Oxidative functionalisation of alkanes: synthesis, molecular structure and catalytic implications of anionic vanadium(V) oxo and peroxo complexes containing bidentate *N,O* ligands †

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A mixture of $[NBu_4][VO_3]$ and pyrazine-2-carboxylic acid (Hpca) in acetonitrile catalysed smoothly the reaction of alkanes RH (R = CH_3 or C_6H_{11}) with molecular oxygen (from air) and hydrogen peroxide to give the corresponding alkyl hydroperoxide ROOH as the primary product. The oxo and peroxo anions $[VO_2(pca)_2]^-$ and $[VO(O_2)(pca)_2]^-$, isolated as the tetrabutylammonium or ammonium salts from acetonitrile solution and fully characterised by single crystal structure analyses, are assumed to be involved in the catalytic process. A screening of different *N,O* ligands showed Hpca to be the best co-catalyst, while anthranilic acid (Hana) proved to be almost inactive. The isolation and crystal structure analysis of the analogous oxo compound $[NBu_4][VO_2(ana)_2]$ showed a fundamental difference in the co-ordination of the bidentate *N,O* ligands which might explain the different catalytic activities: while in $[VO_2(pca)_2]^-$ the two pca ligands are bonded through a nitrogen and an oxygen atom (*N,O* co-ordination), in $[VO_2(ana)_2]^-$ the two ana ligands are co-ordinated *via* two oxygen atoms of the carboxylato group (*O,O* co-ordination).
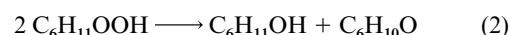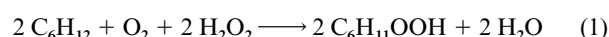
The use of methane as an alternative feedstock for valuable C_1 oxygenates is of great scientific and practical interest due to the considerable reserves of natural gas, although methane is the most inert organic compound.[1,2] Previously we have shown that methane and other saturated hydrocarbons are readily oxidised by molecular oxygen (in air) and hydrogen peroxide in the presence of a catalytic system composed of vanadate(V) and pyrazine-2-carboxylic acid; the reaction takes place either in acetonitrile[3] or in water[4] as solvent. If the reaction is performed under mild conditions (<50 °C) the corresponding alkyl hydroperoxides, formed as primary products, are obtained in good selectivities as major products. At higher temperatures the reaction gives mainly alcohols and ketones.[3,4]

In order to elucidate the function of the catalyst mixture in this remarkable catalytic reaction we decided to study systematically (1) the variation of the co-catalyst and its influence on the catalytic activity, (2) the co-ordination chemistry of vanadate(V) with pyrazine-2-carboxylic acid and related co-catalysts, and (3) the reactivity of the vanadate(V) complex obtained towards hydrogen peroxide. In this paper we report the synthesis and X-ray crystallographic characterisation of the oxo complexes $[VO_2L_2]^-$ [HL = pyrazine-2-carboxylic acid (Hpna) or anthranilic acid (Hana)] and of the peroxo complex $[VO(O_2)(pca)_2]^-$. Their implication in the catalytic process is also discussed.

Results and discussion

The oxidative functionalisation of alkanes with air and hydrogen peroxide is catalysed in acetonitrile by tetrabutylammonium vanadate in the presence of organic acids such as pyrazine-2-carboxylic acid. The primary oxidation products are the corresponding alkyl hydroperoxides which decompose to give a mixture of the alcohols and ketones. In the case of cyclohexane, cyclohexanol and cyclohexanone are obtained in addition to the intermediary cyclohexyl hydroperoxide, eqns. (1) and (2). For analytical reasons, the reaction mixture

$$2\,C_6H_{12} + O_2 + 2\,H_2O_2 \longrightarrow 2\,C_6H_{11}OOH + 2\,H_2O \quad (1)$$

$$2\,C_6H_{11}OOH \longrightarrow C_6H_{11}OH + C_6H_{10}O \quad (2)$$

obtained is treated with triphenylphosphine which transforms the cyclohexyl hydroperoxide quantitatively into cyclohexanol and triphenylphosphine oxide,[3b,5] eqn. (3).

$$C_6H_{11}OOH + PPh_3 \longrightarrow C_6H_{11}OH + OPPh_3 \quad (3)$$
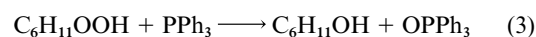
1 Variation of the co-catalyst

In order to understand the prerequisites of the co-catalyst in the catalytic reaction we studied the oxidation of cyclohexane under standard conditions with various compounds, mainly organic acids with N- and O-containing functions, as co-catalysts.

The oxidation reaction was carried out in a thermostatted glass vessel. For the screening, the reaction temperature was chosen to be 40 °C, and the reactions were stopped after 24 h. The results are compiled in Table 1, giving the concentration of cyclohexanol and cyclohexanone after reaction with PPh_3 (which transforms the cyclohexyl hydroperoxide quantitatively into cyclohexanol). The results clearly show that the best co-catalysts are pyrazine-2,3-dicarboxylic acid (Hpda), pyrazine-2-carboxylic acid (Hpca) and picolinic acid (Hpic), all of them being heteroaromatic and acidic. They have in common a six-membered aromatic cycle containing at least one nitrogen ring atom and at least one carboxylato substituent in the α position with respect to the nitrogen atom.

Five-membered heterocycles containing two or three nitro-

N   COOH
N   COOH
Pyrazine-2,3-dicarboxylic acid
(pdaH)

N   COOH
N
Pyrazine-2-carboxylic acid
(pcaH)

N   COOH
N   NH$_2$
3-Aminopyrazine-2-carboxylic acid
(NH$_2$pcaH)

N   COOH
Picolinic acid
(picH)

COOH
H N   COOH
Imidazole-4,5-dicarboxylic acid
(idaH)

H N   COOH
N
4-Imidazole carboxylic acid
(icaH)

H N   N   COOH
HOOC
Pyrazole-3,5-dicarboxylic acid
(poldaH)

COOH
NH$_2$
Anthranilic acid
(anaH)

OH
O=Cl=O
O
Perchloric acid
(HClO$_4$)

CH$_3$
HO   O
Acetic acid
(MeCOOH)

N
N H   H N
2,6-bis(pyrrolidin-2-yl)-pyridine
(bpp)

C$_6$H$_5$
N
N   N
H$_3$C   COOH
5-Methyl-2-phenyl-1,2,3-triazole-
4-carboxylic acid
(MePhtcaH)

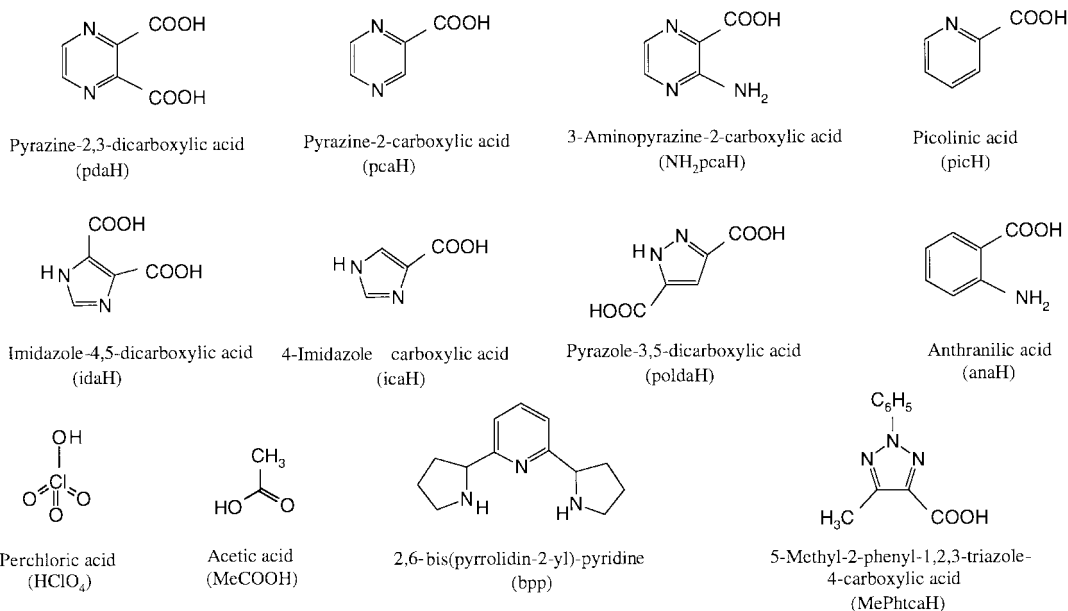**Table 1** Oxidation of cyclohexane catalysed by [NBu$_4$][VO$_3$] in the presence of various co-catalysts[a]

Co-catalyst	Cyclohexanone[b]/ 10^2 M	Cyclohexanol[b]/ 10^2 M	Total TON[c]
Hpda	0.72	10.40	1112
Hpca	0.55	10.44	1100
Hpic	0.51	9.20	971
Hida	0.12	4.20	432
Hica	0	0.66	66
Hpolda	0	0.32	32
NH$_2$pcaH	0	0.20	20
Hana	0	0.09	9
MePhtcaH	0	0.08	8
HClO$_4$	0	3.80	380
CH$_3$CO$_2$H	0	0.65	65
bpp	0	0.21	21

[a] Reaction conditions: CH$_3$CN; [NBu$_4$][VO$_3$], 1×10^{-4} M; co-catalyst, 4×10^{-4} M; cyclohexane, 0.464 M; H$_2$O$_2$, 0.5 M; 40 °C; 24 h. [b] GC analysis after reaction of the products with PPh$_3$. [c] Total turnover number: (mol cyclohexanol + mol cyclohexanone)/mol [NBu$_4$][VO$_3$].
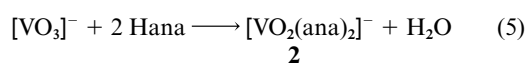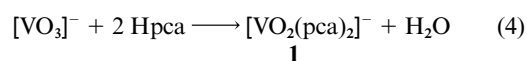
gen ring atoms and one or two carboxylato substituents are less active. The ring size, however, is not a crucial factor, since anthranilic acid (Hana), a six-membered aromatic cycle containing a carboxylato and an amino substituent, is almost inactive. Some results seem to be contradictory and are not easy to explain: on the one hand, the most important feature of an active co-catalyst seems to be its acid function, since perchloric acid and acetic acid are weakly active (without having an aromatic function or a nitrogen atom); on the other hand, nitrogen-containing heteroaromatics such as 2,6-bis(pyrrolidin-2-yl)pyridine[6] also work as weak co-catalysts (without containing an acid function).

In order to understand the role of the co-catalyst in the vanadate-catalysed oxidation of alkanes, we decided to study the action on the vanadate anion of pyrazine-2-carboxylic acid, one of the best co-catalysts, and of anthranilic acid, which is almost inactive as a co-catalyst. This is based on the assumption that the co-catalyst co-ordinates to vanadium in some way in order to activate the vanadium center for the catalytic transformations.

2 Reaction of [NBu$_4$][VO$_3$] with pyrazine-2-carboxylic acid and with anthranilic acid

Tetrabutylammonium vanadate reacts in refluxing acetonitrile with the pyrazine-2-carboxylic acid or with anthranilic acid to give the disubstituted vanadate derivatives [VO$_2$(pca)$_2$]$^-$ **1** and [VO$_2$(ana)$_2$]$^-$ **2**, respectively, eqns. (3) and (4). The anions **1** and

$$[VO_3]^- + 2 \text{ Hpca} \longrightarrow [VO_2(pca)_2]^- + H_2O \quad (4)$$
$$\mathbf{1}$$

$$[VO_3]^- + 2 \text{ Hana} \longrightarrow [VO_2(ana)_2]^- + H_2O \quad (5)$$
$$\mathbf{2}$$

2 can be isolated as tetrabutylammonium salts in the form of air-stable, yellow (**1**) or violet (**2**) crystals. In the infrared spectra two characteristic absorptions at 862 and 873 cm^{-1} (**1**) and 825 and 875 cm^{-1} (**2**) are assigned to the symmetric and the anti-symmetric stretches of the cis-VO$_2$ moiety.[7] A strong absorption at 1668 (**1**) and 1623 cm^{-1} (**2**) is attributed to the asymmetric vibration of the carboxylato function of the ligand. In the ^{1}H NMR spectra of both compounds the expected four signals of the tetrabutylammonium cation are observed in the aliphatic region as well as the expected signals of the ligands in the aromatic region: three for the pca units in **1** and four for the ana units in **2**. The integral ratio of the methyl triplet of the cation at δ 0.94 (in both cases) and of the most deshielded ligand signal assigned to the α-proton with respect to the carboxylato function (**1**: δ 9.20, d. **2**: δ 7.87, dd) being 6:11 approximately, is in accordance with the 1:1 cation:anion stoichiometry. The ^{51}V NMR spectra show only one signal for both complexes: at δ −525 for **1** and −503 for **2** (with respect to VOCl$_3$, in d$_6$-acetone). This is in accordance with other cis-dioxovanadate complexes, where the vanadium resonances have been found between δ −500 and −560.[8–11,15]

Suitable crystals for X-ray analysis of [NBu$_4$][VO$_2$(pca)$_2$] and of [NBu$_4$][VO$_2$(ana)$_2$] have been obtained by crystallisation from a mixture of dichloromethane and cyclohexane. In both cases the anionic vanadium complex is found to have an octahedral co-ordination geometry with the two terminal oxo ligands in the cis positions. The O=V=O angle is 106.5(6)° in complex **1** and 105.99(7)° in **2**, the vanadium–oxygen distances are 1.620(1) and 1.634(1) Å in **1**, and 1.631(1) and 1.613(1) Å in **2**, being in line with those found for V=O bonds in other vanadate comlexes.[10–16]
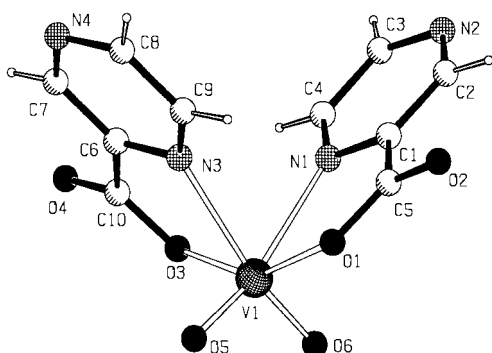
In complex **1** (Fig. 1, Table 2) the two pca ligands are co-ordinated by an oxygen atom of the carboxylato function and by a nitrogen atom of the aromatic cycle (in the α position with respect to the carboxylato substituent). The two chelating ligands form with the vanadium atom an almost planar five-membered metallacyclic moiety. The V–O bonds are 1.996(1) and 1.990(1) Å, the V–N bonds 2.316(1) and 2.343(2) Å. Simi-

Table 2 Selected bond lengths (Å) and angles (°) for anion **1**

V(1)–O(5)	1.6203(13)	O(6)–V(1)–O(3)	97.12(6)
V(1)–O(6)	1.6340(12)	O(1)–V(1)–O(3)	150.81(5)
V(1)–O(1)	1.9895(13)	O(5)–V(1)–N(3)	88.48(6)
V(1)–O(3)	1.9961(13)	O(6)–V(1)–N(3)	164.07(6)
V(1)–N(3)	2.3158(14)	O(1)–V(1)–N(3)	83.32(5)
V(1)–N(1)	2.3434(15)	O(3)–V(1)–N(3)	74.31(5)
		O(5)–V(1)–N(1)	162.36(6)
O(5)–V(1)–O(6)	106.50(6)	O(6)–V(1)–N(1)	90.29(6)
O(5)–V(1)–O(1)	97.36(6)	O(1)–V(1)–N(1)	73.98(5)
O(6)–V(1)–O(1)	99.71(6)	O(3)–V(1)–N(1)	82.29(5)
O(5)–V(1)–O(3)	100.49(6)	N(3)–V(1)–N(1)	75.42(5)

Table 3 Selected bond lengths (Å) and angles (°) for anion **2**

V(1)–O(5)	1.6132(14)	O(6)–V(1)–O(3)	100.46(6)
V(1)–O(6)	1.6312(13)	O(1)–V(1)–O(3)	141.11(6)
V(1)–O(1)	1.9868(14)	O(5)–V(1)–O(4)	93.96(6)
V(1)–O(3)	1.9987(14)	O(6)–V(1)–O(4)	155.49(6)
V(1)–O(4)	2.3079(13)	O(1)–V(1)–O(4)	86.99(5)
V(1)–O(2)	2.3476(15)	O(3)–V(1)–O(4)	60.12(5)
		O(5)–V(1)–O(2)	155.85(7)
O(5)–V(1)–O(6)	105.99(7)	O(6)–V(1)–O(2)	89.51(6)
O(5)–V(1)–O(1)	97.93(7)	O(1)–V(1)–O(2)	59.75(5)
O(6)–V(1)–O(1)	103.80(6)	O(3)–V(1)–O(2)	90.82(5)
O(5)–V(1)–O(3)	104.04(7)	O(4)–V(1)–O(2)	76.87(5)

Fig. 2 Molecular drawing of the anion $[VO_2(ana)_2]^-$ **2**.
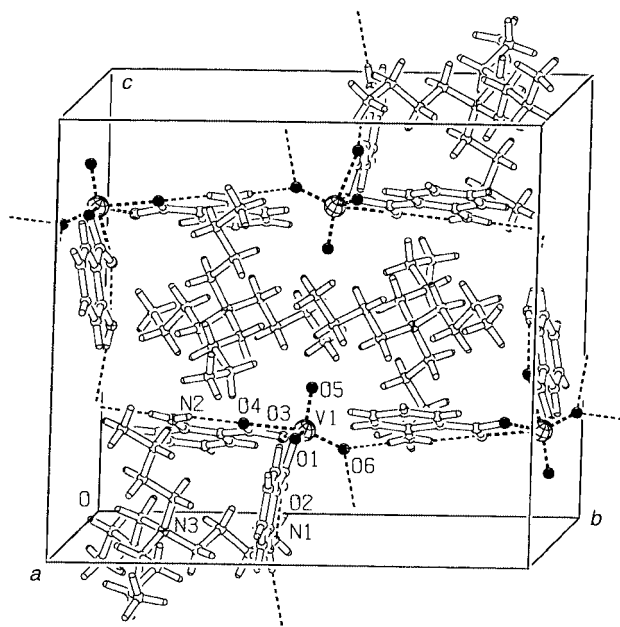
Fig. 3 Representation of the unit cell of $[NBu_4][VO_2(ana)_2]$.

Fig. 1 Molecular drawing of the anion $[VO_2(pca)_2]^-$ **1**.

lar values have been observed in other *N,O*-disubstituted vanadate derivatives: $[NH_4][VO_2(pic)_2]\cdot 2H_2O$,[12] $[NH_4][VO_2(edda)]$ (H_2edda = ethylenediiminodiacetic acid),[10] $Na_3[VO_2(edta)]$ (H_2edta = ethylenenitrilotetraacetic acid),[13] and $[NH_4][VO_2(H_2\text{-}edta)]\cdot H_2O$,[14] $[NBu_4][VO_2(qnl)_2]$ (Hqnl = 8-hydroxyquinoline).[15] By contrast, in the neutral complex $[VO_2(Hpmide)]\cdot 4H_2O$ (H_2pmide = *N*-2-pyridylmethyliminodiethanol)[11] both the V–O bond [1.876(1) Å] and the V–N bond [2.141(1) Å] to the ligand are shorter. The deviation of the angles from the octahedral geometry in **1** (Table 2) is due to the five-membered ring structure of the two chelating ligands. Only the two angles involving the terminal oxo ligands are almost 90°: O(6)–V(1)–N(1) 90.29(6)° and O(5)–V(1)–N(3) 88.48(6)°.

Surprisingly, the crystal structure analysis reveals an *O,O* co-ordination of the ana ligands in complex **2** (Fig. 2, Table 3): both ana ligands are co-ordinated by the two oxygen atoms of the carboxylato function, while the nitrogen atom of the ana ligand is not co-ordinated. The two V–O bonds of the two four-membered metallacycles are quite different in length: V(1)–O(1) 1.987(1), V(1)–O(2) 2.348(2) and V(1)–O(3) 1.999(1), V(1)–O(4) 2.308(1) Å. In both ana ligands the long vanadium–oxygen bonds are those which are *trans* with respect to the terminal oxo ligands. This is in line with the findings in the bis(oxalato) derivative $[NH_4]_3[VO_2(ox)_2]\cdot 2H_2O$ (H_2ox = oxalic acid) where the V–O bonds *trans* to the V=O bonds measure 2.235(2) and 2.185(2) Å, while the remaining two V–O bonds are shorter [1.972(2) and 1.988(2) Å], although in this case the oxygen atoms of the two different carboxylato functions of

the ligands are co-ordinated.[16] The two angles O(1)–V–O(2) [59.75(5)°] and O(3)–V–O(4) [60.12(5)°] are very small and considerably distort the octahedral geometry of the complex, being due to the four-membered metallacyclic system formed by the chelating ligand (Table 3).

The presence of a non-co-ordinated NH_2 group in the ana ligands of complex **2** is responsible for the formation of hydrogen bonds within and between the $[VO_2(ana)_2]^-$ anions. There are intramolecular interactions between N(1)–H$\cdots$O(2) (2.72 Å) and N(2)–H$\cdots$O(4) (2.70 Å), as well as intermolecular interactions between O(6) of a $[VO_2(ana)_2]^-$ molecule and NH_2 of a neighbouring $[VO_2(ana)_2]^-$ anion (N(1)–H$\cdots$O(6^a) 3.06, N(2)–H$\cdots$O(6^b) 3.01 Å. Symmetry operations: a $-x + 1$, $-y + 1$, $-z + 2$; b $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$). Hydrogen bonding involving the tetrabutylammonium cation has not been observed (Fig. 3).

The different co-ordination mode of the ligands (*N,O* for pca and *O,O* for ana) may explain the different activity of the acids Hpca and Hana as co-catalysts in the oxidative functionalisation of alkanes catalysed by the vanadate anion.

As expected, complex **1** is catalytically active, whereas **2** is almost inactive in this reaction. For the catalytic oxidation of cyclohexane under the same conditions, almost the same selectivity and activity is obtained for the systems $[NBu_4][VO_3]$:Hpca 1:4 and $[NBu_4][VO_2(pca)_2]$:Hpca 1:2 (Table 4), suggesting the role of a catalytic intermediate for complex **1**.

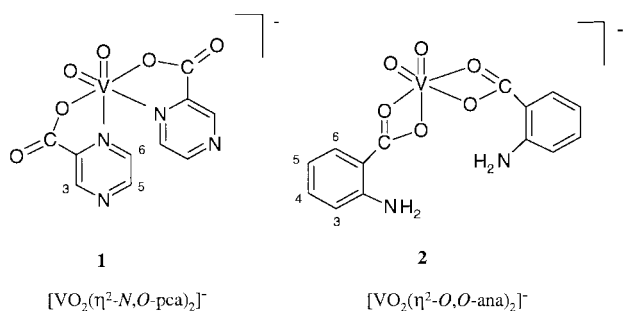## 3 Reaction of $[VO_2(pca)_2]^-$ with hydrogen peroxide

Given the hypothetical role of the complex $[VO_2(pca)_2]^-$ **1** as a catalytic intermediate in the oxidation of alkanes by molecular

**Table 4** Oxidation of cyclohexane catalysed by the system vanadate/pyrazine-2-carboxylate[a]

Catalyst	Co-catalyst (concentration/M)	Cyclohexanone[b]/ 10^2 M[b]	Cyclohexanol[b]/ 10^2 M[b]	Total TON[c]
[NBu$_4$][VO$_3$]	Hpca (4×10^{-4})	0.55	10.44	1100
	Hpca (2×10^{-4})	0	3.30	330
	Hpca (1×10^{-4})/HClO$_4$ (3×10^{-4})	0.45	3.30	375
	Hpca (4×10^{-4})/HClO$_4$ (4×10^{-4})	0.47	9.20	967
[NBu$_4$][VO$_2$(pca)$_2$]	—	0.15	2.00	215
	Hpca (2×10^{-4})	0.84	8.4	924
	HClO$_4$ (2×10^{-4})	0.52	8.4	892

[a] Reaction conditions: CH$_3$CN; catalyst, 1×10^{-4} M; cyclohexane, 0.464 M; H$_2$O$_2$, 0.5 M; 40 °C; 24 h. [b] GC analysis after reaction of the products with PPh$_3$. [c] Total turnover number: (mol cyclohexane + mol cyclohexanone)/mol catalyst.

1

[VO$_2$(η^2-N,O-pca)$_2$]$^-$

2

[VO$_2$(η^2-O,O-ana)$_2$]$^-$

oxygen and hydrogen peroxide, it was interesting to study the reaction of **1** with these components. As **1** is air stable, molecular oxygen obviously does not attack this anion, however a smooth reaction is observed between **1** and H$_2$O$_2$, eqn. (6). If

$$[\text{VO}_2(\text{pca})_2]^- + \text{H}_2\text{O}_2 \longrightarrow [\text{VO}(\text{O}_2)(\text{pca})_2]^- + \text{H}_2\text{O} \quad (6)$$
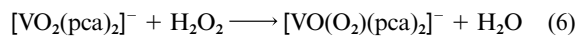
the reaction is carried out with the tetrabutylammonium salt of **1** in acetonitrile at 40 °C (the conditions of the catalytic alkane oxidation) an immediate change from yellow to red indicates the formation of the peroxo complex [VO(O$_2$)(pca)$_2$]$^-$ **3**. The solid isolated by crystallisation from a mixture of acetone and diethyl ether turns out to be the double salt [NBu$_4$]$_2$[VO$_2$(pca)$_2$][VO(O$_2$)(pca)$_2$] containing both anions **1** and **3**. The infrared spectrum of this double salt shows, in addition to the ν(VO$_2$) bands of anion **1** at 857 and 875 cm^{-1}, an absorption at 847 cm^{-1}, assigned to the ν(V=O) vibration in anion **3**. The asymmetric vibrations of the carboxylato functions of both anions give rise to two very strong bands at 1651 and 1674 cm^{-1}. Two bands at 546 and 578 cm^{-1} are assigned to the symmetrical and antisymmetrical vibration of the vanadium peroxo unit in **3**, based on a comparison with the known peroxo complex [VO(O$_2$)(pic)$_2$]$^-$ described in the pioneering paper of Mimoun et al.[17] In the ^{1}H NMR spectrum the two anions of the double salt give rise to three sets of badly resolved signals for the pca ligands in the aromatic region: δ(CDCl$_3$) 8.67 (dd), 8.76 (d) and 9.24 (d) for the two pca ligands in **1**, and 9.00 (d), 9.16 (d), 9.31 (d), 9.38 (s), 9.49 (s), 9.89 (d) for the two nonequivalent pca ligands in **3**. The ^{51}V NMR spectrum in acetone-d$_6$ shows the signal of **1** at δ −520 and a resonance at δ −540 for anion **3**. In D$_2$O **3** resonates at δ −600 in accordance with the findings for the known complex [VO(O$_2$)(H$_2$O)(pca)] (δ −585.5).[18]

Both anions, [VO$_2$(pca)$_2$]$^-$ **1** and [VO(O$_2$)(pca)$_2$]$^-$ **3**, can also be identified by ^{51}V NMR spectroscopy in the reaction mixture of the cyclohexane oxidation with O$_2$/H$_2$O$_2$ catalysed by [NBu$_4$][VO$_3$]:Hpca (1:4), if the reaction is carried out in CD$_3$CN: anion **1** gives a signal at δ −540 (in the isolated double salt, anion **1** resonates at δ −537), while **3** gives a signal at δ −551 (in the isolated double salt, anion **3** resonates at δ −558). This observation confirms the presence of both anions **1** and **3** in the catalytic system.

A single crystal structure analysis of the double salt [NBu$_4$]$_2$-
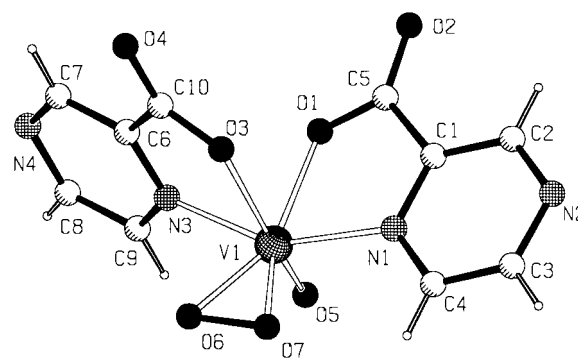
Fig. 4 Molecular drawing of the anion [VO(O$_2$)(pca)$_2$]$^-$ **3b**.

[VO$_2$(pca)$_2$][VO(O$_2$)(pca)$_2$] reveals for anion **3** a pentagonal bipyramidal structure **3a**, which derives from the octahedral structure of anion **1** by replacing one of the two oxo ligands by a peroxo ligand. The two pca ligands are N,O co-ordinated, the two nitrogen atoms being cis with respect to each other. Unfortunately the structure analysis is not good enough for publication ($R > 10\%$), due to the disorder of the tetrabutylammonium cations.

isomer **3a**
(from acetonitrile solution)

isomer **3b**
(from water solution)
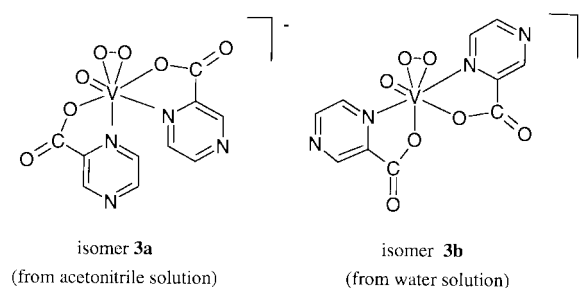
In order to characterise the peroxo complex [VO(O$_2$)(pca)$_2$]$^-$ **3** unambiguously, and to separate it from anion **1**, with which it tends to crystallise as the tetrabutylammonium double salt, we decided to synthesize **3** in aqueous solution and to crystallise it as the ammonium salt. The compound NH$_4$VO$_3$ was found to react in water with Hpca and H$_2$O$_2$ to give [NH$_4$][VO(O$_2$)-(pca)$_2$], which crystallises directly from water upon addition of ethanol. In the infrared spectrum of this salt, an absorption at 939 cm^{-1} is assigned to the ν(V=O) vibration and one at 1668 cm^{-1} to ν_{asym}(CO$_2$), in accordance with the known complex [VO(O$_2$)(pic)$_2$]$^-$.[19a] The symmetrical and antisymmetrical vibrations of the vanadium peroxo unit are found at 533 and 553 cm^{-1}. The ^{1}H NMR in CD$_3$OD shows the signals of the co-ordinated pca at δ 9.2275 (d), 9.3815 (d), 9.410 (d), 9.4925 (d), 9.922 (m). The ^{51}V NMR spectrum shows a resonance at δ −600 in D$_2$O, in accordance with the resonance found for the peroxo complex in the double salt.

The single-crystal structure analysis of [NH$_4$][VO(O$_2$)(pca)$_2$] (Fig. 4) revealed the presence of two water molecules of crystallisation per molecule of complex. As found for complex **1**, the

Table 5 Selected bond lengths (Å) and angles (°) for anion **3b**

|			
V(1)–O(5)	1.5977(12)	O(5)–V(1)–O(3)	163.65(6)
V(1)–O(6)	1.8908(13)	O(6)–V(1)–O(3)	85.78(5)
V(1)–O(7)	1.8634(13)	O(7)–V(1)–O(3)	91.45(5)
V(1)–O(1)	2.0865(12)	O(1)–V(1)–O(3)	76.15(5)
V(1)–O(3)	2.1892(12)	O(5)–V(1)–N(3)	92.20(6)
V(1)–N(3)	2.1148(14)	O(6)–V(1)–N(3)	78.82(5)
V(1)–N(1)	2.1405(14)	O(7)–V(1)–N(3)	122.55(6)
O(6)–O(7)	1.4119(19)	O(1)–V(1)–N(3)	78.72(5)
		O(3)–V(1)–N(3)	75.08(5)
O(5)–V(1)–O(6)	102.03(6)	O(5)–V(1)–N(1)	97.95(6)
O(5)–V(1)–O(7)	104.20(6)	O(6)–V(1)–N(1)	123.47(6)
O(6)–V(1)–O(7)	44.18(6)	O(7)–V(1)–N(1)	79.81(5)
O(5)–V(1)–O(1)	91.51(6)	O(1)–V(1)–N(1)	75.32(5)
O(6)–V(1)–O(1)	154.12(5)	O(3)–V(1)–N(1)	89.36(5)
O(7)–V(1)–O(1)	152.19(5)	N(3)–V(1)–N(1)	152.30(5)

vanadium atom is at the center of an irregular octahedron, and both pca ligands are *N,O* co-ordinated. Surprisingly, the orientation of the two *N,O*-pca ligands in **3b** is different from that in **1** and also from that found for **3a** in the double salt [NBu$_4$]$_2$-[VO$_2$(pca)$_2$][VO(O$_2$)(pca)$_2$]: whereas for anion **3a** in the double salt both pca ligands (like in **1**) are found to be *N,O* co-ordinated with the two nitrogen atoms being *cis* with respect to each other, anion **3b** in the salt [NH$_4$][VO(O$_2$)(pca)$_2$] contains two pca ligands *N,O* co-ordinated with the nitrogen atoms being *trans* with respect to each other as was also found by X-ray crystallography[19b] for the picolinato analogue [VO(O$_2$)-(pic)$_2$]$^-$.[17,19a] This co-ordination generates an equatorial plane containing all of the oxygen atoms, the oxygen atoms from the oxo and the peroxo group being *cis* to each other. Selected bond distances and angles are included in Table 5.

The O–V–O angle of the peroxo group is 44.18(6)°, in accordance with the complexes [VO(O$_2$)(pic)]·2H$_2$O,[17] [VO(O$_2$)-(H$_2$O)(dipic)]$^-$ (H$_2$dipic = pyridine-2,6-dicarboxylic acid),[20] and [{VO(O$_2$)(H$_2$tart)}(μ-H$_2$O)]$^{2-}$ (H$_4$tart = L-tartaric acid),[21] for which this angle was found to be 45.06(8), 45.3(1) and 44.5(2)°, respectively. In the analogue [VO(O$_2$)(pic)$_2$]$^-$ this angle is slightly smaller: 40.8(5)°.[19b] The vanadium–oxygen distances of the peroxo group are 1.863(1) and 1.891(1) Å in line with the findings in the complexes cited above.[17,19b,20,21] The V=O distance [1.598(1) Å] and the angles O(5)–V(1)–O(6) [102.03(6)°] and O(5)–V(1)–O(7) [104.20(6)°] are similar to those found in anion **1**, whereas the V–N distances are slightly shorter (**3b**, average 2.1 Å; **1**, average 2.3 Å) (Fig. 4).

The presence of an ammonium cation and two water molecules per unit of anion **3b** generates hydrogen bonds. The interactions between anion **3b** and the ammonium cation result in hydrogen bonds N(5)–H · · · O(2) (2.92), N(5)–H · · · N(2^d) (2.98), N(5)–H · · · O(4^e) (2.95), N(5)–H · · · O(6^f) (3.04) and N(5)–H · · · N(4^g) (3.04 Å) (symmetry operations: d $-x + 1$, $-y$, $-z + 1$; e $-x + 2$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$; f x, $y - 1$, z; g $-x + 2$, $-y$, $-z + 2$). The water molecules containing the oxygen atoms O(8) and O(9) interact with anion **3b** to give hydrogen bonds O(8)–H · · · O(4) (2.87), O(8)–H · · · O(3) (3.27) and O(9)–H · · · O(1) (2.85 Å), and the intermolecular interactions between the water molecules are O(8)–H · · · O(9^h) (2.81) and O(9)–H · · · O(8^j) (2.81 Å) (symmetry operations: h $-x + 2$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$ and j x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$), forming a three-dimensional hydrogen bonded network (Fig. 5).

The different arrangement of the two pca ligands in the anion [VO(O$_2$)(pca)$_2$]$^-$ **3** is probably due to the different solvents used: in acetonitrile the two pca ligands co-ordinate to vanadium as *N,O*-chelates with the two nitrogen atoms *cis* to each other, which gives rise to the formation of isomer **3a** upon reaction with hydrogen peroxide. In aqueous solution the two pca ligands undergo *N,O* co-ordination with the two nitrogen atoms *trans* to each other, resulting in isomer **3b**, upon reaction with H$_2$O$_2$.

A catalytic test using anion **3b** as a catalyst for the oxidation
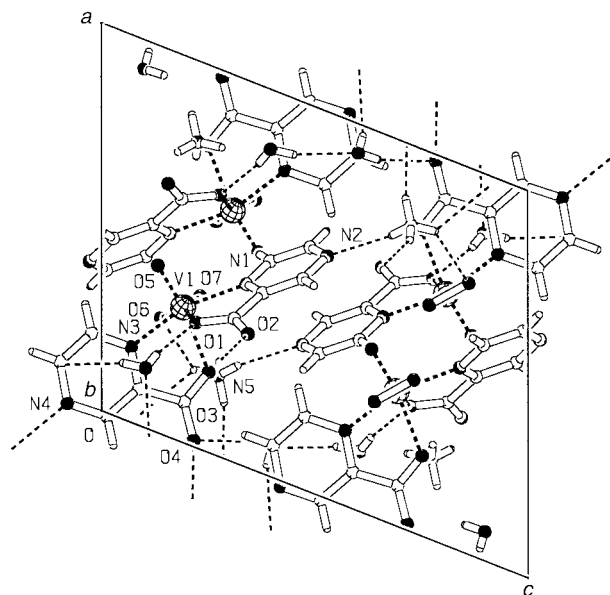
Fig. 5 Representation of the unit cell of [NH$_4$][VO(O$_2$)(pca)$_2$].

of cyclohexane under standard conditions (CH$_3$CN, 1 × 10^{-4} M [NH$_4$][VO(O$_2$)(pca)$_2$], 2 × 10^{-4} M Hpca, 0.5 M H$_2$O$_2$, 40 °C, 24 h) reveals a selectivity (cyclohexanone 0.74 × 10^{-2} M, cyclohexanol 10.46 × 10^{-2} M) and an activity (total TON 1120) comparable to those of VO$_3^-$/4 Hpca and [VO$_2$(pca)$_2$]$^-$/2 Hpca (compare Table 4). This observation suggests the peroxo complex [VO(O$_2$)(pca)$_2$]$^-$ **3** to be a member of the catalytic cycle of the alkane oxidation catalysed by the system tetrabutylammonium metavanadate and pyrazine-2-carboxylic acid.

Experimental

All the reactions were carried out in air. Acetonitrile (Fluka) was distilled over CaH$_2$; all other solvents were distilled over appropriate drying agents prior to use. Tetrabutylammonium vanadate was prepared according to the literature method.[22] All organic acids (Fluka) were used without purification. Hydrogen peroxide 30% in water (Fluka) was stored in a refrigerator (maximum 4 °C) after each use. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer with TMS for ^{1}H and VOCl$_3$ for ^{51}V as external references, infrared spectra with a Perkin-Elmer 1720x FT-IR spectrometer and mass spectra (electrospray) using a LCQ Finnigan instrument. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium of the ETH Zürich, Switzerland. Gas chromatographic analyses were recorded with a Dani 86.10 Doppler instrument (with CH$_3$NO$_2$ as internal reference) using a capillary Cp-wax 52-CB (25 m × 0.32 mm) column from Chrompack, and a Chrom Jet integrator (Spectra-Physics).

Preparations

[NBu$_4$][VO$_2$(pca)$_2$]. The compound NBu$_4$VO$_3$ (681 mg, 2 mmol) was dissolved in 20 ml of CH$_3$CN. After complete dissolution, pyrazine-2-carboxylic acid (492 mg, 4 mmol) was added, and the solution stirred under reflux for 5 h. After filtration of the green solution, evaporation of the solvent gave a yellow-green powder, which was dissolved in the minimum quantity of CH$_2$Cl$_2$. Addition of the same volume of cyclohexane led, after a few days, to the formation of light yellow crystals. Yield 61% (Found: C, 54.64; H, 7.32; N, 12.33. C$_{26}$H$_{42}$N$_5$O$_6$V requires C, 54.63; H, 7.41; N, 12.25%). IR (cm^{-1}): 862s, 873s and 1668vs. ^{1}H NMR (acetone-d$_6$): δ 0.9406 (12 H, t, J = 7.5, CH$_3$), 1.4227 (8 H, m, J = 7.3, CH$_2$), 1.8298 (8 H, m,

	1	**2**	**3b**
Formula	$C_{26}H_{42}N_5O_6V$	$C_{30}H_{48}N_3O_6V$	$C_{10}H_{10}N_5O_7V\cdot 2\,H_2O$
M	571.59	597.65	399.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pbcn$	$P2_1/c$	$P2_1/c$
$a/\text{Å}$	13.6607(8)	11.1906(8)	12.1752(7)
$b/\text{Å}$	17.9727(16)	18.1294(16)	9.2884(5)
$c/\text{Å}$	23.6191(16)	16.5682(10)	14.3963(9)
$\beta/°$		105.831(7)	111.386(6)
$V/\text{Å}^3$	5799.0(7)	3233.8(4)	1515.95(15)
Z	8	4	4
μ/mm^{-1}	0.389	0.350	0.716
Reflections measured	32314	24916	11496
Independent reflections	5613	6031	2918
Observed reflections	3493	4359	2410
R_{int}	0.0590	0.0435	0.0318
$R1\ [I > 2\sigma(I)]/R1$ (all data)	0.0333/0.0641	0.0383/0.0577	0.0260/0.0339
$wR2\ [I > 2\sigma(I)]/wR2$ (all data)	0.0682/0.0736	0.0972/0.1028	0.0706/0.0731

$J = 7.5$, CH$_2$), 3.4976 (8H, m, $J = 8.1$, CH$_2$), for NBu$_4{}^+$; 8.521 (2 H, dd, J(H5–H3) = 1.46 and J(H5–H6) = 2.64, H5), 8.8547 (2 H, d, J(H6–H5) = 2.68, H6) and 9.1828 (2 H, d, J(H3–H5) = 1.48 Hz, H3) for pca ligand. ^{51}V NMR (acetone-d$_6$): δ −525. MS (electrospray, negative): m/z 329.

[NBu$_4$][VO$_2$(ana)$_2$]. The compound NBu$_4$VO$_3$ (681 mg, 2 mmol) was dissolved in 20 ml of CH$_3$CN. After complete dissolution, anthranilic acid (547 mg, 4 mmol) was added and the solution stirred under reflux during 4 h. After filtration, evaporation of the solvent gave a yellow-green powder, which was dissolved in the minimum quantity of CH$_2$Cl$_2$. Addition of the same volume of cyclohexane led, after a few days, to the formation of light violet crystals. Yield 78% (Found: C, 60.17; H, 8.06; N, 7.08. C$_{30}$H$_{48}$N$_3$O$_6$V requires C, 60.29; H, 8.09; N, 7.03%). IR (cm^{-1}): 825s, 875s and 1623vs. ^{1}H NMR (acetone-d$_6$): δ 0.9410 (12 H, t, $J = 7$, CH$_3$), 1.4045 (8 H, m, $J = 6.6$, CH$_2$), 1.774 (8 H, m, CH$_2$), 3.421 (8H, m, CH$_2$) for NBu$_4{}^+$; 6.507 (2 H, ddd, J(H4–H3) = 8, J(H4–H5) = 6.8 and J(H4–H6) = 1, H4), 6.7065 (2 H, dd, J(H3–H4) = 8 and J(H3–H5) = 0.6, H3), 7.154 (2 H, ddd, J(H5–H6) = 8.4, J(H5–H4) = 7 and J(H5–H3) = 1.8, H5), 7.867 (2 H, dd, J(H6–H5) = 7.2 and J(H6–H4) = 1, H6) for ana ligand. ^{51}V NMR (acetone-d$_6$): δ −503. MS (electrospray, negative): m/z 354.7.

[NH$_4$][VO(O$_2$)(pca)$_2$]. The compound NH$_4$VO$_3$ (100 mg, 0.855 mmol) was dissolved in 20 ml of water and pyrazine-2-carboxylic acid (212 mg, 1.7 mmol) in 20 ml of water. The solutions were mixed, and 30% H$_2$O$_2$ (87 μl, 0.9 mmol) was added. The resulting solution was stirred at room temperature for 1 h. Slow evaporation of the solvent at room temperature to $ca.\ \tfrac{2}{3}$ of its volume and addition of the same volume of ethanol led after a few days at −18 °C to the formation of light red crystals. Yield 64% (Found: C, 33.14; H, 2.71; N, 19.03; O, 30.96. C$_{10}$H$_{10}$N$_5$O$_7$V requires C, 33.07; H, 2.78; N, 19.28; O, 30.84%). IR (cm^{-1}): 533s, 553s, 939s and 1668vs. ^{1}H NMR (CD$_3$OD): δ 9.2275 (1 H, d, $J = 3$), 9.3815 (2 H, d, $J = 3$), 9.410 (1 H, d, $J = 1.2$), 9.4925 (1 H, d, $J = 1$ Hz) and 9.922 (1 H, m) for pca ligand. ^{51}V NMR (D$_2$O): δ −600. MS (electrospray, negative): m/z 344.9.

[NBu$_4$]$_2$[VO$_2$(pca)$_2$][VO(O$_2$)(pca)$_2$]. The salt [NBu$_4$][VO$_2$-(pca)$_2$] (500 mg, 0.875 mmol) was dissolved in 5 ml of CH$_3$CN and, after complete dissolution, 30% H$_2$O$_2$ (90 μl, 0.88 mmol) added. The solution was stirred at 0 °C during 4 h. After filtration of the red solution, evaporation of the solvent gave a red powder, which was dissolved in the minimum amount of acetone. Addition of the same volume of diethyl ether led, after a few days at room temperature, to crystallisation of light red crystals. Yield 56%.

Catalytic runs

In a typical experiment the oxidation of cyclohexane was carried out in thermostatted cylindrical glass vessels equipped with reflux condensers, with vigorous stirring in air. The reagents (catalyst, co-catalyst and CH$_3$NO$_2$ as internal standard) were dissolved separately in acetonitrile and added to cyclohexane. After addition of H$_2$O$_2$ (30% aqueous solution), the reaction solution (total volume 10 cm^3) was stirred at 40 °C during 24 h. The reaction was monitored by withdrawing aliquots (0.5 cm^3) and, after addition of triphenylphosphine to saturation, the samples were analysed by GLC.

Crystallography

Single crystals of the tetrabutylammonium salts of complexes **1** (yellow) and **2** (violet) were obtained by slow diffusion of cyclohexane into their dichloromethane solutions. Single crystals of the ammonium salt of **3** (**3b**) were obtained by slow diffusion of ethanol into an aqueous solution containing [NH$_4$][VO(O$_2$)(pca)$_2$] at −18 °C.

Data collection, solution and structure refinement. Single crystals of the compounds **1**, **2** and **3** were measured on a Stoe Imaging Plate Diffractometer System at −50 °C. Crystallographic details are given in Table 6.

The structures were solved by direct methods using the program SHELXS 97[23] and refined by full-matrix least squares on F^2 with SHELXL 97.[24] The positions of the hydrogen atoms in the amino groups in anion **2** and those of the ammonium cation and the two water molecules in anion **3b** were derived using Fourier difference maps and refined isotropically. The remaining hydrogen atoms in all the complexes were included in calculated positions and treated as riding atoms using SHELXL 97 default parameters. In anion **2** a partial disorder was found in the tetrabutylammonium cation. The molecules in the complex are connected by hydrogen bonds involving the amino groups of the organic ligand and the oxygen atoms O(2), O(4) and O(5), so forming an extended hydrogen bonded network. The crystal containing the anion **3b** crystallises with two water molecules per molecule of complex. The figures were drawn with PLATON/PLUTON.[25]

CCDC reference number 186/1595.

See http://www.rsc.org/suppdata/dt/1999/3169/ for crystallographic files in .cif format.

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Paper 9/04844H