bromido-bridged vanadium(II) ions at the centers of these cofacial bioctahedra are rather similar, with a $V \cdots V$ distance of $3.146(6)$ Å reported in reference [12] and $3.112(2)$ Å in the title complex. The average $V-Br$ bond lengths in each of these dinuclear complexes are essentially identical.

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