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Dichlorobis(tetrahydrofuran)(*N*,*N*′-di-*tert*-butylethane-1,2-diamine)vanadium(II)

Antonio Carlos Niedwieski,[a] G. Jeffery Leigh,[b] Tai Hasegawa[c] and Fábio Souza Nunes[a]*

[a]Universidade Federal do Paraná, Departamento de Química, CP 19081, CEP 81531-990, Curitiba - PR, Brazil, [b]University of Sussex, School of Chemistry, Physics and Environmental Science, Brighton, BN1 9QJ, England, and [c]Henry Taube Institute, 897 Embarcadero Road, Palo Alto, CA 94303, USA

Correspondence e-mail:
fsnunes@quimica.ufpr.br

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.137
Data-to-parameter ratio = 22.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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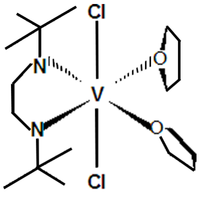
The title complex, [VCl_2(dtbeda)(thf)$_2$] (dtbeda is *N*,*N*′-di-*tert*-butylethane-1,2-diamine), was prepared from the reaction of [V_2Cl_3(thf)$_6$]$_2$[Zn_2Cl_6] with dtbeda in refluxing thf. The crystal structure of [VCl_2(dtbeda)(thf)$_2$] exhibits chlorides in *trans* positions in a distorted octahedral geometry around the vanadium site. The asymmetric unit consists of one-half of the complex, which is located on a twofold rotation axis in space group *C*2/*c*.

Comment

In recent years, vanadium has attracted the attention of bioinorganic chemists, after proof of its presence at the active site of vanadium-nitrogenase (Eady, 1996). Vanadium(II) trinuclear complexes have been identified as functional models of the reducing site of vanadium-nitrogenase (Luvena *et al.*, 1982; Shilov, 1987). It is known that *trans*-[VCl_2(tmeda)$_2$] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) is a good starting material for the synthesis of trinuclear vanadium(II) complexes (Edema *et al.*, 1990; Hitchcock *et al.*, 1997).

In tetrahydrofuran solutions *trans*-[VCl_2(tmeda)$_2$] is in equilibrium with [$V_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})_2(\text{tmeda})_3]^+$, which can be prepared by a self-assembly mechanism when *trans*-[VCl_2(tmeda)$_2$] reacts with a halide-removing species, such as sodium tetraphenylborate, at room temperature. However, this mechanism is not completely understood. Apparently, the self-assembly is strongly dependent on the electronic and steric effects imposed by the diamine (Niedwieski *et al.*, 2003).



(I)

This present work is part of a systematic study of the electronic and steric effects which govern the thermodynamic stability and reactivity of *trans*-[VCl_2(diamine)$_2$] complexes toward the formation of the trinuclear species. In an attempt to synthesize *trans*-[VCl_2(dtbeda)$_2$] (dtbeda = *N*,*N*′-di-*tert*-butylethane-1,2-diamine), we ended up isolating the title complex, (I), which has only one dtbeda coordinated to vanadium, the coordination sphere being completed by two solvent molecules. [VCl_2(dtbeda)(thf)$_2$] is the first dtbeda–vanadium(II) complex to be structurally characterized.

A view of [VCl_2(dtbeda)(thf)$_2$] is shown in Fig. 1. The molecule lies on a crystallographic twofold rotation axis, with thf molecules in a *cis* configuration. Selected bond distances

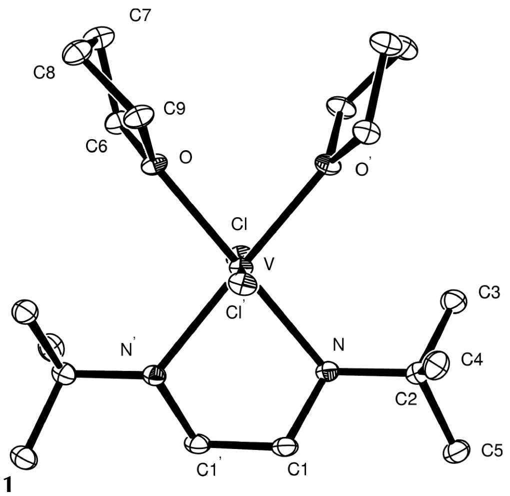


Figure 1
View of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Primed atoms are related to unprimed atoms by twofold rotation.

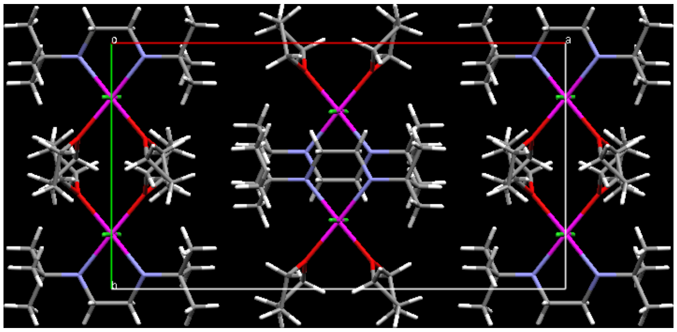


Figure 2
The molecular packing, viewed along the *c* axis.

and angles are listed in Table 1. The vanadium(II) ion occupies an octahedral environment, with the chloride ligands bound axially to it at a distance of 2.4888 (7) Å, with a $Cl^{i}—V—Cl$ angle of 178.11 (4)° (symmetry code as in Table 1). The same configuration was reported for related bis(diamine) complexes, $[VCl_2(diamine)_2]$ (diamine: tmeda = *N,N,N′,N′*-tetramethylethane-1,2-diamine and deeda = *N,N′*-diethylethane-1,2-diamine), where V—Cl distances of 2.487 (1) and 2.4936 (14) Å, respectively, were found (Niedwieski *et al.*, 2003). The octahedron is distorted, due to the space requirements of the bulky dtbeda.

Angles of 81.76 (6)° [for N—V—Cl and $N^{i}—V—Cl^{i}$ (symmetry code as in Table 1] and 96.78 (6)° (for $N—V—Cl^{i}$ and $N^{i}—V—Cl$) indicate an organic skeleton slightly twisted above and below the mean OO'NN' plane. The two *tert*-butyl groups are in a *gauche* conformation with respect to each other.

Experimental

All operations were carried out under an inert atmosphere using standard Schlenk techniques. The solvent was dried by a standard procedure and distilled twice under dinitrogen prior to use (Perrin & Armarego, 1997). Liquid dtbeda was refluxed over sodium and distilled under dinitrogen. The starting material $[V_2Cl_3(thf)_6]_2$\\-forcelb][Zn_2Cl_6] was prepared as described by Bouma *et al.* (1984).

The title complex was prepared as follows. Addition of dtbeda (2.65 ml, 12.4 mmol) to a light green suspension of $[V_2Cl_3$\\-forcelb]$(thf)_6]_2[Zn_2Cl_6]$ (1.0 g, 0.62 mmol) in refluxing thf (40 ml) produced a blue–green solution, with immediate precipitation of a very fine pale-green solid. Upon cooling to room temperature, the suspension was filtered off and the resulting solution kept for 4 d at 253 K, after which green crystals suitable for X-ray study were isolated; yield 50%. FAB–MS: *m*/*z* 381 (25%, $\{VCl_2(tbeda)(thf)_2\}^+$); magnetochemistry: $\mu_{eff} = 3.47\ \mu_B$ (compared with the spin-only value of 3.87 μ_B).

UV–vis data: the electronic spectrum of (I) in CH_2Cl_2, along with its bigaussian analysis, shows bands at 470, 561, 648 and 741 nm with low intensities, typical of *d*–*d* Laporte-forbidden transitions. The spectrum was rationalized on the basis of C_{2v} symmetry and assigned as transitions from the ground state $^4B_{1g}$ to the following excited states (in order of decreasing energy): $^4B_{2g}(2)$, $^4A_{2g}$, $^4B_{2g}$ (1), $^4A_{1g}$.

IR data: typical V—O and V—N stretching bands at 442 and 378 cm^{-1} were observed.

Crystal data

$[V(C_4H_8O)_2(C_8H_{22}N_2)Cl_2]$
$M_r = 436.34$
Monoclinic, $C2/c$
$a = 20.915$ (2) Å
$b = 10.3733$ (9) Å
$c = 11.4042$ (13) Å
$\beta = 113.236$ (5)°
$V = 2273.6$ (4) Å^3
$Z = 4$

$D_x = 1.275$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 335 reflections
$\theta = 3.7$–27.5°
$\mu = 0.69$ mm^{-1}
$T = 173$ (2) K
Prism, green
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.813$, $T_{max} = 0.903$
8029 measured reflections
2597 independent reflections

2003 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 27$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.137$
$S = 1.07$
2597 reflections
114 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 4.9995P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V—O	2.2165 (19)	N—C1	1.483 (4)
V—N	2.274 (2)	N—C2	1.511 (4)
V—Cl	2.4888 (7)	$C1—C1^{i}$	1.508 (6)
O—C9	1.453 (3)	C2—C3	1.520 (4)
O—C6	1.451 (3)		
$O—V—O^{i}$	80.02 (10)	$O^{i}—V—Cl$	91.38 (5)
O—V—N	171.80 (7)	N—V—Cl	81.76 (6)
$N—V—N^{i}$	79.80 (12)	$Cl^{i}—V—Cl$	178.11 (4)
O—V—Cl	90.07 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*;

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program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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