[Pt(C2H8N2)(C12H8N2)]Cl2·2H2O AND [Pt(C2H8N2)(C12H8N2)](PF6)2

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1091). Services for accessing these data are described at the back of the journal.

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endo-{6,6'-Diethoxy-2,2'-[(R)-propane-1,2-diylbis(nitrilomethylidene)]diphenolato-O,N,N',O'}oxovanadium(IV)

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Abstract

In the title mononuclear oxovanadium(IV) complex, [VO(C$_{21}$H$_{24}$N$_2$O$_4$)], the methyl group of the central diamine moiety in the Schiff base ligand is directed opposite to the oxo ligand. This *endo* isomer elutes more slowly than the *exo* isomer when subjected to high-performance liquid reversed-phase chromatography using CH$_3$CN–H$_2$O (1:1 *v/v*) as the eluent. Crystals of both the *endo* and *exo* isomers decompose at 473 K, with no solid-state isomerization from *endo* to *exo* or vice versa.

Comment

The solid-state thermal isomerization of Schiff base–oxovanadium(IV) complexes has been investigated previously by Kojima *et al.* (1994) and Hoshina, Ohba *et al.* (1999). However, the mechanism of isomerization is still unclear at present. Thus, the title complex, (I), was prepared and studied by X-ray crystallography and the results are presented here.

(I)
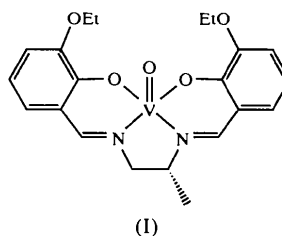
There are two possible geometrical isomers for (I), *exo* and *endo*, which are defined as having the substituted group (the methyl on C18) of the central diamine moiety in the Schiff base ligand directed outside or inside the O$_{oxo}$N$_2$ plane (O2, N7 and N8) of the VN$_2$O$_3$ square pyramid, respectively. In the present study, the slower eluate by high-performance liquid reversed-phase chromatography was determined to be the *endo* isomer. The methyl on C18 is in an axial position, almost antiparallel to the V1═O2 bond axis. This is in contrast to the equatorial methyl orientation of the sal-(*R*)(*S*)-pn ligand (sal = salicylidene; pn = 1,2-propylenediamine) in crystals of *endo*-(chlorotriphenylstannyloxy)[*N*,*N*'-1,2-propylenebis(salicylideneamino)]vanadium(IV) (Cashin *et al.*, 1989).
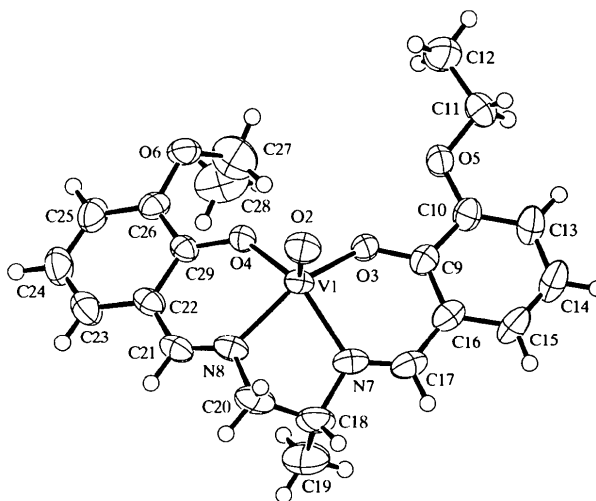

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of (I) showing the atom-numbering scheme and 50% probability ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Although Schiff base–oxovanadium(IV) complexes with two ethoxy substituents at the 3-positions have a tendency to connect with a water molecule for crystallization *via* two bifurcated hydrogen bonds (Zamian *et al.*, 1995; Kasahara *et al.*, 1996; Hoshina *et al.*, 1998; Hoshina, Tsuchimoto & Ohba, 1999), the title crystal is an exception as it is unhydrated. The O6 ethoxy group is directed perpendicular to the salicylidene moiety, which may be due to the packing efficiency.

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A crystal of [VO(sal-*meso*-bn)] [H$_2$sal-*meso*-bn = *N*,*N*′-disalicylidene-(*R,S*)(*S,R*)-2,3-butanediamine] shows thermal isomerization from *endo* to *exo* in the solid state at 483 K (Hoshina, Tsuchimoto & Ohba, 1999). However, crystals of both the *endo* and *exo* isomers of the present complex decomposed at *ca* 473 K, with no isomerization having taken place.

Experimental

The H$_2$3-EtOsal-(*R*)-pn ligand was prepared by the reaction of (*R*)-1,2-propylenediamine (1.48 g, 20 mmol) with two equivalents of 3-ethoxysalicylaldehyde (6.64 g, 40 mmol) in ethanol. To a hot methanol solution (500 ml) of oxovanadium(IV) sulfate (5.06 g, 20 mmol) was added H$_2$3-EtOsal-(*R*)-pn (7.69 g, 20 mmol) and pyridine (50 ml), and the mixture was stirred for 1 h at 333 K. The resulting green precipitate was collected by filtration and washed with ether {yield of [VO(3-EtOsal-(*R*)-pn)] 6.87 g, 79.0%}. The reaction product was a mixture of *exo* and *endo* isomers (*exo:endo* ≃ 1:5). The ratio of isomers was estimated by high- performance liquid reversed-phase chromatography using CH$_3$CN–H$_2$O (1:1 *v/v*) as the eluent. Green plate-like crystals of the *exo* isomer and green prisms of the *endo* isomer, (I), were grown from an acetonitrile solution. The two isomers of the present complex have similar solubilities.

Crystal data

[VO(C$_{21}$H$_{24}$N$_2$O$_4$)]
M_r = 435.37
Orthorhombic
$P2_12_12_1$
a = 12.783 (4) Å
b = 16.645 (3) Å
c = 9.834 (3) Å
V = 2092.2 (8) Å^3
Z = 4
D_x = 1.382 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14.4–15.0°
μ = 0.508 mm^{-1}
T = 298 K
Prism
0.40 × 0.37 × 0.27 mm
Green

Data collection

Rigaku AFC-5S diffractometer
$\theta/2\theta$ scans
Absorption correction:
  by integration (numerical; Coppens *et al.*, 1965)
  T_{min} = 0.780, T_{max} = 0.878
2737 measured reflections
2737 independent reflections

2203 reflections with $I > 2\sigma(I)$
θ_{max} = 27.5°
h = 0 → 16
k = 0 → 21
l = 0 → 12
Intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.048
$wR(F^2)$ = 0.120
S = 1.250
2714 reflections ($I \geq 0$)
263 parameters

$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

H atoms: see below
$w = 1/[\sigma^2(F^2) + 0.00348(F^2)^2]$
$(\Delta/\sigma)_{max}$ = 0.001

Absolute structure:
  Flack (1983)
  Flack parameter = 0.03 (4)

Table 1. *Selected geometric parameters (Å, °)*

V1—O2	1.598 (3)	V1—N7	2.066 (4)
V1—O3	1.938 (3)	V1—N8	2.053 (4)
V1—O4	1.918 (3)		
O3—V1—O4	86.9 (1)	O4—V1—N8	87.1 (1)
O3—V1—N7	86.6 (1)	N7—V1—N8	78.4 (2)
V1—N7—C18—C19	103.2 (5)	C26—O6—C27—C28	63.1 (7)
C10—O5—C11—C12	−173.7 (4)		

The coordinates of all H atoms were calculated geometrically and fixed with U_{iso}(H) = 0.076 Å^2. The absolute structure was assigned based on the absolute configuration of the 3-EtOsal-(*R*)-pn ligand, and was confirmed by the Flack (1983) parameter.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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