

at 253 K for several months afforded a mass of purple cube-shaped crystals.

Crystal data

[Nd(C₃H₅O₃)₂(NO₃)(H₂O)]
M_r = 402.41
 Monoclinic
*P*2₁/*c*
a = 6.2457 (11) Å
b = 11.9757 (9) Å
c = 17.1228 (14) Å
 β = 90.081 (2)°
V = 1280.7 (3) Å³
Z = 4
D_x = 2.087 Mg m⁻³
D_m = 2.1 Mg m⁻³
D_m measured by flotation

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 23 reflections
 θ = 12.23–17.76°
 μ = 4.098 mm⁻¹
T = 293 (2) K
 Block
 0.33 × 0.33 × 0.23 mm
 Light purple

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: by integration
T_{min} = 0.412, *T_{max}* = 0.483
 2465 measured reflections
 2245 independent reflections
 1823 reflections with *I* > 2σ(*I*)

R_{int} = 0.021
 θ_{\max} = 25°
 h = 0 → 7
 k = 0 → 14
 l = -20 → 20
 2 standard reflections
 frequency: 120 min
 intensity decay: -5.3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.088
S = 1.222
 2245 reflections
 165 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0540P)^2 + 1.1239P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = -0.001
 $\Delta\rho_{\max} = 1.781 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.738 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O10—H1W...O1 ⁱ	0.87	2.00	2.816 (7)	154
O10—H2W...O5 ⁱⁱ	0.77	2.49	3.069 (7)	134

Symmetry codes: (i) 1 - *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*; (ii) *x* - 1, *y*, *z*.

The water H atoms were placed in the locations obtained from the difference map, while those attached to carbon were placed in calculated positions. All were included as riding contributions with fixed isotropic displacement parameters 20% larger than those of the attached atoms. The largest features in the final difference map are 0.78–0.97 Å from the Nd atom, but there is no obvious source.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD4* (Harms & Wocadlo, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Siemens, 1994). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1460). Services for accessing these data are described at the back of the journal.

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Dichloro(tetrahydrofuran-*O*)[tris(1-pyrazolyl-*N*²)borato]vanadium(III)

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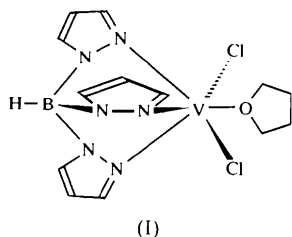
Abstract

The title compound, [HB(pz)₃]VCl₂(thf) or [VCl₂-(C₉H₁₀BN₆)(C₄H₈O)] (pz = pyrazolyl, thf = tetrahydrofuran), is an analogue of the unknown η⁵-CpVCl₂ (Cp =

cyclopentadienyl). The pyrazolyl complex was prepared from $\text{VCl}_3(\text{thf})_3$ and $\text{K}[\text{HB}(\text{pz})_3]$. The molecule adopts a structure comparable to the piano-stool arrangement of a half-sandwich complex.

Comment

Tris(pyrazolyl)borato complexes are often considered counterparts of cyclopentadienyl complexes due to the fact that both ligand systems possess a six-electron donor system. At least as far as the catalytic properties of these compounds in olefin polymerization are concerned, this view appears to be reasonable (Scheuer *et al.*, 1995). In this context, we were interested in synthesizing an analogue of the V^{III} half-sandwich $\eta^5\text{-CpVCl}_2$ (Cp = cyclopentadienyl, C_5H_5), a compound which does not exist by itself but needs stabilization, either by two triethylphosphines (Niemann *et al.*, 1980) or *via* oligomerization (methyl-substituted Cp: Ting *et al.*, 1997; Abernethy *et al.*, 1997). $[\text{HB}(\text{pz})_3]\text{VCl}_2(\text{thf})$ (thf = tetrahydrofuran) was first prepared by Manzer (1975) in tetrahydrofuran solution. Later, $[\text{HB}(\text{pz})_3]\text{VCl}_2(\text{dmf})$ (dmf = dimethylformamide) was prepared in dimethylformamide (Mohan *et al.*, 1992), and the dimethyl derivative $[\text{HB}(3,4\text{-Me}_2\text{pz})_3]\text{VCl}_2(\text{dmf})$ has been structurally characterized with two benzene molecules of crystallization (Kime-Hunt *et al.*, 1989). The same authors note that solvents other than dimethylformamide lead to a decomposition of the pyrazolylborate. We have now been able to obtain crystals of the title compound, (I), containing the unsubstituted pyrazolylborate, by reacting $\text{VCl}_3(\text{thf})_3$ with potassium tris(pyrazolyl)borate in dichloromethane.



The crystal structure reveals a piano-stool arrangement of the ligands with respect to the three donor-N atoms, very much reminiscent of that found for half-sandwich complexes of the type $\eta^5\text{-CpML}_3$ [where L is any ligand appropriate to satisfy the electronic and configurational requirements of the metal ion M ; for $M = \text{V}$, see, for example, Alt *et al.* (1998) and Hessen *et al.* (1990)], *i.e.* V is in the centre of a slightly distorted octahedron, with one of the octahedral faces occupied by the six-electron system of the tridentate tris(pyrazolyl)borate, and the opposite face by the two Cl atoms and the tetrahydrofuran. The dis-

tortions from octahedral geometry mainly concern the O1-V-N3 angle [$168.48(13)^\circ$]. For all other angles, deviations from ideal angles amount to a maximum of *ca* 5° . The bond lengths V-N [$2.103(3)$, $2.110(3)$ and $2.114(3)$ Å] and V-Cl [$2.298(2)$ and $2.369(1)$ Å], and the bond angles Cl1-V-Cl2 [$98.66(5)^\circ$], N1/3-V-Cl [$90.4(1)$ – $95.7(1)^\circ$], N1/N5-V-Cl [$175.93(10)$ and $176.78(10)^\circ$] and N-V-N [$83.64(13)$, $84.53(13)$ and $86.38(13)^\circ$], compare favourably with those for other structurally characterized V^{III} , V^{IV} and V^{V} complexes containing the tris(pyrazolyl)- or tris(dimethylpyrazolyl)borate ligand (Herberhold *et al.*, 1998; Collison *et al.*, 1997; Scheuer *et al.*, 1995; Mohan *et al.*, 1992; Kime-Hunt *et al.*, 1989). The bonding angles at the B atom are close to those for a tetrahedral geometry [$108.6(3)$, $107.5(3)$ and $105.8(3)^\circ$], underlining the overall unstrained ligand arrangement in the complex.

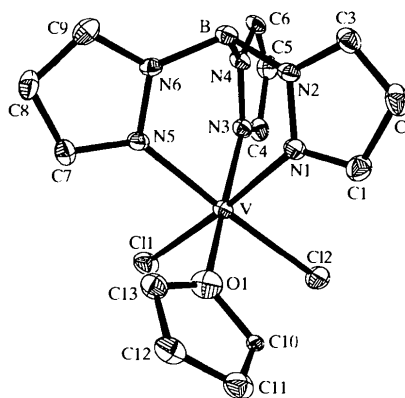


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

$\text{VCl}_3(\text{thf})_3$ (360 mg, 1 mmol) was dissolved in CH_2Cl_2 (20 ml), treated with $\text{K}[\text{HB}(\text{pz})_3]$ (300 mg, 1.2 mmol) and stirred at room temperature for 12 h, to yield a purple solution, possibly containing $\eta^2\text{-}[\text{HB}(\text{pz})_3]\text{VCl}_2(\text{thf})_2$ (with the pyrazolylborate acting as a bidentate ligand; Kime-Hunt *et al.*, 1989). The solution was filtered and its volume reduced to 3 ml *in vacuo*. Upon standing for a couple of weeks, blue-green crystals of $[\eta^3\text{-HB}(\text{pz})_3]\text{VCl}_2(\text{thf})$ were obtained suitable for X-ray analysis. Addition of pentane (100 ml) to the mother liquor yielded the main portion of the product, which was filtered off, washed with three 20 ml portions of pentane and dried (yield: 290 mg, 74%). Analysis calculated for $\text{C}_{13}\text{H}_{18}\text{BCl}_2\text{N}_6\text{OV}$: C 38.36, H 4.46, N 20.65%; found: C 38.16, H 4.42, N 20.78%; $\nu_{\text{BH}} = 2489 \text{ cm}^{-1}$.

Crystal data

$[\text{VCl}_2(\text{C}_9\text{H}_{10}\text{BN}_6)(\text{C}_4\text{H}_8\text{O})]$
 $M_r = 406.98$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic

 $P2_1/n$ $a = 8.553 (4) \text{ \AA}$ $b = 12.860 (5) \text{ \AA}$ $c = 15.530 (7) \text{ \AA}$ $\beta = 104.08 (4)^\circ$ $V = 1656.9 (13) \text{ \AA}^3$ $Z = 4$ $D_x = 1.632 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Hilger & Watts Y290 four-circle diffractometer

 $2\theta/\omega$ scans

Absorption correction: none

3819 measured reflections

3819 independent reflections

2805 reflections with

 $I > 2\sigma(I)$

Cell parameters from 25 reflections

 $\theta = 21.2\text{--}26.7^\circ$ $\mu = 0.935 \text{ mm}^{-1}$ $T = 153 (2) \text{ K}$

Block

 $0.3 \times 0.2 \times 0.2 \text{ mm}$

Blue-green

 $R_{\text{int}} = 0.019$ $\theta_{\text{max}} = 27.56^\circ$ $h = -1 \rightarrow 11$ $k = -1 \rightarrow 16$ $l = -20 \rightarrow 19$

3 standard reflections

every 97 reflections

intensity decay: 1%

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.057$ $wR(F^2) = 0.151$ $S = 1.031$

3819 reflections

217 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 3.8059P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.841 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.943 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

The title structure was solved using direct methods. All non-H atoms were refined anisotropically. The H atoms of the pyrazolyl ligand were found explicitly and were refined isotropically. All other H atoms were fixed at ideal positions with common isotropic displacement parameters.

Data collection: Y290 (Abeln & Kopf, 1993). Cell refinement: Y290. Data reduction: Y290. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1019). Services for accessing these data are described at the back of the journal.

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Bromotricarbonyl(3,3'-dimethyl-2,2'-bi-quinoline-*N,N'*)rhenium(I)

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Abstract

In the title compound, [ReBr(C₂₀H₁₆N₂)(CO)₃], the Re atom has a slightly distorted octahedral coordination, with Re—Br = 2.6299 (9), Re—N = 2.217 (4) and Re—C = 1.902 (6)–1.927 (7) Å.

Comment

The coordination chemistry of transition metal complexes containing polypyridinic ligands has led to a significant amount of work over the last few decades, both because this type of compound shows interesting photo-physical and photochemical behaviour and because they are potential candidates as models in photosynthesis processes (Juris *et al.*, 1988; Moya *et al.*, 1994, 1996; Sartori *et al.*, 1992; Ferraudi *et al.*, 1995; Kutal *et al.*, 1987; Kubow *et al.*, 1988, and references therein; Kallianasundaram, 1992; Gratzel, 1983).