Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

trans-Diaquadichlorooxovanadium(IV) bis[2-(2-pyridylamino)pyridinium] dichloride

Jens Hartung,[a] Philipp Schmidt,[b] Ingrid Svoboda[c] and Hartmut Fuess[c]*

[a]Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany, [b]Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and [c]Strukturforschung, FB11 Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany

Correspondence e-mail:
hartung@chemie.uni-kl.de

Received 16 May 2005
Accepted 26 May 2005
Online 10 June 2005

The neutral complex *trans*-[$VOCl_2(H_2O)_2$] co-crystallizes with di-2-pyridylamine hydrochloride to provide the title compound, $(C_{10}H_{10}N_3)_2[VCl_2O(H_2O)_2]Cl_2$. The V-bound aqua ligands form two hydrogen bonds each. The amine functionality of the 2-(2-pyridylamino)pyridinium cation participates as a monovalent donor in the hydrogen bonding. In both instances, interstitial Cl^- ions serve as hydrogen-bond acceptors. The three hydrogen bonds that are formed per anion give rise to one-dimensional chains along [100].

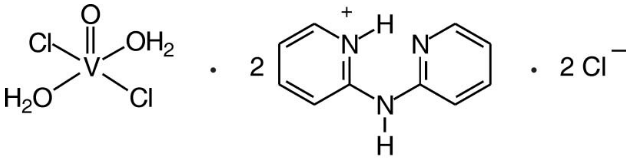
Key indicators

Single-crystal X-ray study
T = 303 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.097
Data-to-parameter ratio = 15.3

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

Comment

The title compound, (I), is a hydrogen-bonded adduct that is formed upon treatment of a solution of triethyl vanadate(V) with (2,2′-dipyridyl)amine and HCl in hot EtOH. The identity of (I) was established by X-ray diffraction analysis and the structure is presented here.



(I)

Compound (I) crystallizes in the triclinic space group $P\bar{1}$. The unit cell (Z = 2) contains two neutral *trans*-[$VOCl_2(H_2O)_2$] complexes, four Cl^- ions and four *N*-(pyridinium-2-yl)-*N*-(2-pyridyl)amine cations. The nitrogen base is

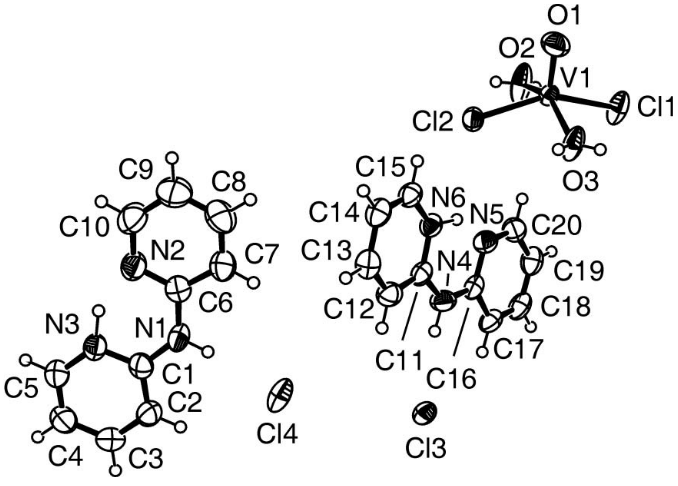


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

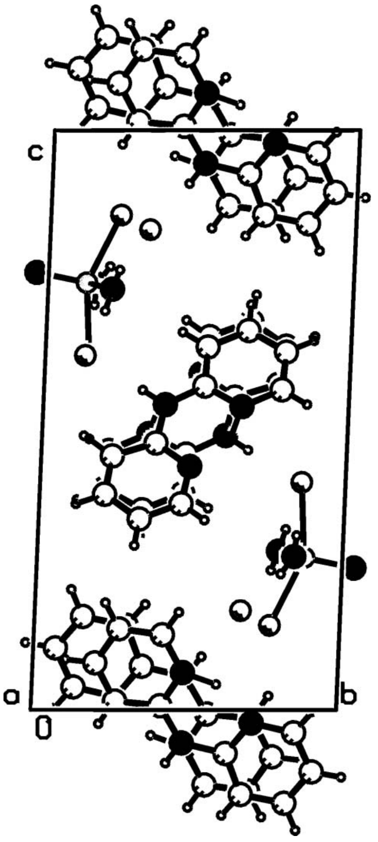


Figure 2
The packing of (I) in the solid state, viewed along [100].

protonated in both crystallographically independent cations at one of the two pyridine N atoms, *viz*. N3 and N6 (Fig. 1). The positive charge that is imposed upon protonation gives rise to Coulomb attractions between N3—H3···N2 and N6—H6···N5, thus leading to a *syn*-planar arrangement of the two heterocyclic N atoms [N3—C1—N1—C6 = 0.2 (4), N2—C6—N1—C1 = 0.6 (4), N6—C11—N4—C16 = 0.7 (4) and N5—C16—N4—C11 = −1.4 (4)°]. The cations are stacked to form columns along the *a* axis (Fig. 2).

The V atom in *trans*-[$VOCl_2(H_2O)_2$] is located 0.568 (1) Å above the basal plane of a square-pyramidal coordination polyhedron [atom O3 deviates by 0.032 (4) Å from the plane of atoms Cl1, Cl2 and O2]. The oxido ligand is located at the apex of this pyramid, which gives rise to a symmetry that is close to C_{2v} (Fig. 2). The V1—O1 distance suggests a V═O double bond (Table 1) (Priebsch & Rehder, 1990*a*; Brand *et al.*, 1990). The V1—Cl1 and V1—Cl2 bond lengths, as well as the distances between V1 and atoms O2 and O3 of the aqua ligands, correspond to reference values that have been reported for structurally related neutral vanadium(IV) complexes (Priebsch & Rehder, 1990*a*,*b*; Azuma *et al.*, 1994). The magnitudes of the Cl1—V1—Cl2 and O2—V1—O3 angles are similar to data that have been reported in the literature for hydrogen-bonded adducts between *trans*-[$VOCl_2(H_2O)_2$] and selected crown ethers (Azuma *et al.*, 1994).

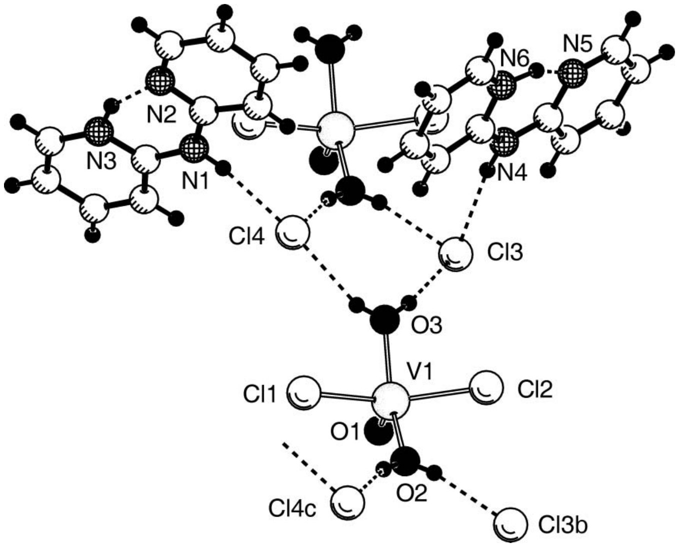


Figure 3
A view of the hydrogen bonding (dashed lines) in (I). Atoms Cl3b and Cl4c are related by the symmetry operator (−*x*, 1 − *y*, 1 − *z*).

The V-bound aqua ligands form two hydrogen bonds each. The amine functionality of the *N*-(pyridinium-2-yl)-*N*-(2-pyridyl)amine cation participates as a monovalent donor in the hydrogen bonding. In both instances, interstitial Cl^- ions serve as hydrogen-bond acceptors. The three hydrogen bonds that are formed per anion give rise to one-dimensional chains along [100] (Table 2 and Fig. 3).

Experimental

A solution of triethyl vanadate(V) (202 mg, 1.00 mmol) in anhydrous EtOH (2 ml) was treated at 298 K with (2,2-dipyridyl)amine (342 mg, 2.00 mmol) and hydrochloric acid (0.5 ml of a 10 *M* aqueous solution). The reaction mixture was heated for 5 min at 351 K. The colour changed during that time from yellow to brown, and upon standing for 24 h at 298 K it changed to blue. The blue solution was filtered to afford 167 mg (28%) of turquoise prisms of compound (I), which were suitable for X-ray diffraction analysis.

Crystal data

$(C_{10}H_{10}N_3)_2[VCl_2O(H_2O)_2]Cl_2$
M_r = 589.19
Triclinic, $P\bar{1}$
a = 7.838 (2) Å
b = 9.609 (1) Å
c = 17.739 (3) Å
α = 86.68 (1)°
β = 86.10 (2)°
γ = 75.32 (1)°
V = 1288.3 (4) Å^3
Z = 2
D_x = 1.519 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
θ = 3.2–10.1°
μ = 0.83 mm^{-1}
T = 303 (2) K
Prism, turquoise
0.25 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.735, T_{max} = 0.918
6971 measured reflections
5048 independent reflections
3771 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 26.0°
h = −9 → 3
k = −11 → 11
l = −21 → 21
3 standard reflections
frequency: 120 min
intensity decay: 0.1%

m1254 Hartung *et al.* • $(C_{10}H_{10}N_3)_2[VCl_2O(H_2O)_2]Cl_2$ *Acta Cryst.* (2005). E**61**, m1253–m1255

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.01$
5048 reflections
331 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.4055P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—V1	1.572 (2)	V1—Cl2	2.3030 (8)
O2—V1	1.975 (2)	V1—Cl1	2.3169 (8)
O3—V1	1.979 (2)		
O1—V1—O2	106.9 (1)	O3—V1—Cl2	86.13 (6)
O1—V1—O3	106.2 (1)	O1—V1—Cl1	105.55 (8)
O2—V1—O3	147.0 (1)	O2—V1—Cl1	85.55 (6)
O1—V1—Cl2	103.59 (8)	O3—V1—Cl1	85.80 (6)
O2—V1—Cl2	86.12 (7)	Cl2—V1—Cl1	150.85 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···Cl4	0.87 (3)	2.29 (3)	3.149 (2)	170 (3)
N3—H3N···N2	1.07 (3)	1.62 (3)	2.608 (3)	150 (2)
N4—H4N···Cl3	0.86 (3)	2.32 (3)	3.168 (2)	169 (3)
N6—H6N···N5	1.07 (3)	1.66 (3)	2.624 (3)	148 (2)
O2—H2*A*···Cl3^{i}	0.84 (1)	2.19 (1)	3.016 (2)	170 (3)
O2—H2*B*···Cl4^{i}	0.84 (1)	2.20 (1)	3.026 (2)	167 (3)
O3—H3*B*···Cl4^{ii}	0.84 (1)	2.22 (1)	3.026 (2)	162 (3)
O3—H3*B*···Cl4^{ii}	0.84 (1)	2.22 (1)	3.026 (2)	162 (3)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

H atoms bound to C atoms were positioned geometrically and treated as riding atoms (C—H = 0.93 Å). Water H atoms were refined with restrained geometry (Nardelli, 1999), *viz*. O—H distances were restrained to 0.85 Å and H···H distances to 1.34 Å, determining an H—O—H angle of 107°. H atoms on N atoms were located in a difference Fourier map and their positions were refined. All displacement parameters of H were constrained to 1.2 times U_{eq} of the parent atom.

Data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *CAD-4 Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2003* (Spek, 2003) and *ORTEP3* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 347 – Selektive Reaktionen Metall-aktivierter Moleküle).

References

Azuma, N., Ozawa, T. & Ishizu, K. (1994). *Polyhedron*, **13**, 1715–1723.
Brand, S. G., Edelstein, N., Hawkins, C. J., Shalimoff, G., Snow, M. R. & Tiekink, E. R. T. (1990). *Inorg. Chem.* **29**, 434–438.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (2005). *ORTEP3*. University of Glasgow, Scotland.
Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.
Enraf–Nonius (1993). *CAD-4 Diffractometer Control Software*. Release 5.1. Enraf-Nonius, Delft, The Netherlands.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Priebsch, W. & Rehder, D. (1990*a*). *Inorg. Chem.* **29**, 3013–3019.
Priebsch, W. & Rehder, D. (1990*b*). *Acta Cryst.* C**46**, 568–570.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Acta Cryst. (2005). E**61**, m1253–m1255 Hartung *et al.* • $(C_{10}H_{10}N_3)_2[VCl_2O(H_2O)_2]Cl_2$ **m1255**