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New scorpionate oxovanadium complexes: syntheses and crystal structures of a series of vanadium (IV) complexes with mixed ligands of polypyrazolylborates and substituted acetylacetonates

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The reaction of $[VO(R_1\text{-acac})_2]$ (R_1 = Me or Et; acac = acetylacetonate) with $Na[HB(pz)_3]$ (pz = pyrazole) or $Na[HB(3,5\text{-}Me_2pz)_3]$ in MeOH gave a series of new oxovanadium (IV) complexes: $[VO\{HB(pz)_3\}(Me\text{-acac})]$ (**1**), $[VO\{HB(3,5\text{-}Me_2pz)_3\}(Me\text{-acac})]$ (**2**), $[VO\{HB(pz)_3\}(Et\text{-acac})]$ (**3**) and $[VO\{HB(3,5\text{-}Me_2pz)_3\}(Et\text{-acac})]$ (**4**), respectively. All complexes have similar distorted octahedral coordination about vanadium, [VO(N3O2)], in which the basal plane is defined by the N_4, N_6 atoms from the tridentate ligand and the O_2, O_3 atoms from the R_1-acac ligand. However, the dihedral angles between the plane formed by O_2, V and O_3, and the plane of the pentane-2, 4-dionato ligand (O2, C1, C2, C3 and O3) are variously different; 3.59° for **1**, 74.54° for **2**, 0.92° for **3**, and 29.50° for **4**, respectively. In addition, *ab initio* calculations on **1**, **2**, **3** and **4** have given the energies and characters of the selected MOs, the atomic net charge and the NBO bond order. The order of stability of the complexes is $\mathbf{1} \cong \mathbf{2} \cong \mathbf{4} > \mathbf{3}$.

Keywords: oxovanadium complexes, polypyrazolylborates, crystal structures, quantum chemistry

Vanadium complexes containing N, O and S donor ligands are of considerable current interest because such complexes have been used as insulin-mimetics and are potential therapeutic agents to treat diabetes mellitus.[1-3] Up to now, several types of vanadyl complexes with different combinations of coordinating atoms such as VO(O4),[4,5] VO(N2O2),[6] VO(S2N2),[7] VO(N3O2),[8] and VO(S2O2)[7] have been proposed to be effective to treat hypoglycemia of STZ-rats on oral administration.[7]

Among these vanadium complexes, little is known about the coordination structure of the vanadium-containing active site, although the complexes had been evaluated by a variety of physical methods such as elemental analysis, IR, UV-vis, NMR, and EPR spectroscopies and bioactivity experiments. In addition, significant differences among the geometric, electronic, structural and spectroscopic features of vanadium complexes reflect a structural diversity that accompanies their functional variability. Despite extensive research, understanding of structure–function relationships at the molecular level is incomplete, and many questions remain unanswered concerning the detailed mechanisms and fundamental chemistry underlying vanadium bioactivity in biology. In our studies of the relationship between the structures of model complexes and bioactivities (insulin-like activity) to achieve the best relevant modeling complexes for medicinal or biochemical research, we have turned our attention to vanadium complexes with the tri(pyrazolyl)borate ligands, which can in many ways mimic histidine nitrogen ligation, since the pyrazole ring of tripyrazolylborate ligands is similar to the imidazolyl group. Although these ligands have been used in modeling, a number of important metallo-biochemical motifs,[9,10] to our knowledge, relatively little is known about their vanadium complexes, especially structural information. Recently, $[VCl_3\{HB(pz)_3\}$, $[VCl_2\{HB(pz)_3\}(THF)]$,[11] $[VCl_2\{HB(Me_2pz)_3\}(DMF)]$, [12]$[VCl_2\{HB(Me_2pz)_3\}(Me_2pz)]^-$, $[VOCl\{HB(Me_2pz)_3\}(DMF)]$, $[VOCl_2\{HB(Me_2pz)_3]$ and $[HB(Me_2pz)_2VOCl_2]_2(THF)$,[13] $[HB(pz)_3)_2V_2(\mu\text{-}O)(\mu\text{-}C_3H_5O_2)_2]$,[14] $[V(N\text{-}t\text{-}Bu)Cl_2\{HB(pz)_3\}]$,[15] and $[V_2O(O_2CR)_2L_2]$ (where L = $HB(pz)_3^-$; R = CH_3, C_6H_5, C_2H_5, H, *etc.*) have been reported.[16] We have synthesised some vanadium complexes with tripyrazolylborate ligands,[17-18] and we now report the synthesis and characterisation of a series of new oxo vanadium (IV) complexes with the tripyrazolylborate or tris(3,5-dimethylpyrozolyl)borate ligands and provide X-ray structural characterisation for these complexes.

Experimental

Methods and materials

The reactions were carried out at room temperature. Solvents were dried by molecular sieve (4Å). All other reactants were used as purchased. IR spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer (200–4000 cm^{-1}, with pressed KBr pellets). Uv-vis spectra were recorded on a JASCO V-570 spectrometer (200–1100 nm, CH_2Cl_2 solution). Elemental analysis was performed on a Yanaco CHN CORDER MT-6 automatic analyser. $Na[HB(pz)_3]$[19] and $Na[HB(3,5\text{-}Me_2pz)_3]$[20] were prepared according to the literature methods.

Synthesis of precursors $[VO(Me\text{-acac})_2]$ and $[VO(Et\text{-acac})_2]$

These precursors were synthesised by a slight modification of the method in ref. 21. Vanadyl sulfate ($VOSO_4{\cdot}3H_2O$, 0.66 g, 3 mmol) was dissolved in 3 ml of 10% H_2SO_4. Then 3-methyl-2-4-pentanedione (0.75 g, 6 mmol, excess 10%) or 3-Ethyl-2-4-pentanedione (0.84 g, 6 mmol, excess 10%) were added, respectively, and the pH value of the resulting blue solution was adjusted with solid sodium hydrogen carbonate to pH=4. A blue-green precipitate began to form immediately. After keeping overnight, the precipitates were separated by filtration, washed with distilled water extensively and dried. For $[VO(Me\text{-acac})_2]$ the yield was 0.75 g, 85.27% (based on $VOSO_4$). Anal. Calcd for $C_{12}H_{18}O_5V$: C, 48.8; H, 6.1. Found: C, 48.5; H, 6.1%. For $[VO(Et\text{-acac})_2]$, yield was 0.64 g, 66.40% (based on $VOSO_4$). Anal. Calcd for $C_{14}H_{22}O_5V$: C, 52.3; H, 6.85. Found: C, 52.2; H, 6.75%.

Preparation of $[VO(Me\text{-acac})\{HB(pz)_3\}]$ (**1**): To $Na[HB(pz)_3]$ [0.24 g (1 mmol) in 5 ml of dry MeOH] was added $[VO(Me\text{-acac})_2]$ [(0.29 g, 1 mmol) in 5 ml of MeOH]. The mixture solution was stirred for 4 h, resulting in a solution colour change from violet to yellow-green. Then the solvent was removed by vacuum to dryness, the residue was redissolved in CH_2Cl_2 and filtered to take off some insoluble solid, and the filtrate was evaporated by vacuum to drynes. A violet solid was obtained, which was washed with MeOH, and dried in air. Yield 0.25 g, 64% (based on vanadium). It was crystallised from CH_2Cl_2. Anal. Calcd for $C_{15}H_{19}BN_6O_3V$ (F. W. 393.11): C, 45.8; H, 4.8; N, 21.4. Found: C, 45.7; H, 4.6; N, 21.6%.

Preparation of $[VO(Me\text{-acac})\{HB(3,5\text{-}Me_2pz)_3\}]$ (**2**): A mixture of $Na[HB(3,5\text{-}Me_2pz)_3]$ (0.32 g, 1 mmol) and $[VO(Me\text{-acac})_2]$ (0.29 g, 1 mmol) was dissolved in MeOH (10 ml) and stirred for 4 h to give a yellow-green solution which gradually turned orange. After the reaction finished, the solution was concentrated to about 5 ml by vacuum, producing a large quantity of pale blue precipitate which was filtered and washed with MeOH, then ether extensively and dried in air. Yield 0.38 g, 80% (based on vanadium). The pale blue solid could be recrystallised from $MeOH/CH_2Cl_2$. Anal. Calcd for

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$C_{21}H_{31}BN_6O_3V$ (F. W. 477.27): C, 52.8; H, 6.5; N, 17.6. Found: C, 52.6; H, 6.5; N, 17.45%.

Preparation of [VO(Et-acac)(HB(pz)₃)] (**3**): A mixture of Na[HB(pz)$_3$] (0.24 g, 1 mmol) and [VO(Et-acac)$_2$] (0.32 g, 1 mmol) was dissolved in MeOH (10 ml) and stirred for 4 h to get a clear yellow-green solution. Then the solvent was removed by vacuum to dryness, and the residue was redissolved in CH_2Cl_2 and filtered to remove some insoluble solid, and the filtrate was evaporated by vacuum to dryness again. A yellow-green solid was obtained and washed with MeOH, and dried in air. Yield 0.20 g, 49% (based on vanadium). The pale yellow-green solid could be recrystallised from MeOH/CH_2Cl_2. Anal. Calcd for $C_{16}H_{21}BN_6O_3V$ (F. W. 407.14): C, 47.2; H, 5.2; N, 20.6. Found: C, 47.5; H, 5.1; N, 20.3%.

Preparation of [VO(Et-acac)(HB(3,5-Me₂pz)₃)] (**4**): A mixture of Na[HB(3,5-Me$_2$pz)$_3$] (0.32 g, 1 mmol) and [VO(Et-acac)$_2$] (0.32 g, 1 mmol) was dissolved in MeOH (10 ml) and stirred for 4 h to give a yellow-green solution that gradually turned dark orange and deposited a large quantity of yellow-green precipitate. The precipitate was filtered, washed with MeOH and dried in air. Yield 0.25 g, 51% (based on vanadium). The yellow-green solid could be recrystallised from MeOH/CH_2Cl_2. Anal. Calcd for $C_{22}H_{32}BN_6O_3V$ (F. W. 491.3): C, 53.8; H, 6.5; N, 17.1. Found: C, 53.4; H, 6.4; N, 17.3%.

X-ray data collection and refinement of the crystal structures

Crystals of 1, 2, 3 and 4 were mounted on a glass fibre for X-ray measurement, respectively. Reflection data were collected at room temperature on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation (λ = 0.7107 Å) and an ω-2θ scan mode. Intensity data were corrected for Lorentz-Polarisation effects and absorption (φ scans). The crystal data, data collection, and refinement details are summarised in Table 1.

The structures were solved by the direct method using SHELXS–86 and refined using the SHELXL–97 program. All the non-hydrogen atoms were refined anisotropically and the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. Atomic scattering factors and anomalous dispersion terms were as in SHELXL – 97 program. The drawings were made with Diamond program, and all calculations were performed on a pentium4 computer.

Methods of quantum chemistry calculation

MP2 calculations at 3-21G* basis sets level were carried out for the complexes with the Gussian 98W program. The calculation included 45 atoms, 292 basis functions, 489 primitive Gaussians for complex 1; 63 atoms, 370 basis functions, 615 primitive Gaussians for complex 2; 48 atoms, 305 basis functions, 510 primitive Gaussians for complex 3; 66 atoms, 383 basis functions, 636 primitive Gaussians for complex 4. The parameters of the molecular structure come from the crystal structure data, and the molecular point group and its symmetry (C_s) are also considered. The electronic structure and the bonding characters of the complex were analysed with ab initio calculations and natural bonding orbital (NBO) analysis. The result of calculation gives the constitution and the energy of the molecular orbital, NBO atomic charge and NBO bond orders.

Results and discussion

Synthesis

The synthetic strategy is outlined in the Scheme. Previously, we have prepared VO (IV) complexes with tripyrazolylborate ligand (Tp or Tp^{Me}) via similar methods.[22]

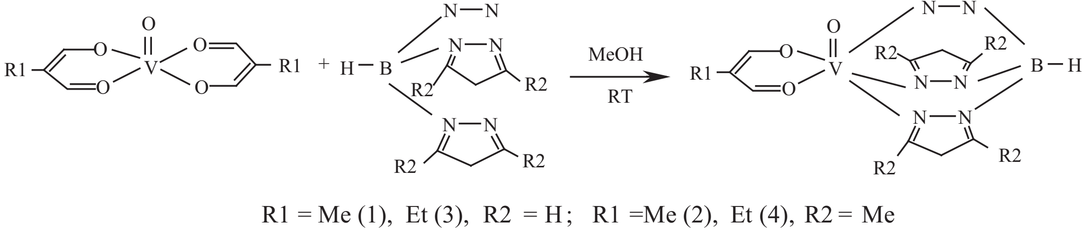
Although similar framework complexes have been reported,

Table 1 Crystal parameters of complexes **1**, **2**, **3** and **4**[a]

Complexes	1	2	3	4
Empirical Formula	$C_{15}H_{19}BN_6O_3V$	$C_{21}H_{31}BN_6O_3V$	$C_{16}H_{21}BN_6O_3V$	$C_{22}H_{33}BN_6O_3V$
F.M (g mol^{-1})	393.11	477.27	407.14	491.29
Color	Violet	Pale blue	Yellow green	Yellow green
Size(mm)	0.50 × 0.10 × 0.05	0.40 × 0.50 × 0.20	0.15 × 0.10 × 0.05	0.30 × 0.15 × 0.10
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	Pnma	Pnma	P2$_1$/c	Pnma
a (Å)	11.892(3)	13.061(3)	7.791(2)	13.154(2)
b (Å)	19.953(3)	19.009(4)	11.961(2)	19.265(2)
c (Å)	7.616(3)	9.923(2)	21.083(4)	10.003(2)
α (°)	90	90	90	90
β (°)	90	90	91.14(2)	90
γ (°)	90	90	90	90
V (Å^3)	1807.3(10)	2463.5(9)	1964.1(7)	2534.7(7)
Z	4	4	4	4
D_{calc} g cm^{-3}	1.445	1.311	1.377	1.311
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
F(000)	812	1004	844	1036
μ(Mo–Kα)/cm^{-1}	0.95	0.82	0.90	0.82
2 θ (°)	5.32–55.14	5.16–55.06	5.16 – 54.98	5.12– 55.06
Reflections collected	2235	3028	4892	2699
Independent reflections(I>2σ(I))	1067	2035	1883	698
Parameters	135	169	247	175
Δ(ρ) (e Å^{-3})	0.672 and–0.637	0.345 and–0.480	0.510 and–0.455	0.280 and–0.367
Goodness–of–fit	1.044	1.033	0.968	0.912
R[a]	0.0581(0.1682)[b]	0.0451(0.073)[b]	0.0670(0.2001)[b]	0.0645(0.3233)[b]
wR$_2$[a]	0.1475(0.1925)[b]	0.1307(0.1470)[b]	0.1615(0.1615)[b]	0.1201(0.1854)[b]

[a] $R = \Sigma\,||Fo|-|Fc||\,/\,\Sigma\,|Fo|$, $wR_2 = [\,\Sigma\,(w(Fo^2-Fc^2)^2\,/\,[\Sigma\,(w(Fo^2)^2)^{1/2}$ [Fo>4σ(Fo)].

[b] Based on all data.



R1 = Me (1), Et (3), R2 = H; R1 =Me (2), Et (4), R2 = Me

Scheme 1 Reaction process of oxovanadium complexes **1–4**.

such as [VCl2{HB(3,5-Me$_2$pz)$_3$}(dmf)] (dmf = dimethylformamide),[23a] [V(N^{t}Bu)Cl$_2$ {HB(3,5-Me$_2$pz)$_3$}](NBu^t)],[23a] [NEt$_4$][V(CN)3{HB(3,5-Me$_2$pz)$_3$}]·H$_2$O,[23b] [VO(acac){HB(3,5-Me$_2$pz)$_3$}](acac = pentane-2,4-dionato),[24] [VO(DMF) {HB (Me$_2$pz)$_3$}], [VOCl$_2${HB(Me$_2$pz)$_3$}][13] *etc*., the examples of structurally characterised highly hindered Tp^R (R = H and Me) complexes of vanadium are rare, and crystal structures of Me- or Et-substituted acetylacetonato-oxovanadium complexes with tripolypyrazolylborate ligands (Tp or Tp^{Me2}) are not known so far. Systematic investigation of various vanadium complexes having the same Tp^R ligand may provide insight into properties of their various structures and the effect of the supporting ligands. Our new oxovanadium (IV) complexes have been isolated as shining crystals, light blue to yellow-green in colour, in moderate yields (80–49%) by reactions involving stoichiometric amounts of [VO(R-acac)$_2$], and Na[HB(pz)$_3$] or Na[HB(3,5-Me$_2$pz)$_3$], in MeOH at room temperature. Crystals for X-ray were fom CH$_2$Cl$_2$, MeOH/CH$_2$Cl$_2$ (1:2), MeOH/CH$_2$Cl$_2$ (1:4-5), or MeOH/CH$_2$Cl$_2$ (1:3), respectively.

IR spectra

In the region of 3200–2850 cm^{-1}, we found weak and medium absorptions involving $\nu_{(C\text{-}H)}$ and $\nu_{(CH3)}$. The medium sharp bands observed in the IR spectrum at about 2500 cm^{-1} are characteristic of the B-H stretching vibration mode. Bands in the range of 1600–1000 cm^{-1} can be attributed to pyrazolyl ring stretching modes according to a vibration study of pyrazole by Durig *et al.*[25] A strong and sharp vibration band of the V = O stretch appears around 960 cm^{-1} which is close to those found in [VO(acac) {HB(3,5-Me$_2$pz)$_3$}] (957 cm^{-1})[24] and [VOCl(DMF){HB(3,5Me$_2$pz)$_3$}] (965 cm^{-1}).[13] These values agree well with V = O frequencies generally falling in the range of 900–1000 cm^{-1}.[26] Below 800 cm^{-1}, we can find those normal modes corresponding to pyrazolyl ring torsions, as well as bending movements (in-plane and out-of-plane) of the CH$_3$ groups in the region around 700 cm^{-1}. Between 400 and 200 cm^{-1} bands should be attributed to the V–O, V–N, N–V–N stretching modes. Detail comparison of related IR spectra data is given in Table 2.

UV-visible absorption spectroscopy

The electronic absorption spectra of complexes **1, 2**, **3** and **4** in dichloromethane present similar absorption patterns with a high-energy intense absorption in approximately the range of 237–341 nm. The high-energy absorption bands: 237nm for **1**, 241 nm for **2**, 238nm for **3** and 242 nm for **4** are assigned as π–π* transitions of the aromatic-like chromophore from tri(pyrazolyl)borate or tris(3,5-Me$_2$pyrazolyl)borate. Bands at 341 nm for **1**, 331 nm for **2,** 339 nm for **3** and 338 nm for **4** are attributed to the ligand- to-vanadium charge-transfer absorption(LMCT), respectively.

Structural discussion

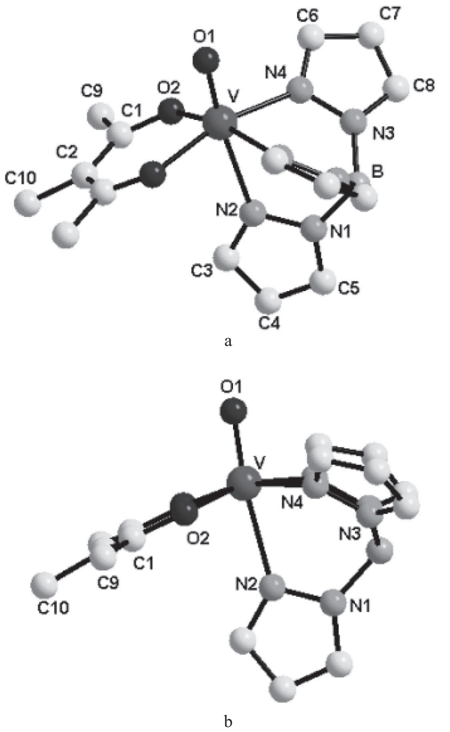
The structures of all complexes have been determined by single-crystal X-ray diffraction. The molecular structures are shown in Figs 1–4. Selected bond lengths and angles of **1**, **2**, **3** and **4** are listed in Table 3. The vanadium atom in each molecule is six coordinate, existing in a distorted octahedral geometry in which the basal plane is defined by two nitrogen atoms (N4, N6) derived from the tridentate ligand of trypyrazolylborate, and two oxygen atoms (O2, O3) from the methyl substituted acac ligand. The apical position are occupied by the O$_1$ atom and the N$_2$ atom from the tridentate ligand. Detailed description of structures are held as supplementary material for the complexes, **1**, **2**, **3** and **4**.

Although the coordination modes of **1** and **2** are the similar, their geometry and the corresponding bonding distances and angles are somewhat different. The bonding distance of V–O$_1$ [1.590(5)Å] in **1** is close to that of **2** [1.597(2)Å]; however, the V–O$_{acac}$(O2 or O3) distance of **1** [1.966(3) Å] is slightly shorter than that of **2** [1.989(2)Å]. The V–N bond distances of **1** is slightly longer than those in **2** [for **1**: 2.122(4), 2.122(4), 2.361(5)Å; for **2**: 2.099(2), 2.099(2), 2.353(2)]. For **1**, the equatorial plane is a perfect plane, but not that in **2**, which is slightly out of the plane by 0.047(1)Å. The angles of the O–V–O group are in the range of 86.4(2) to 100.9(2)° for **1**, and 85.36(10)° to 98.25(8)° for **2**. The angles of the N–V–N group range from 79.8(1)° to 86.0(2)° for **1**, and 80.90(6)° to 87.08(10)° for **2**.

In **3** and **4**, with the 3-ethyl-2,4-pentanedionate ligand, the V–O$_1$ bonding distance in **3** [1.598(4)Å] is close to that of **4** (1.594(6)Å). The V–O$_{acac}$ (O2, O3) bonding distances in **3** [(1.956(4) and 1.974(4)Å] are slightly shorter than those in **4** [1.989(5) and 1.989(5)Å]. The V–N bond distances of **3** are lightly longer than those in **4** [for **3**: 2.116(4), 2.143(4), 2.378(4) Å; for **4**: 2.093(6), 2.093(6), 2.348(8) Å]. The equatorial plane of **4** is a perfect plane, but not in **3**, which is slightly out of the plane by 0.004(2), –0.004(2), –0.004(2) and 0.004(2) Å for O2, O3, N4 and N6, respectively. The angle of O$_1$–V–N$_2$ for **3** [172.2(2)°] is close to that of **4** [173.7(4)°]. The angles of the O–V–O and N–V–N groups for **3** are in the range of 86.4(1)° to 102.2(2)°, and 80.7(2)° to 86.2(2)°, respectively; while in the range of 84.9(3)° to 99.2(3)° and 81.0(2)° to 87.7(4)° for **4**, respectively. In addition, for complex **3** and **4**, the C$_2$–C$_{15}$–C$_{16}$ angles of the ethyl group of 2, 4-pentanedione are different from each

Table 2 IR spectra (cm^{-1}) for complexes **1**, **2**, **3** and **4**

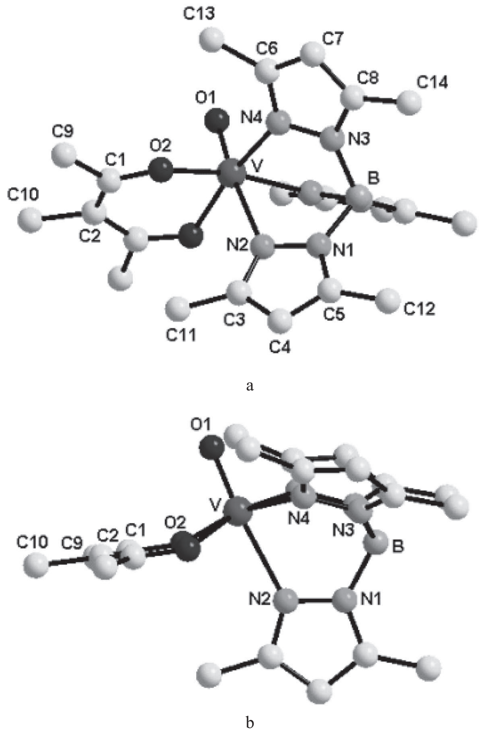
1	2	3	4	Assignment
3135	3128	3131	3133	C–H
2966	2925	2965	2926	–CH$_3$
2479	2523	2479	2522	B–H
1574, 1503	1575, 1540	1573, 1503	1569, 1541	C=C C–N
1462	1448	1462	1448	δCH$_{3sym}$
1404	1418	1404	1417	δCH$_{3asym}$
1390,1324,	1384,1353,	1390,1325,	1384,1328	
1307	1329	1307	C–C	
1262, 1212,	1294,1207,	1262,1212,	1292,1265,	N–N
1175, 1116	1190	1175,1116	1207,1187	
1070, 1048, 1001	1075, 1065, 1039	1070, 1048, 1001	1074, 1064, 1039	C–CH$_3$
967	982	966	998	V=O
884, 815	857, 814	884, 815	855, 811	ρCH$_3$
790, 760, 721,	723, 697,	790, 759, 720,	728,698,	
666, 619, 600	649, 600	666, 619, 600	696 619	Pyrazolyl ring C–C, C–H, C–N *etc.*
471, 431	468	469, 431	470	V–O
379,340	376,344	379,340	375,342	V–N



a

b

Fig.1 A view of structure of complex **1**, with hydrogen atoms being omitted for clarity.



a

b

Fig.2 A view of structure of complex **2**, with hydrogen atoms being omitted for clarity.

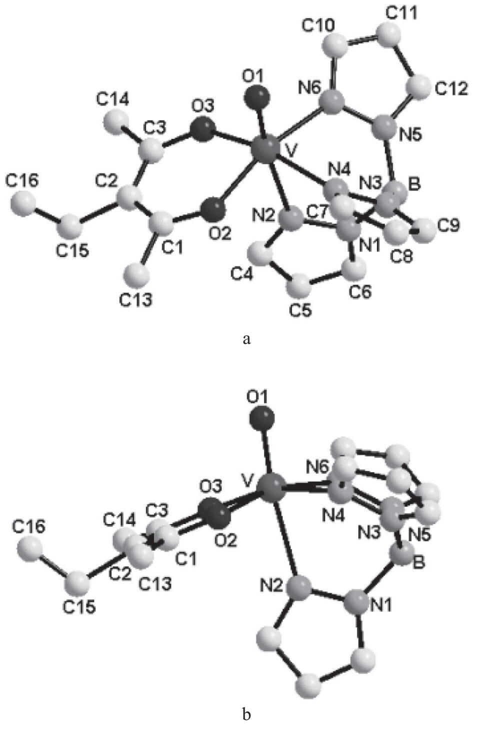


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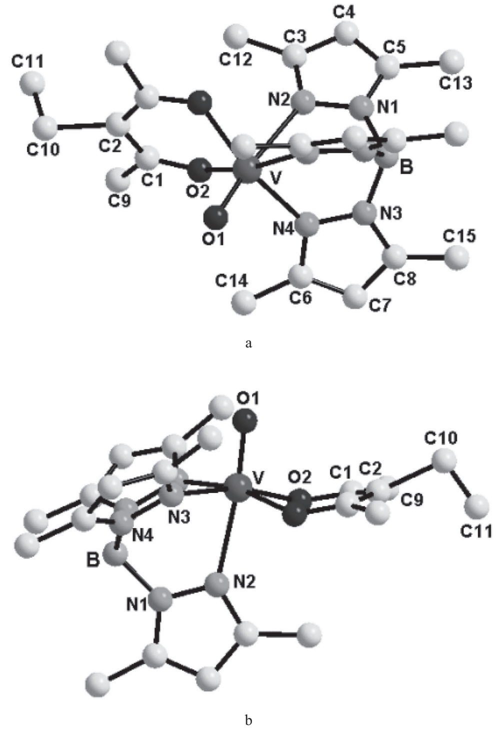
Fig.3 A view of structure of complex **3**, with hydrogen atoms being omitted for clarity.



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b

Fig.4 A view of structure of complex **4**, with hydrogen atoms being omitted for clarity.

other; **3** is 111.9(12)°, **4** is 100.0(2)°. Their bonding lengths are not close, C_2–C_{15} is 1.720(2)Å for **3**, but 1.584(10)Å for **4**. This is maybe because of steric crowding between the methyl groups of the tripyrazolyborate and Et-acac ligands.

Comparison of the bond lengths and angles of methyl or ethyl-substituted acac oxovanadium complexes with tripyrazolylborate ligands is given in Table 3. In complexes, **1**, **2**, **3** and **4**, the V = O1 bond lengths are in the order of **1** < **4** < **3** ≅ **2**; the V–O_2 or V–O_3 bonding length is 1.966(3) Å for **1**, 1.980(2) Å for **2**, 1.956(4) Å for **3** and 1.989(5) Å for **4**, respectively, the bond distances order of which is **3** < **1** < **2** ≅ **4**. The V–N_{trans} (N is *trans* to O1) bond lengths are **2** < **4** < **1** < **3**, while, another two average bond lengths(V–N4, V–N6), which is in the base plane, are in the order of **2** ≅ **4** < **1** < **3**.

Table 3 Comparison of related bond lengths (Å) and angles (°) of complexes **1**, **2**, **3** and **4**

Complexes	**1**	**2**	**3**	**4**
(i) The coordination sphere				
V–O_1	1.590(5)	1.597(2)	1.598(4)	1.594(6)
V–O_2	1.966(3)	1.9897(17)	1.956(4)	1.989(5)
V–O_3	1.966(3)	1.9897(17)	1.974(4)	1.989(5)
V–N_2	2.361(5)	2.353(2)	2.378(4)	2.348(8)
V–N_4	2.122(4)	2.099 (2)	2.143(4)	2.093(6)
V–N_6	2.122(4)	2.099 (2)	2.116(4)	2.093(6)
O_1 –V–O_2	100.9(2)	98.25(8)	102.3(2)	99.2(3)
O_1 –V– O_3	100.89(1)	98.25(8)	100.8(2)	99.2(3)
O_2 –V– O_3	86.4(2)	85.36(10)	86.4(1)	84.9(3)
O_1 –V–N_2	173.4(2)	174.17(10)	172.2(2)	173.7(4)
O_1 –V–N_4	95.36(16)	94.90(8)	94.2(2)	94.5(3)
O_1 –V– N_6	95.36(16)	94.90(8)	96.3(2)	94.5(3)
O_2 –V–N_2	83.91(12)	86.02(6)	84.9(2)	85.4(2)
O_2 –V–N_4	91.51(13)	92.28(7)	163.3(2)	92.1(2)
O_2 –V– N_6	163.7(1)	166.85(7)	88.9(2)	166.3(2)
O_3 –V–N_2	83.9(1)	86.02(6)	82.5(2)	85.4(2)
O_3 –V–N_4	163.7(1)	166.85(7)	93.6(2)	166.3(2)
O_3 –V– N_6	91.5(1)	92.28(7)	162.9(2)	92.1(2)
N_2 –V–N_4	79.8(1)	80.90(6)	78.5(2)	81.0(2)
N_2 –V– N_6	79.8(1)	80.90(6)	80.7(2)	81.0(2)
N_4 –V– N_6	86.0(2)	87.08(10)	86.2(2)	87.7(4)
V–O_2 –C_1	130.9(3)	126.0(2)	131.0(3)	125.3(6)
V–O_3 –C_3	130.9(3)	126.0(2)	130.8(3)	125.3(6)
V–N_2 –N_1	119.2(3)	117.7(2)	118.9(3)	117.1(6)
V–N_2 – C_4	136.0(5)	136.4(2)	134.5(3)	137.0(8)
V–N_6 –N_5	122.0(3)	121.8(1)	122.6(3)	121.7(5)
V–N_4 –N_3	122.0(3)	121.8(1)	121.4(3)	121.7(5)
V–N_4 – C_7	131.1(3)	131.3(2)	131.7(4)	130.8(5)
V–N_6 –C_{10}	131.1(3)	131.3(2)	131.0(4)	130.8(5)
(ii) The HB$(pz)_3$ or HB$(Me_2pz)_3$ ligand				
B–N_1	1.530(9)	1.522(4)	1.529(7)	1.507(14)
B–N_3	1.531(6)	1.542(3)	1.543(7)	1.552(9)
B– N_5	1.531(6)	1.542(3)	1.549(7)	1.552(9)
N_1 –N_2	1.374(7)	1.371(3)	1.352(5)	1.379(11)
N_2 – C_4	1.330(7)	1.335(3)	1.356(6)	1.352(12)
C_1 –C_2	1.401(5)	1.393(3)	1.391(7)	1.399(9)
C_1 – C_{13}	1.504(6)	1.509(4)	1.524(7)	1.520(10)
N_1 – C_6	1.349(8)	1.354(3)	1.346(6)	1.337(12)
N_3 –N_4	1.365(5)	1.375(2)	1.368(5)	1.382(7)
N_3 – C_9	1.352(6)	1.353(3)	1.345(6)	1.366(9)
N_4 – C_7	1.341(6)	1.337(3)	1.332(6)	1.335(9)
B–N_1–N_2	117.6(5)	118.7(2)	118.7(4)	119.8(8)
B–N_1– C_6	132.5(6)	130.9(2)	131.1(4)	129.9(10)
B–N_3– C_9	131.1(5)	130.8(2)	130.0(5)	129.6(7)
B–N_3–N_4	120.9(4)	119.9(2)	120.8(4)	120.2(7)
N_1–B–N_3	108.4(4)	108.7(2)	108.6(4)	108.2(6)
N_1–B–N_5	108.4(4)	108.7(2)	109.1(4)	108.2(6)
N_3–B–N_5	109.6(5)	109.5(2)	108.1(4)	109.0(9)
(iii) The acac ligand				
C_1–O_2	1.283(5)	1.283(3)	1.271(6)	1.270(8)
C_3–O_3	1.283(5)	1.283(3)	1.287(6)	1.270(8)
C_2–C_{15}	1.511(9)	1.530(5)	1.720(2)	1.584(10)
C_{15}–C_{16}			1.330(17)	1.343(14)
O_2 –C_1 –C_2	125.5(4)	125.8(2)	125.4(5)	125.2(9)
O_3 –C_3 –C_2	125.5(4)	125.8(2)	124.4(5)	125.2(9)
O_3 –C_3 –C_{14}	113.4(4)	112.8(3)	114.0(5)	113.7(8)
O_2 –C_1 – C_{13}	113.4(4)	112.8(3)	113.6(5)	113.7(8)
C_2 –C_3 –C_{14}	121.1(4)	121.4(2)	121.6(5)	121.0(7)
C_2 –C_{15}–C_{16}			111.9(12)	100.0(2)

For their angles around the V centre, the O–V–O angles range from 101.25(8)° to 88.92(7)° for **1**, 98.25(8)° to 85.36(10)° for **2**; 100.9(2)° to 86.39(17)° for **3**; 99.2(3)° to 84.9(3)° for **4**, while, the N_{cis}–V–N_{cis} angles range from 87.01(7) to 79.08(7)° for **1** and 86.0(2)° to 79.8(1)° for **3**, respectively. The carbon–oxygen and carbon–carbon bond lengths within the methyl-substituted pentane-2,4-dionato ligands are comparable to those observed in other oxovanadium (IV) pentane-2,4 –dionato complexes.[21] In addition, it is found also that the dihedral angles between the plane formed by O_2, V and O_3, and the plane of the pentane-2, 4-dionato ligand are variously different, *i.e.* 3.59° for **1**, 74.54° for **2**, 0.92° for **3**, 29.50° for **4**, respectively.

Compared with related bonding distances and angles of oxo-vanadium analogues, [VO(acac){HB(3,5-Me_2pz)}](**I**)[27], [VO(acac){HB(3,5-Pr^i_2pz)}](**II**)[27] and [VOCl {HB(3,5-Me_2pz)} (DMF)] (**III**)[13], it is found that the V–Ot distances of **1**, **2**, **3** and **4** are close to that of complex (**I**) [1.596(2) Å]; shorter than those in complexes, (**II**) [1.626(4) Å] and (**III**) [1.649(5) Å]. The V–N_{trans} distances are longer than those in complexes **(I)** [2.328(2) Å]; **(II)** [2.329(4) Å]; **(III)**, [2.329(6) Å]. The V–N_{cis} distances are close to those in **(I)** [average, 2.115(2) Å], **(II)** [average, 2.108(5) Å] and **(III)** [average, 2.113(5) Å]. The angle of O–V–O for complex **3** [average, 96.7(2)°] is bigger than those corresponding to oxovanadium complexes **(I)** [average, 93.6(1)°] and **(II)** [average, 94.5(2)°]; ones for **(1)** [93.64(2)°], **2** [91.8(1)°] and **4** [92.1(3)°] are close to those in complexes **(I)** and **(II)**. The angle of N_{cis}–V–N_{cis} for **4** [average, 84.35(3)°)] is close to that of **(I)** [average, 83.3(1)°], **(II)** [average, 83.6(2)°] and **(III)**, [average, 83.3(2)°]; the average angle of N_{cis}–V–N_{cis} for **1** [81.9(1)°], **2** [82.0(1)°] and **3** [81.81(3)°] are slightly smaller than those in complexes **(I)**, **(II)** and **(III)**.

Quantum chemistry calculation of complexes

The energies and characters of the selected MOs for **1**, **2**, **3** and **4** are presented in Table 4. According to molecular orbital theory, the frontier orbital and nearby molecular orbitals are the most important factors to the activity. The more different the frontier orbitals are, the more stable the molecular structure is. The value of ΔE ($\Delta E = E_{LUMO}–E_{HOMO}$) is 0.1928, 0.19703, 0.16578 and 0.20346, respectively, which shows tha thet order of stability of the complexes is **1** ≅ **2** ≅ **4** > **3**.

The atomic net charges for complexes calculated from NBO analysis are listed in Table 5, the charge of the central V metal changes from 2.368887 to 2.39284 for **1, 2, 3** and **4**, *i.e.* less than +4. Obviously, V has been coordinated by the ligands, which transfers electron density to vanadium. The net charge of the coordinated O_1, O_2, O_3, and N_2, N_4, N_6 atoms are negative, in comparison, the net charge of O_1 is more negative than those of O_2, O_3, and also more negative those of the N atoms. The change in the charge distribution value of the coordinated N atoms (N_2, N_4, N_6) is more than that of the uncoordinated N atoms (N_1, N_3, N_5). The charge distribution value of the carbon atoms of the pyrazole ring changes and it is found that methyl-substituted tripyrazolylborate is more negative than that of tripyrazolylborate.

The NBO bond order (Table 6) between V and O_1 is stronger than that of V–O_2 (or O_3), showing that V–O_1 possess double character, whilst V–O_2(or O_3) have single bond character. The bond order of V–N_2 is weaker than that of V–N_4 and V–N_6. For all complexes, the bond order of V–O(O1, O2, O3) is **1** ≅ **3** > **2** ≅ **4**; while the bond orders of V–N (N2, N4, N6) are **1** ≅ **3** < **2** ≅ **4**. All calculated results are consistent with the experiment results of X-ray diffraction.

Supplementary material

Tables of atomic coordinates, an isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC: 606409–606412, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http: //www.ccdc.cam.ac.uk).

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Table 4 Frontier molecular orbitals' energy values in Hartree for **1**, **2**, **3** and **4**

				HOMO	LUMO	Δ
1	–0.3481	–0.3352	–0.3194	–0.0887	0.1041	0.1928
2	–0.32131	–0.31974	–0.31449	–0.08759	0.10944	0.19703
3	–0.34501	–0.33244	–0.32557	–0.09291	0.07287	0.16578
4	–0.32056	–0.31035	–0.30982	–0.08831	0.11515	0.20346

Table 5 The atomic net charges for complexes **1**, **2**, **3** and **4**

	1	2	3	4
V	2.268887	2.39284	2.37452	2.39092
O_1	–0.90098	–0.93427	–0.91265	–0.93445
O_2	–0.83003	–0.83369	–0.83058	–0.82797
O_3	–0.83003	–0.83369	–0.83058	–0.82797
N_2	–0.45407	–0.47793	–0.44605	–0.48763
N_4	–0.49610	–0.52658	–0.49008	–0.51940
N_6	–0.49610	–0.52658	–0.49008	–0.51940
N_1	–0.43532	–0.4497	–0.42960	–0.44798
N_3	–0.41954	–0.43132	–0.42422	–0.43545
N_5	–0.41954	–0.43132	–0.42422	–0.43545
B	0.84752	0.83813	0.87690	0.84032

Table 6 Selected NBO bond order (a.u.) for complexes **1**, **2**, **3** and **4**

Bond orders	1	2	3	4
V-O1	0.7261	0.6869	0.7135	0.6886
V-O2	0.2247	0.2114	0.2239	0.2096
V-O3	0.2247	0.2114	0.2239	0.2096
V-N4	0.1842	0.1936	0.1838	0.1942
V-N2	0.1140	0.1237	0.1075	0.1247
V-N6	0.1842	0.1936	0.1838	0.1942
N1-N2	0.8401	0.8315	0.8643	0.8243
N3-N4	0.8451	0.8250	0.8457	0.8257
B-N1	0.6677	0.6745	0.6616	0.6771
B-N3	0.6682	0.6651	0.6525	0.6643
B-N5	0.6682	0.6651	0.6525	0.6643

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