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PII:	S0277-5387(17)30221-8		
DOI:	http://dx.doi.org/10.1016/j.poly.2017.03.033		
Reference:	POLY 12548		
To appear in:	Polyhedron		
Received Date:	8 November 2016		
Revised Date:	15 March 2017		
Accepted Date:	19 March 2017		



Please cite this article as: P.A. Petrov, A.I. Smolentsev, A.S. Bogomyakov, S.N. Konchenko, Novel Vanadium Complexes Supported by a Bulky Tris(pyrazolyl)borate Ligand, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.03.033

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#### Novel Vanadium Complexes Supported by a Bulky Tris(pyrazolyl)borate Ligand

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(Received 2016)

Keywords: Vanadium, Tris(pyrazolyl)borates, Crystal structure, Magnetic susceptibility

### Abstract

The V(III) complex  $[V(Tp^{tBu_2})Cl_2]$  (**1**,  $Tp^{tBu_2}$  = hydrotris(3,5-di-*tert*-butylpyrazolyl)borate) was synthesized by the reaction of  $[VCl_3(THF)_3]$  (prepared *in sit*)*u* and  $K(Tp^{tBu_2})$ . Reduction of **1** with potassium mirror afforded the V(II) complex  $[V(Tp^{tBu_2})Cl]$  (**2**). Both complexes were characterized by means of a single crystal X-ray diffraction. **1** represents the first example of pentacoordinated vanadium tris(pyrazolyl)borate (Tp) complexes. The V(III) ion environment is a distorted trigonal bipyramid. **2** is the first V(II) Tp-complex. The V(II) ion has tetrahedral environment, and the CI atom is deviated from the B–V axis ( $\angle B(1)-V(1)-Cl(1) = 157.8^\circ$ ). Magnetic susceptibility measurements showed reasonable  $\mu_{eff}$  values at 300 K: 2.80 (**1**) and 3.78 (**2**)  $\mu_B$ , those prove the oxidation states of V: +3 (**1**) and +2 (**2**).

### 1. Introduction

Since their discovery in the mid-1960s [1], tris(pyrazolyl)borates ( ${}^{R}Tp^{R1,R2}$ )<sup>-</sup> (Scheme 1), often nicknamed *scorpionates*, have become important ancillary ligands in modern coordination, organometallic and bioinorganic chemistry [2–6]. Usually coordinated in tridentate  $\kappa^{3}$ -*N*,*N'*,*N''* manner, tris(pyrazolyl)borates are considered as cyclopentadienyl analogues, and their complexes with most transition and post-transition metals are known. The main feature of ( ${}^{R}Tp^{R1,R2}$ )<sup>-</sup> is the ease of variation of substituents R1 and R2 in pyrazole cycles, and (to lesser extent) R on boron atom. Reasonable choice of the substituents makes Tp ligands a powerful

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instrument to stabilize the desired oxidation state and coordination polyhedron of the central ion providing consequently a possibility for a fine tuning of the steric and electronic properties of the metal complexes. For instance, tetrahedral complexes of the first row transition metals with hydrotris(pyrazolyl)borates containing bulky R1 (<sup>t</sup>Bu, <sup>i</sup>Pr, neopentyl (Np), etc.) and small R2 (Me, H) substituents proved to be really attractive catalysts and/or pre-catalysts for small molecule activation [7].



Fig. 1. The tris(pyrazolyl)borate  $({}^{R}Tp^{R1,R2})^{-}$  ligands.

The more bulky hydrotris(pyrazolyl)borate –  $(Tp^{tBu_2})^-$  – has been designed as a more stable ligand system shielding both the B–H moiety and metal ion, but surprisingly it has not attracted much attention. To the best of our knowledge, only two complexes of *d*-metals are described:  $[Zn(Tp^{tBu_2})I]$  and  $[Cd(Tp^{tBu_2})I]$  [8]. At the same time, the use of  $(Tp^{tBu_2})^-$  was very fruitful for synthesis of unusual monomeric compounds of group 13 elements  $[M(Tp^{tBu_2})]$  (M = Ga, In) exhibited very interesting chemistry towards group 16 elements as well [9–14]. A few V(III) tris(pyrazolyl)borates are known, but only with small substituents in the pyrazole cycles allowing coordination of additional ligand completing the coordination polyhedron to a distorted octahedron:  $[V(Tp^{R_2})Cl_2(L)]$  (R = H, Me; L = DMF, THF, *p*-(Me\_2N)Py) [15–18]. The V(II) Tp-complexes and the low-coordinated V(III) were still not reported.

In order to discover the interesting chemical and physical properties of the low-valent lowcoordinated vanadium Tp-complexes, we have started a systematic study of such compounds. This work is focused on the synthesis and structural characterization of two compounds:  $[V(Tp^{tBu_2})Cl_2]$  (1) and  $[V(Tp^{tBu_2})Cl]$  (2), which can be used as starting reagents for preparation of unusual derivatives.

#### 2. Experimental

#### 2.1. General

All reactions were performed using standard Schlenk and vacuum-line techniques under argon atmosphere or in evacuated ampoules. VCl<sub>3</sub> (Sigma Aldrich) was used as received. The starting compound K(Tp<sup>tBu</sup>) was prepared as described [8]. Solvents were pre-dried by using an MBraun SPS-800 solvent purification system and then dried by refluxing over Na/K alloy, degassed and stored over Na/K *in vacuo*. Elemental analyses were performed using Euro EA 3000 analyzer. Magnetic susceptibility measurements were performed on polycrystalline samples with Quantum Design MPMSXL SQUID magnetometer in the temperature range 2–300 K with magnetic fields up to 5 kOe. The susceptibilities of the samples were corrected for the sample holder contribution, previously measured under the same conditions, and for the diamagnetic contribution of the constituent atoms by using Pascal constant tables. The effective magnetic moment was calculated as  $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$ . Infrared spectra (in KBr pellets) were recorded using a Scimitar FTS 2000 spectrometer in 4000 to 400 cm<sup>-1</sup> range.

### 2.2. Synthesis and characterization

### 2.2.1. Synthesis of [V(Tp<sup>tBu2</sup>)Cl<sub>2</sub>] (1)

Solid VCl<sub>3</sub> (0.315 g, 2 mmol) was placed into a Schlenk tube equipped with J. Young PTFE stopcock. THF (*ca.* 40 mL) was condensed into the reaction vessel under reduced pressure and the mixture was heated at 70°C for 24 h. Solid K( $Tp^{tBu_2}$ ) (1.18 g, 2 mmol) was added and the heating was continued for another 14 h. Reaction mixture slowly turned blue and a colorless powder precipitated. All volatiles were removed under reduced pressure and the residue was extracted with toluene for 12 h at 100°C. The extract was filtered and dried *in vacuo*. Extraction of the crude product with *n*-heptane (20 mL) in the sealed two-necked tube afforded blue crystals suitable for an X-ray experiment. Yield 1.21 g (90 %). Anal. Found C 58.80, H 8.70, N 12.20. Calc. for C<sub>33</sub>H<sub>58</sub>BCl<sub>2</sub>N<sub>6</sub>V: C 59.02, H 8.70, N 12.52. IR (KBr): 2960 (s), 2926 (m), 2869 (m), 2594 (m), 1728 (w), 1518 (s), 1486 (m), 1463 (m), 1434 (m), 1413 (s), 1394 (w), 1362 (m), 1338 (m), 1317 (m), 1249 (s), 1225 (s), 1170 (s), 1136 (m), 1110 (m), 1068 (m), 1047 (m), 1015 (m), 929 (w), 856 (w), 813 (m), 797 (m), 741 (m), 707 (m), 619 (m), 561 (w), 515 (w), 484 (w), 407 (m).

### 2.2.1. Synthesis of [V(Tp<sup>tBu2</sup>)Cl] (2)

The synthesis was carried out in a double-section ampoule shown in ESI (Fig. S1–S6). A piece of potassium (0.3 g, 7.67 mmol) was placed onto the bottom of the section A of the ampoule

evacuated to  $10^{-3}$  Torr. Heating of the section A from the bottom by a Bunsen burner causes deposition of K as a mirror on the cold walls over the heated zone. In a glove-box solid [V(Tp<sup>rBu2</sup>)Cl<sub>2</sub>] (0.070 g, 0.104 mmol) and a glass-coated magnetic stir bar were added to the Kmirror thus obtained. Then the ampoule was connected to a vacuum line and n-hexane (Ca. 15 mL) was condensed into the section A following by flame sealing of the ampoule (ESI, Fig. S1). The mixture was stirred and heated at 50°C for 72 h (ESI, Fig. S2). After settling of a precipitate the reaction solution was decanted to the section B (ESI, Fig. S3). The solvent was condensed back to the section A (ESI, Fig. S4), stirred for some time for saturation and left for settling. Then the solution was again decanted to the section B. The condensation-decantation cycle was repeated several times to complete extraction of 2 which started to crystallize in the section B during this process. The crystallization was completed by keeping the final extract at +5°C overnight (ESI, Fig. S5). Purple crystals of 2 were isolated and dried by decantation of the mother liquor to the section A following by its cooling with liquid nitrogen. Finally the sections A and B were flame separated (ESI, Fig. S6). The crystals of 2 were retrieved from the ampoule in a glove-box. Yield 0.054 g (82 %). Single crystal suitable for an X-ray experiment was found in the bulk material. Anal. Found C 62.15, H 9.30, N 13.00. Calc. for C<sub>33</sub>H<sub>58</sub>BClN<sub>6</sub>V: C 62.31, H 9.19, N 13.21. IR (KBr): 3205 (m), 2964 (s), 2926 (m), 2908 (m), 2870 (m), 2622 (m), 1731 (w), 1615 (w), 1568 (s), 1520 (m), 1488 (m), 1462 (m), 1412 (s), 1364 (w), 1343 (m), 1326 (m), 1291 (m), 1250 (s), 1225 (s), 1173 (s), 1147 (m), 1110 (m), 1064 (m), 1045 (m), 1008 (m), 930 (w), 801 (m), 736 (m), 710 (m), 616 (m), 555 (w), 516 (w), 452 (w).

### 2.3. Crystal structure determination

Single crystals of **1** and **2** were selected under a microscope and mounted to the tip of the thin glass fiber with epoxy resin. X-ray intensity data were collected on a Bruker X8 Apex CCD diffractometer at 100.0(2) and 150.0(2) K for **1** and **2**, respectively (graphite monochromator,  $\lambda(Mo \alpha) = 0.71073$  Å,  $\varphi$ -scanning). Data reduction and multi-scan absorption were carried out using SADABS [19]. The structures were solved by the direct methods and refined by least-squares methods against  $F^2$  using the SHELXTL program suite [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated on idealized positions and refined with a riding model. Crystallographic data and selected refinement details are summarized in Table 1.

	1	2	
Chemical formula	C <sub>33</sub> H <sub>58</sub> BCl <sub>2</sub> N <sub>6</sub> V	C <sub>33</sub> H <sub>58</sub> BCIN <sub>6</sub> V	
Formula weight	671.50	636.05	
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c	Triclinic, <i>P</i> 1	
Temperature (K)	100	150	
<i>a</i> (Å)	19.9451(16)	10.8738(5)	
b (Å)	10.1263(7)	13.0509(5)	
<i>c</i> (Å)	20.3500(16)	13.2217(5)	
α (°)	90	95.614(1)	
β (°)	115.907(1)	93.541(1)	
γ (°)	90	101.767(1)	
V (Å <sup>3</sup> )	3697.0(5)	1821.65(13)	
Ζ	4	2	
$d_{\rm calcd}$ (g cm <sup>-3</sup> )	1.206	1.160	
μ (mm <sup>-1</sup> )	0.443	0.375	
Crystal size (mm)	0.18 × 0.16 × 0.14	0.30 × 0.18 × 0.15	
F(000)	1440	686	
Θ range (°)	2.01-27.49	2.10–27.52	
h, k, l limits	$-25 \le h \le 21,$ $-12 \le k \le 13,$ $-26 \le l \le 25$	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -17 ≤ l ≤ 15	
Measured reflections	17341	16592	
Observed reflections $[l > 2\sigma(l)]$	5032 ( <i>R</i> <sub>int</sub> = 0.078)	6668 ( <i>R</i> <sub>int</sub> = 0.033)	
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.0535, 0.0927	0.0539, 0.1394	
R indices (all data)	0.1118, 0.1063	0.0693, 0.1465	
Goodness-of-fit on F <sup>2</sup>	0.902	1.080	
No. of parameters	410	431	
No. of restraints	0	12	
$\Delta \rho_{max}$ , $\Delta \rho_{min}$ (e Å <sup>-3</sup> )	0.39, -0.40	1.92, -0.66	
CCDC	1513374	1513375	

Table 1. Cry	ystal Data	and Data	Collection	and Refine	ment Details
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#### 3. Results and Discussion

### 3.1. Synthesis

The first structurally characterized V(III) Tp-complex  $[V(Tp^{Me_2})Cl_2(DMF)]$  was obtained by the reaction of  $K(Tp^{Me_2})$  with VCl<sub>3</sub> in DMF following by recrystallization of the initially formed

 $[V(Tp^{Me_2})Cl_2(DMF)(H_2O)]$  from benzene [15]. The authors of this work have noted that "DMF appears to be the solvent of choice" for the synthesis of Tp-complexes starting from VCl<sub>3</sub> as a vanadium source, synthesis in other solvents, such as THF or CH<sub>2</sub>Cl<sub>2</sub>, invariably yields a complicated mixture [15]. Nevertheless, later the compounds  $[V(Tp^{R_2})Cl_2(THF)]$  were prepared in THF by using  $[VCl_3(THF)_3]$  as vanadium source in the reactions with  $K(Tp^{H_2})$  [17] or  $[Sn(Tp^{Me_2})ClBu_2]$  [18]. Taking all these results into account, we carried out the synthesis as a one-pot procedure. The first step is to prepare  $[VCl_3(THF)_3]$  by heating  $VCl_3$  in THF over 24 h, and the second step is to react with  $K(Tp^{tBu_2})$ , which was added directly to the mixture prepared at the first step. We found that the compound **1** was obtained in a nearly quantitative yield by using the procedure described above (Scheme 1).



Scheme 1. Synthesis of  $[V(Tp^{tBu_2})Cl_2]$  (1) and  $[V(Tp^{tBu_2})Cl]$  (2).

The V(II) complex **2** was prepared by reduction of **1** with potassium in hexane. For this reaction potassium was used as a mirror prepared by vacuum deposition. The whole synthesis was carried out in a pre-evacuated flame-sealed ampoule without any protecting gas. This technic allows one to prevent the product from oxidation by trace impurities in Ar or N<sub>2</sub> in the Schlenk line. The ampoule (see ESI) was finally opened in a glove-box where atmosphere contains less than 0.1 ppm of oxygen. The fully conversion of the V(III) to the V(II) compound was verified by IR spectrum, i.e., in the spectrum of **2** the v<sub>B-H</sub> band is shifted by almost 30 cm<sup>-1</sup> to range of higher frequencies related to that of **1** (2622 and 2594 respectively).

#### 3.2. Structures of the complexes 1 and 2

Molecular structures of **1** and **2** were determined by means of single crystal X-ray analysis (Fig. 2, 3). The coordination numbers of V metal center are 5 and 4, respectively. These coordination numbers are unusual for V(III) and V(II) complexes. Most common coordination sphere for the

V metal in any oxidation state is with 6 coordination sites. The bulky <sup>t</sup>Bu moieties in **1** and **2** prohibited V atoms from coordinating more than one ligand or dimerizing *via* chloride bridges. The coordination geometry of V atom in complex **1** (Fig. 2) can be described as a trigonal bipyramid with N(11), N(13) and Cl(2) atoms in the equatorial plane. The basal distance V(1)– N(21) (2.312(3) Å) is significantly longer than two equatorial V–N ones (2.074(2) and 2.076(3) Å). Such V–N bond length pattern is quite common for Tp-complexes, but earlier it was rather observed for vanadyl complexes with six-coordinated V and the ligands strongly differing in size [20-32]. All the pyrazole rings in the (Tp<sup>tBu2</sup>)<sup>-</sup> ligand are twisted in a propeller-like fashion, the angles between them and the V(1)–B(1) axis are 12.4°, 30.8° and 39.2°. The maximal angle is found for N(31)N(32)C(31)C(32)C(33) ring. Strong deviation of the pyrazole moiety leads to a simultaneous shortening of the V(1)...N(32) distance to 2.657 Å *vs.* 2.942 and 2.921 for V(1)...N(22) and V(1)...N(12), respectively.



**Fig. 2.** Molecular structure of **1**. Hydrogen atoms and methyl groups omitted for clarity. Selected bond lengths (Å): V1–N11 2.074(2), V1–N21 2.312(2), V1–N31 2.076(2), V1–Cl1 2.2590(9), V1–Cl2 2.2394(8).

The coordination environment of V atom in complex **2** (Fig. 3) is a highly distorted tetrahedron. The pyrazole rings are also twisted, but to a less intensity compared to complex **1**: the angles between the V(1)–B(1) axis and the ring planes are 14.7, 21.6 and 28.3°. Similarly to complex **1**, the strongest twisting occurs again for the ring N(31)N(32)C(31)C(32)C(33) which has the

shortest distance to Cl(1). The latter is significantly shifted from the V(1)–B(1) axis with B(1)–V(1)–Cl(1) angle of 157.8°.

The distorted coordination of the V atom may be due to Jahn-Teller effect that one could expect for  $V^{2+}$  ( $d^3$  configuration) in tetrahedral environment [33]. To the best of our knowledge, complex **2** is the first example of the divalent V ion in a (distorted) tetrahedral environment. Other structurally characterized V(II) species, such as dihalides VHal<sub>2</sub> [34–36], ternary phases AVHal<sub>3</sub> (A = alkali metal) [37, 38], possess an octahedral environment where Jahn-Teller effect is not expected.



**Fig. 3.** Molecular structure of **2**. Hydrogen atoms and methyl groups omitted for clarity. Selected bond lengths (Å): V1–N11 2.1286(18), V1–N21 2.1348(19), V1–N31 2.1162(18), V1–Cl1 2.3347(7).

Despite the absence of the V(II) Tp-complexes, several examples of classical Jahn-Teller ions  $Cu^{2+} (d^9)$ ,  $Cr^{2+} (d^4)$  and  $Co^{1+} (d^8)$  tetrahedrally coordinated with Tp ligands are present in the Cambridge Structural Database [39-45]. An averaged B–Cu–Hal angle of 166° is observed for 7 structures of formula [Cu(Tp)Hal]. The B–Cu–O angles are 169.5 and 173.8° for [Cu(Tp<sup>H,tBu</sup>)OH] [44] and [Cu(Tp<sup>*i*Pr,tBu</sup>)(CF<sub>3</sub>SO<sub>3</sub>)] [45], respectively. For the three examples of [Cr(Tp<sup>Me,tBu</sup>)X] complexes (X = Cl, Et and Ph) [41], the B–Cr–Cl and B–Cr–C angles fall in the range 130.8–150.7°. The B–Co–C and B–Co–N angles in [{Co(Tp<sup>Np</sup>)}<sub>2</sub>(µ–N<sub>2</sub>)] and [Co(Tp<sup>Np</sup>)(CO)] are 145.4° and 153.4° respectively, which was explained by occurrence of Jahn-Teller effect based on DFT

calculations [42]. Theoretical study focused on magnetic anisotropy in [M(Tp)Cl] complexes (M = first-row transition-metals) also supports this conclusion [43]. Therefore we believe that the small B(1)-V(1)-Cl(1) angle in **2** is attributed to Jahn-Teller effect.

#### 3.3. Magnetic measurements

Oxidation states of vanadium atom in **1** and **2** have been confirmed by using magnetic susceptibility measurements (Fig. 4). For the complexes **1** and **2** the values of  $\mu_{eff}$  values are 2.80 and 3.78  $\mu_B$  at 300 K and do not change with lowering the temperature to 20 K. Below 20 K the  $\mu_{eff}$  values decrease slightly to 2.51  $\mu_B$  for **1** at 5 K and to 3.52  $\mu_B$  for **2** at 2 K. The  $\mu_{eff}$  values are in a good agreement with spin-only ones for paramagnetic centers with *S* = 1 (2.83  $\mu_B$  for *g* = 2.000 for  $d^2$  configuration) and *S* = 3/2 (3.87  $\mu_B$  for *g* = 2.000 for  $d^3$  configuration). Slightly lower value for **2** can be caused by the partial decomposition of the sample during its transfer from a glove box to a magnetometer. The constancy of  $\mu_{eff}$  values in the 300–20 K temperature range suggests a good separation of the paramagnetic centers both in **1** and **2**. Very weak antiferromagnetic exchange interactions operating below 20 K can cause the decrease in  $\mu_{eff}$  at low temperature.



Fig. 4. Temperature dependence of effective magnetic moment for  $1 (\blacksquare)$  and  $2 (\triangledown)$ .

#### 4. Conclusions

In conclusion, the first V(III) complex  $[V(Tp^{tBu_2})Cl_2]$  with sterically demanding tris(pyrazolyl)borate ligand has been synthesized *via* salt metathesis reaction between K(Tp<sup>tBu\_2</sup>)

and  $[VCl_3(THF)_3]$  generated from VCl\_3 in hot THF. Reduction of  $[V(Tp^{tBu_2})Cl_2]$  with potassium mirror leads to  $[V(Tp^{tBu_2})Cl_2]$ , which is the first V(II) tris(pyrazolyl)borate complex. The vanadium oxidation states in the complexes have been reliably proved by magnetic measurements. Both  $[V(Tp^{tBu_2})Cl_2]$  and  $[V(Tp^{tBu_2})Cl]$  characterized by means of single crystal X-ray analysis. The complexes are monomeric, and the tris(pyrazolyl)borate ligand is strongly twisted in both cases. The coordination environment of V ion is distorted trigonal bipyramid for V(III) and distorted tetrahedron for V(II). The distortion of the latter is likely attributed to Jahn-Teller effect.

#### Acknowledgements

CCF

This work was supported by the Russian Science Foundation (project No. 16-13-10294).

### Appendix A. Supplementary data

CCDC 1513374 and 1513375 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/\*\*\*\*\*\*\*\*

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Novel vanadium complexes  $[V(Tp^{tBu_2})Cl_2]$  and  $[V(Tp^{tBu_2})Cl]$  with bulky tris(3,5-di-*tert*-butylpirazolyl)borate ligand have been synthesized and structurally characterized. The oxidation states of vanadium (+3 and +2, respectively) have been unambiguously confirmed by magnetic susceptibility data.

