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# Preparation, Crystal and Molecular Structure of Aquadichlorobis(ethylpyridine)-oxovanadium

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## Abstract

The compound $VOCl_2 \cdot 2(3\text{-Etpy}) \cdot H_2O$ (Etpy = ethylpyridine) was prepared by slow hydrolysis of the toluene suspension obtained from the reaction of $VCl_4$ with 3-ethylpyridine The crystal was found to be monoclinic $C2/c$, $Z = 4$, $\rho(\text{calc.}) = 1.426 \times 10^3$ kg m$^{-3}$, $a = 13.281(5)$, $b = 13.989(7)$, $c = 9.277(8)$ Å, $V = 1723(2)$ Å$^3$, $\beta = 90.53(5)°$.

Final full matrix least-square refinement with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.039$, $R_w = 0.042$, $R_g = 0.053$. The vanadium atom is hexacoordinate with the pyridine ligands in mutually *trans* positions in the plane containing the Cl atoms. The O vanadyl atom is in an axial position *trans* to the coordinated $H_2O$ molecule, and the O–V–O line is a binary axis for the molecule.

## Introduction

A large number of oxohalide complexes of vanadium with coordinated monodentate ligands are known at present. A survey of these compounds shows that (i) pentacoordination with a square pyramidal geometry is implicitly assumed to be the prevalent structure, the oxygen occupying the unique axial position and (ii) among the compounds known with unidentate nitrogen donor ligands it seems that only $VOCl_2(Me_3N)_2$ has been subject to X-ray studies [1] which revealed a trigonal bipyramidal structure; this has been attributed to stereochemical constraints. However, despite wide exploration of the synthetic aspects of vanadyl chemistry, the paucity of structural information on the compounds prepared is rather surprising [2].

Our interest in the adducts of group 4 halides with P- and N-donor ligands [3] led us to prepare the hexacoordinate vanadyl compound $VOCl_2 \cdot 2EtPy \cdot H_2O$ (**1**). To our knowledge it is one of the rare vanadyl compounds having this geometry. We report herein its synthesis and the study of its crystal structure which throws some light on vanadium–nitrogen bonding.

## Results

A number of vanadyl dichloride adducts with pyridine were described some time ago [4]. Compounds of composition 1/2, 1/3 and 1/2/methanol and 1/3/0.5 methanol were isolated as blue–green crystalline substances. They were prepared from $VOCl_2 \cdot 3$methanol and pyridine, but apart from the compositional formula, no other details were given.

In a previous work [3] we have shown by ESR that soft donor ligands such as phosphines form 1/2 adducts (V/P) with $VCl_4$. The octahedral geometry could be deduced from the frozen solution spectra which exhibited an axial g tensor. We found later that controlled hydrolysis of these compounds leads to vanadyl dihalide adducts without loss of the donor ligands. This constitutes an alternative method for the preparation of vanadyl dichloride compounds, and has been used in a few cases in the literature to prepare $VOCl_2 \cdot 2CH_3CN$ and $VOCl_2 \cdot 2$Dioxane (dioxane = $C_2H_8O_2$) [5]. We decided therefore to study the reaction of pyridines with $VCl_4$ and track the formation of the products resulting from their hydrolysis.

$VCl_4$ reacts with pyridine in toluene to form a dark red complex of composition $VCl_4 \cdot 2py$ (py = pyridine) [6]. Although the compound is reported to be insoluble in toluene, we found that the solution obtained by mixing the reactants in roughly 1/2 (V/py) proportions yielded an ESR spectrum typical of an octahedral vanadium(IV) compound with the two ligands occupying the axial positions. No s.h.f. splitting with the $^{14}N$ nucleus of the pyri-

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dine ligand was observed (see Table III). Slow and controlled hydrolysis gave only a green sticky material. The reaction with 3-ethylpyridine proceeds in the same manner with the formation of a red–brown precipitate. The ESR parameters of the toluene solution (see Table III) are very close to those of the pyridine compound and reflect the same geometry.

Controlled hydrolysis this time yielded single crystals of **1** suitable for X-ray study.

## Experimental

### *Preparation of the Compound*

All operations were conducted under argon. Pure commercial toluene was freed from residual olefins by washing with sulfuric acid, then water, dried over KOH and distilled over $AlLiH_4$. Ethylpyridine was dried by the usual methods and distilled also over $AlLiH_4$ before use. $VCl_4$ (Alfa) was dissolved in toluene in a Schlenck tube. Ethylpyridine (twofold molar ratio in toluene) was added via a syringe while stirring. The solution became immediately red–brown and a suspension was formed. A small air inlet was made through the septum and the suspension was allowed to stand for a few days. Green crystals suitable for the above study deposited at the bottom of the flask. Samples for ESR measurements of $VCl_4$ adducts were prepared in a specially designed apparatus which allows the introduction of the solution into the ESR tube without transfer with a syringe, thus avoiding contact with traces of humidity.

### *Crystal Data*

Preliminary Laue and precession photographs led to a monoclinic unit cell. The angular coordinates of 25 reflexions, which were centered with monochromatic Mo K$\alpha$ radiation ($\lambda = 0.71069$) were least-squares refined to yield the lattice parameters: $a = 13.281(5)$, $b = 13.989(7)$, $c = 9.277(8)$ Å; $\beta = 90.53(5)°$, $V = 1723(2)$ Å$^3$, $Z = 4$, $\rho = 1.426 \times 10^3$ kg m$^{-3}$. The observed systematic absences for $|hkl|$ of $h + k = 2n + 1$ and for $|h0l|$ of $l = 2n + 1$ are compatible with two space groups $Cc$ and $C2/c$. The centrosymmetric space group was chosen under the basis of statistical tests and confirmed by subsequent results. Four molecules per unit cell imply that some atoms lie on special positions. Each molecule lies along a two-fold axis which passes through the vanadium and two oxygen atoms. See also 'Supplementary Material'.

### *Data Collection*

Intensity data were collected on a Phillips PW 1100 diffractometer/radiation Mo K$\alpha$, take off angle 5° $\theta$–$2\theta$ scan width 1.8° mn$^{-1}$ in Bragg angle; $1.4 + 0.3$ tg $\theta$ scan length; background measurements half of the scan time, before and after every scan. Three standard reflections 0.06, $6\bar{6}0$, $00\bar{6}$ were measured every other hour. A total of 1610 reflections was collected at room temperature to $\theta = 23°$. Intensities were corrected for Lorentz and polarization factors; Psi-scan curves were roughly linear so that no absorption correction was made. $\mu = 0.73$ cm$^{-1}$ (Mo K$\alpha$).

For every observed structure factor, a standard deviation was computed: $\sigma(F) = \sigma(I)/2\ F$, where $\sigma(I)$ is the error on the integration intensity. 1108 independent reflections with $F > 3\sigma(F)$ were kept for refinement.

All refinements were carried out using SHELX 76 programs. Scattering factors were taken from International Tables including $\Delta f'$ and $\Delta f''$ for V and Cl.

### *Structural Determination and Refinement*

The structure was solved using direct methods. One solution gave an E-map showing all non-hydrogen atoms. Full-matrix least-squares refinement with isotropic temperature factors resulted in $R = 0.085$. Refinement with anisotropic temperature factors resulted in $R = 0.059$. A Fourrier difference map revealed all hydrogen atoms. The oxygen atom O(1) is bound to a hydrogen atom lying at 0.96 Å; this means that the complex molecule also contains one molecule of water. The positions of the hydrogen atoms were refined with isotropic temperature factors in a block different from the one containing all the other variables.

The final least squares refinement of 100 variables using 1108 observations resulted in the values $R = 0.039$, $R_w = 0.042$, $R_g = 0.053$, goodness of fit = 0.86, $R = \Sigma|\Delta|/\Sigma|F_o|$, $\Delta = |F_o| - |F_c|$, $R_w = \Sigma|\Delta| w^{1/2}/\Sigma|F_o|w^{1/2}$, $R_g = \{\Sigma|\Delta|^2 w/\Sigma|F_o|^2 w\}^{1/2}$, $w = \{\sigma^2(F) + 3.19 \times 10^{-3}|F|^2\}^{-1}$.

The final atomic coordinates are listed in Table I. Bond distances and angles are given in Table II. The molecular geometry and the atom numbering are shown in Fig. 1. Figure 2 is a stereoview of the molecular packing in order to display hydrogen bonds.

TABLE I. Fractional Atomic Coordinates (with e.s.d.s)

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| V | 0.0000 | 0.33421(4) | 0.2500 |
| Cl | −0.04749(5) | 0.35847(5) | 0.49528(7) |
| O(1) | 0.0000 | 0.2208(2) | 0.2500 |
| O(2) | 0.0000 | 0.4938(2) | 0.2500 |
| N | 0.1563(2) | 0.3430(1) | 0.3122(2) |
| C(1) | 0.1932(2) | 0.4041(2) | 0.4121(3) |
| C(2) | 0.2906(2) | 0.4012(2) | 0.4643(3) |
| C(3) | 0.3533(2) | 0.3320(2) | 0.4102(4) |
| C(4) | 0.3179(2) | 0.2699(2) | 0.3056(3) |
| C(5) | 0.2199(2) | 0.2771(2) | 0.2580(3) |
| C(6) | 0.3254(2) | 0.4736(3) | 0.5735(4) |
| C(7) | 0.3590(4) | 0.5647(3) | 0.5023(5) |

TABLE II. Interatomic Distances (Å) and Angles (°) (with e.s.d.s)

| | | | |
|---|---|---|---|
| Metal coordination sphere | | | |
| V–O(1) | 1.587(2) | O(1)–V–O(2) | 180.00 |
| V–N | 2.153(2) | N–V–N′ | 173.4(1) |
| V–O(2) | 2.232(2) | Cl–V–Cl′ | 163.68(4) |
| V–Cl | 2.3911(7) | | |
| | | O(1)–V–Cl | 98.16(2) |
| | | O(1)–V–N | 93.28(5) |
| | | O(2)–V–Cl | 81.84(2) |
| | | O(2)–V–N | 86.72(5) |
| | | Cl–V–N | 89.94(6) |
| | | Cl–V–N′ | 89.13(6) |
| Molecule of water | | | |
| H(2)–O(2) | 0.96(2) | H(2)–O(2)–H(2′) | 107(3) |
| Ethylpyridine | | | |
| N–C(1) | 1.350(3) | N–C(1)–C(2) | 123.8(2) |
| C(1)–C(2) | 1.377(4) | C(1)–C(2)–C(3) | 117.6(3) |
| C(2)–C(3) | 1.375(4) | C(2)–C(3)–C(4) | 119.7(3) |
| C(3)–C(4) | 1.382(4) | C(3)–C(4)–C(5) | 119.6(3) |
| C(4)–C(5) | 1.375(4) | C(4)–C(5)–N | 121.6(3) |
| C(5)–N | 1.350(4) | C(5)–N–C(1) | 117.6(2) |
| C(2)–C(6) | 1.503(5) | C(1)–C(2)–C(6) | 119.9(3) |
| C(6)–C(7) | 1.506(6) | C(3)–C(2)–C(6) | 122.5(3) |
| | | C(2)–C(6)–C(7) | 111.4(3) |
| Intramolecular contacts | | | |
| Cl–O(1) | 3.052(2) | | |
| Cl–O(2) | 3.031(2) | | |
| H(2)–H(1) | 2.46(4) | | |
| Intermolecular contacts | | | |
| H(2)–Cl″ | 2.26(2) | H(2)–Cl–V″ | 134.3(7) |
| | | O(2)–H(2)–Cl″ | 167(3) |

(′) and (″) as superscripts refer to the following equivalent positions relative to the x, y, z set: (′): −x, y, 0.5 − z; (″): −x, 1 − y, 1 − z.

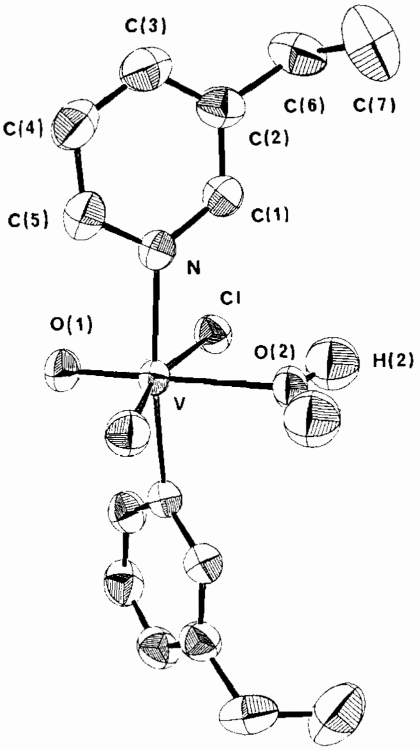

Fig. 1. Crystal structure of $VOCl_2 \cdot 2(Etpy) \cdot H_2O$.

## Discussion

The crystal structure shows that the vanadium atom in **1** is hexacoordinate in a distorted octahedral environment, Fig. 1. The V atom and the two oxygens are located on the binary axis. The N–V–N′ and Cl–V–Cl′ angles are equal to 173.4(1)° and 163.68(4)° so that both V–Cl and V–N bonds are bent towards the water molecule. The N–V–N′

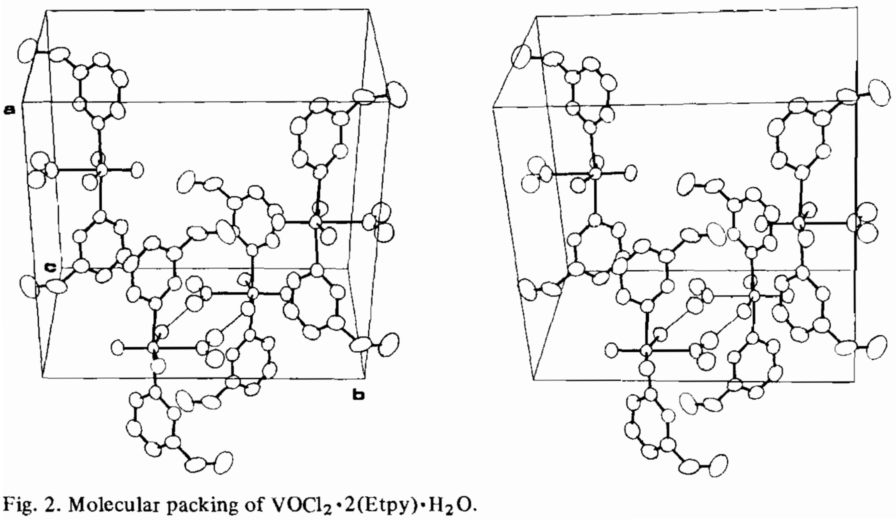

Fig. 2. Molecular packing of $VOCl_2 \cdot 2(Etpy) \cdot H_2O$.

and Cl–V–Cl′ planes remain orthogonal (89.6°). The plane of the water molecule forms an angle of 19.6° with the Cl–V–Cl plane; the pyridine plane is approximately oriented towards the bisector of the Cl–V)O(2) angle. The angle between two pyridine planes is 77.8°. The V–N bond length of 2.153(2) is in good agreement with those found in other V(IV) compounds such as $VOCl_2(NMe_3)_2$ (2.17 and 2.18) [10] and $VCl_4(NCH)_2$ (2.135 and 2.157) [9].

The V–Cl distance of 2.3911 [7] is higher than that found in these latter V(IV) compounds: 2.25 and 2.207 to 2.239 Å respectively. This is due presumably to the strong V–O(1) bond. It is remarkable that the values of Cl•••O(1) = 3.052(2) and Cl•••O(2) = 3.031(2) are 0.15 Å smaller than the sum of Cl and O Van der Waals radii and are very close to each other. The close contact values for Cl••• O(1) and Cl•••O(2) would explain the rather long V–Cl distance and the deformation of the octahedral environment of vanadium.

Figure 2 shows the molecular packing. The distance between $H_2O$ hydrogen atoms and the Cl atoms of adjacent molecules was found to be 2.26(2) Å. It is much smaller than the sum of Van der Waals radii and suggests the presence of some Cl•••H bonding. The existence of this bond explains the positions of the $H_2O$ molecule and could also be responsible for the lengthening of the V–Cl bond. Thus, in $VCl_4(NCH)_2$ [9] the chlorine corresponding to the longer V–Cl distance (2.239 Å) is also implicated in hydrogen bonding.

### *ESR Spectra*

The red solutions obtained by adding pyridine or the red–brown solutions by adding 3-ethyl-pyridine to $VCl_4$ in toluene give well resolved ESR spectra, with at room temperature the typical eight lines isotropic spectrum due to a V(IV) ion. At 140 K the spectrum is resolved into parallel and perpendicular components characteristic of a V(IV) ion in a distorted octahedral ligand field. The $g$ and $A$ values of the vanadyl compound (Table III) are very close to those of the tetrachloride adducts. This shows that the interaction of the unpaired electron with the vanadium nucleus remains virtually unchanged in magnitude for both types of compounds since it resides in a d(xy) orbital of essentially metal character [8].

TABLE III. ESR Parameters at Room and Frozen Solution Temperatures of Some Vanadium Tetrachloride and Vanadyl Dichloride Adducts. $A$ Values in Gauss, 1 G = 0.1 mT

| | $\langle g \rangle$ | $g_\parallel$ | $g_\perp$ | $A_\parallel$ | $A_\perp$ | $\langle A \rangle$ |
|---|---|---|---|---|---|---|
| $VCl_4 \cdot 2py$ | 1.975 | 1.959 | 1.981 | 177 | 61.6 | 101.2 |
| $VCl_4 \cdot 2(3\text{-}Etpy)$ | 1.973 | 1.958 | 1.980 | 176 | 60.0 | 101.4 |
| $VOCl_2 \cdot 2(3\text{-}Etpy \cdot H_2O$ | 1.974 | 1.947 | 1.977 | 177.4 | 61.7 | 103.4 |
| $VCl_4 \cdot 2NMe_3$ | 1.970 | 1.945 | 1.984 | 183.1 | 61.3 | 103.1 |

Finally, it should be mentioned that slow hydrolysis of $VCl_4 \cdot 2py$ or $VCl_4 \cdot 2NMe_3$ did not give the analogous vanadyl dichloride adducts or any other well defined compounds which could be isolated.

## Supplementary Material

Full crystallographic data are available upon request from authors.

## Acknowledgements

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