Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71669 (66 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1066]

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mer-Trichlorotris(pyridine)vanadium(III)

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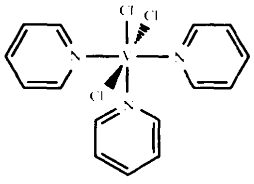
Abstract

The title compound, $[\mathrm{VCl_3(C_5H_5N)_3}]$, adopts an octahedral coordination geometry with three chlorides and three pyridine ligands attached to vanadium(III) in the *mer* configuration and with the pyridine planes twisted significantly from the metal–ligand planes.

Comment

In the course of our recent studies of the synthesis and chemistry of mixed-valence nitride-bridged vanadium compounds, we examined the reaction of pyridine with $[\mathrm{V_3(N)_2Cl_7(THF)_2}]$.THF$_x$ (Sorensen, Lerchen, Ziller & Doherty, 1992). We had formulated this trivanadium dinitrido species as containing a trichlorovanadium(III) center linked to two vanadium(V) nitrido fragments *via* labile bridging interactions; therefore, we expected to observe the formation of the pyridine adduct of vanadium(III) chloride upon addition of this ligand. Crystalline $[\mathrm{VCl_3(C_5H_5N)_3}]$ was isolated from the reaction mixture and its identity confirmed by X-ray crystallography. We describe herein the crystal and molecular structure of this complex (I).


(I)

Although $[\mathrm{VCl_3(C_5H_5N)_3}]$ was first prepared over 25 years ago (Fowles & Greene, 1967), the structure of this compound has not been reported. $[\mathrm{VCl_3(C_5H_5N)_3}]$ is described as a green crystalline solid isolated from the reaction of $[\mathrm{VCl_3(NMe_3)_2}]$ with pyridine in benzene (Fowles & Greene, 1967) or as a blue–violet crystalline compound isolated from the reaction of $\mathrm{VCl_3}$ with pyridine in diethyl ether (Rupp, 1970). We obtained $[\mathrm{VCl_3(C_5H_5N)_3}]$ as pale yellow plates at room temperature from the reaction of $[\mathrm{V_3(N)_2Cl_7(THF)_2}]$.THF$_x$ with approximately 10 equivalents of pyridine in $\mathrm{C_6D_6}$ in a sealed NMR tube (although bulk samples of the crude product appear green in color).

The molecular structure of $[\mathrm{VCl_3(C_5H_5N)_3}]$ shows a roughly octahedral geometry with meridional coordination of the three chlorides and three pyridine ligands, similar to the structure observed at the vanadium(III) center in $[(\mathrm{Me_2NCH_2CH_2NMe_2})\mathrm{Cl_2V^V{=}N:}]\rightarrow[\mathrm{V^{III}Cl_3(Me_2NCH_2CH_2NMe_2)}]$ (Sorensen, Lerchen, Ziller & Doherty, 1992). The pyridine ligands in $[\mathrm{VCl_3(C_5H_5N)_3}]$ are planar, coordinated end-on and twisted about the V—N bond axes by angles of 52 [N(1)–pyridine], 42 [N(2)–pyridine] and 55 [N(3)–pyridine], relative to the N(1)–N(2)–N(3)–Cl(2) ligand plane. We have noted a similar twisting of the pyridine ligands in the solid-state structure of $[\mathrm{V(N)Cl_2(C_5H_5N)_2}]_\infty$, which additionally exhibits a strong intermolecular π-stacking interaction between pyridines on adjacent vanadium–nitride linear chains (Critchlow, Lerchen, Smith & Doherty, 1988). However, a π interaction is not observed between the pyridine ligands on neighboring molecules in the solid-state structure of $[\mathrm{VCl_3(C_5H_5N)_3}]$, suggesting that the orientation of the pyridine ligands may be driven by minimization of intramolecular ligand repulsions.

The V—Cl distances for $[\mathrm{VCl_3(C_5H_5N)_3}]$ are in the range observed for other nitrogen-base adducts of vanadium chlorides, which are found to vary significantly with coordination geometry and oxidation state, from the short V—Cl distances (2.236–2.241 Å) observed in the trigonal-bipyramidal vanadium(III) trimethylamine adduct *trans*-[$VCl_3(NMe_3)_2$] (Greene & Orioli, 1969) to the long V—Cl bonds (2.461 Å) found in the vanadium(II) pyridine complex *trans*-[$VCl_2(C_5H_5N)_4$] (Brauer & Krüger, 1973). In general, $V—N_{pyridine}$ distances show a much smaller variation over the variety of vanadium–pyridine compounds that have been structurally characterized, unless the pyridine ligand is coordinated opposite a good *trans*-labilizing group. An illustrative example is the oxo-bridged divanadium complex [{*mer*-$VCl_2(C_5H_5N)_3$}$_2$(O)], which has normal $V—N_{pyridine}$ distances (2.17–2.18 Å) for the pyridine ligands *cis* to the bridge but significantly longer $V—N_{pyridine}$ distances (2.30–2.31 Å) for the pyridines *trans* to the oxo bridge (Zhang & Holm, 1990). The $V—N_{pyridine}$ distances in [$VCl_3(C_5H_5N)_3$] are comparable to the normal $V—N_{pyridine}$ distances in [{*mer*-$VCl_2(C_5H_5N)_3$}$_2$(O)] and typical of those reported for other vanadium–pyridine compounds.

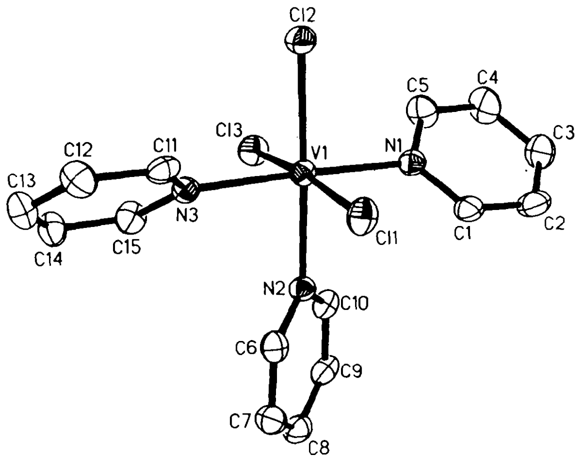


Fig. 1. Thermal ellipsoid plot of [$VCl_3(C_5H_5N)_3$] at the 50% probability level.

Experimental

Crystal data

[$VCl_3(C_5H_5N)_3$]
$M_r = 394.6$
Monoclinic
$P2_1/n$
$a = 9.1175\ (11)$ Å
$b = 12.3971\ (14)$ Å
$c = 15.5602\ (16)$ Å
$\beta = 92.068\ (9)°$
$V = 1757.6\ (3)$ Å^3
$Z = 4$

$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 9.5$–$18.5°$
$\mu = 1.005$ mm^{-1}
$T = 183$ K
Plate
0.40 × 0.40 × 0.10 mm
Yellow

Data collection

Syntex $P2_1$ diffractometer
θ-2θ scans
Absorption correction: semi-empirical (ψ scan)
$T_{min} = 0.695$, $T_{max} = 0.770$
2628 measured reflections
2121 independent reflections
2059 observed reflections [$|F_o| > \sigma(|F_o|)$]

$R_{int} = 0.0101$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 98 min
intensity variation: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.053$
$S = 1.19$
2059 reflections
199 parameters
H-atom parameters not refined

$w = [\sigma^2(|F_o|) + 0.0008(F_o)^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
V(1)	0.00405 (8)	0.41645 (6)	0.75109 (5)	0.0215 (3)
Cl(1)	0.0733 (1)	0.5710 (1)	0.8275 (1)	0.0307 (4)
Cl(2)	−0.1243 (1)	0.5106 (1)	0.6431 (1)	0.0294 (4)
Cl(3)	−0.0484 (1)	0.2498 (1)	0.6876 (1)	0.0310 (4)
N(1)	0.2054 (4)	0.4236 (3)	0.6817 (2)	0.0239 (13)
N(2)	0.1199 (4)	0.3248 (3)	0.8521 (2)	0.0222 (12)
N(3)	−0.1926 (4)	0.4039 (3)	0.8247 (2)	0.0223 (12)
C(1)	0.3314 (5)	0.4585 (4)	0.7190 (3)	0.0302 (16)
C(2)	0.4616 (5)	0.4622 (4)	0.6773 (3)	0.0376 (18)
C(3)	0.4658 (5)	0.4274 (4)	0.5934 (3)	0.0376 (18)
C(4)	0.3359 (6)	0.3935 (4)	0.5536 (3)	0.0418 (19)
C(5)	0.2093 (6)	0.3915 (4)	0.5993 (3)	0.0337 (17)
C(6)	0.0968 (5)	0.3441 (4)	0.9356 (3)	0.0271 (16)
C(7)	0.1645 (5)	0.2849 (4)	1.0018 (3)	0.0315 (16)
C(8)	0.2611 (5)	0.2041 (4)	0.9815 (3)	0.0324 (17)
C(9)	0.2866 (5)	0.1846 (4)	0.8955 (3)	0.0304 (17)
C(10)	0.2134 (5)	0.2455 (3)	0.8338 (3)	0.0263 (15)
C(11)	−0.2677 (5)	0.4931 (4)	0.8450 (3)	0.0252 (15)
C(12)	−0.3954 (5)	0.4892 (4)	0.8911 (3)	0.0324 (17)
C(13)	−0.4465 (5)	0.3906 (4)	0.9169 (3)	0.0320 (17)
C(14)	−0.3701 (5)	0.2989 (4)	0.8970 (3)	0.0314 (17)
C(15)	−0.2448 (5)	0.3092 (4)	0.8510 (3)	0.0307 (17)

Table 2. *Selected geometric parameters* (Å, °)

V(1)—Cl(1)	2.330 (1)	V(1)—Cl(2)	2.326 (1)
V(1)—Cl(3)	2.331 (1)	V(1)—N(1)	2.165 (4)
V(1)—N(2)	2.181 (4)	V(1)—N(3)	2.168 (4)
Cl(1)—V(1)—Cl(2)	94.4 (1)	Cl(1)—V(1)—Cl(3)	172.9 (1)
Cl(2)—V(1)—Cl(3)	92.8 (1)	Cl(1)—V(1)—N(1)	90.1 (1)
Cl(2)—V(1)—N(1)	91.9 (1)	Cl(3)—V(1)—N(1)	89.4 (1)
Cl(1)—V(1)—N(2)	86.9 (1)	Cl(2)—V(1)—N(2)	178.5 (1)
Cl(3)—V(1)—N(2)	86.0 (1)	N(1)—V(1)—N(2)	89.0 (1)
Cl(1)—V(1)—N(3)	90.2 (1)	Cl(2)—V(1)—N(3)	90.8 (1)
Cl(3)—V(1)—N(3)	89.9 (1)	N(1)—V(1)—N(3)	177.3 (1)
N(2)—V(1)—N(3)	88.3 (1)		

The crystal was immersed in a lube oil additive (Exxon Paratone-D), attached to a glass fiber and transferred to the coldnitrogen stream of the diffractometer (Hope, 1987). The structure was solved by direct methods and refined by full-matrix least-squares techniques. Data collection: Siemens *R*3*m*/*V* system. Cell refinement and data reduction: UCI-modified version of the *ULCA Crystallographic Package* (1984) and the *SHELXTL-Plus* (Sheldrick, 1991) program set. Structure solution and refinement: *SHELXTL-Plus*.

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