Vanadyl(IV)–Amide Binding. The Preparation and X-Ray Crystal Structure of [VO(pycac)] {H_2pycac = *N*-[2-(4-Oxopentan-2-ylideneamino)phenyl]pyridine-2-carboxamide}

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Reaction of H_2pycac with bis(pentane-2,4-dionato)oxovanadium(IV) gives the title compound which is the first example of a vanadyl(IV) complex containing a vanadium–amide bond; the X-ray crystal structure of the complex is reported.

In contrast to many other biologically important transition metals (Fe, Cu *etc.*) the role of vanadium in biochemical processes is still poorly understood. The discovery of vanadium in biomolecules such as marine algal bromoperoxidase,[1,2] nitrogenase from *Azobacter vinelandii*,[3,4] marine ascidians[5] and in crude oils[6] has led to considerable attention on its biological activity. In order to understand how vanadium might function in a complex biomolecule it is first necessary to define its basic coordination chemistry with biologically relevant ligands.

Although the interactions of vanadium with hydroxylic compounds are becoming better understood little is yet known about the coordination of vanadium by nitrogen, in particular vanadium–amide binding.[7,8] Herein we describe the first structural characterisation of such a complex, which is part of our programme for preparation and characterisation of vanadium complexes with nitrogen-rich ligands.

The ligand H_2pycac was synthesised by condensing *N*-(2-aminophenyl)pyridine-2-carboxamide and pentane-2,4-dione (Hacac) under argon. The mononuclear brown complex [VO(pycac)] was prepared by refluxing a mixture of bis(pentane-2,4-dionato)oxovanadium(IV) (3.8 mmol) and H_2pycac (4.0 mmol) in dry methanol (35 ml), under argon, for three days (eqn. 1). The resulting brown precipitate was filtered off, washed with methanol and ether and dried *in vacuo* over P_4O_{10} (yield 45%).

$$[\mathrm{VO(acac)_2}] + \mathrm{H_2pycac} \rightarrow [\mathrm{VO(pycac)}] + 2\ \mathrm{Hacac} \qquad (1)$$

The material is stable towards air oxidation in the solid state but decomposes slowly in solution in the presence of air. Crystals of [VO(pycac)] suitable for X-ray diffraction studies were obtained by slow cooling of a hot concentrated solution of the complex in nitromethane. The complex was also characterised by IR spectroscopy, cyclic voltammetry and polarography. Further characterisation by EPR spectroscopy and magnetochemistry is underway.

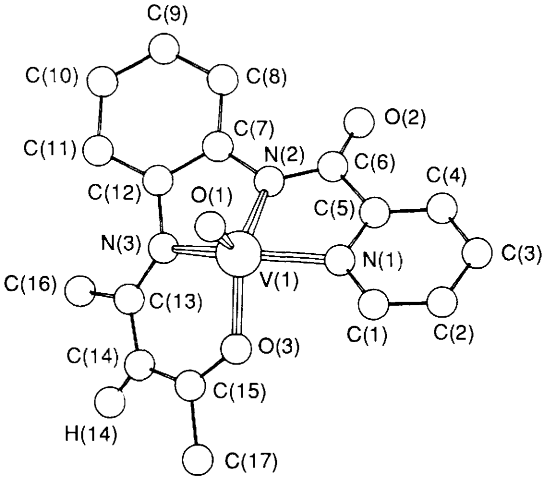

Fig. 1 X-Ray structure of [VO(pycac)] showing the atom labelling scheme. For clarity, hydrogen atoms are omitted. Selected interatomic distances (Å) and angles (°d) for the molecule 1, are as follows: V(1)–O(1) 1.599(2), V(1)–N(1) 2.097(2), V(1)–N(2) 1.984(2), V(1)–N(3) 2.052(2), V(1)–O(3) 1.916(2); N(1)–V(1)–O(1) 107.1(1), N(2)–V(1)–O(2) 111.6(1), N(2)–V(1)–N(1) 77.6(1), N(3)–V(1)–O(1) 106.9(1), N(3)–V(1)–N(1) 143.8(1), N(3)–V(1)–N(2) 78.6(1), O(3)–V(1)–O(1) 112.3(1), O(3)–V(1)–N(1) 88.4(1), O(3)–V(1)–N(2) 136.1(1), O(3)–V(1)–N(3) 90.1(1).

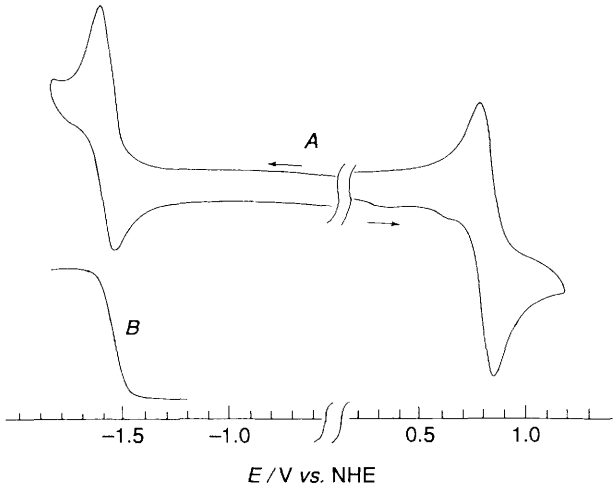

Fig. 2 (*A*) DC cyclic voltammogram for the oxidation and reduction of [VO(pycac)] in MeCN with tetraethylammonium perchlorate (0.1 mmol dm^{-3}) at a glassy carbon electrode and a scan rate of 100 mV S^{-1}. (*B*) DC polarogram of the same solution as in (*A*) at a dropping mercury electrode.

The molecular structure† and atomic numbering scheme of

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† *Crystal data*: $C_{17}H_{15}N_3O_3V$, *M* 360.27, monoclinic, space group $P2_1/n$, $a = 7.5938(3)$, $b = 30.161(1)$, $c = 13.6982(5)$ Å, $\beta = 86.468(1)°$, $V = 3131.5(2)$ Å^3, $Z = 8$, $D_m = 1.52$, $D_c = 1.528$ g cm^{-3}, crystal dimensions $0.23 \times 0.6 \times 0.12$ mm^3, $\mu = 56.87$ cm^{-1}, 5861 data collected, 5298 data unique, data used 4400 with $F_o \geqslant 4.06\ (F_o)$, analytical absorption correction. $F(000) = 1432$, 521 parameters, R $R_w) = 0.0378\ (0.0539)$ for observed data, 0.0490 (0.0559) for all data, weighting scheme $1/w = \sigma^2(F_o) + 0.00013F_o.^2$ Data collected on a Syntex $P2_1$ four-circle diffractometer upgraded by Crystal Logic using Ni-filtered Cu-Kα radiation, θ–2θ scan at 3.0° min^{-1}, θ = 130°. The structure was solved by direct methods and the refinement, based on F, proceeded by full-matrix least squares minimizing $\Sigma w\Delta^2$ with SHELX76.[10] The methyl hydrogen atoms were placed at calculated positions 0.96 Å from the carbon atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[VO(pycac)] are shown in Fig. 1. The structure contains two independent molecules per asymmetric unit but their geometries, bond distances and angles are almost identical. The coordination environment of the vanadium atom approximates to a square pyramid with the oxo ligand occupying the apical position and the donor atoms of the tetradentate ligand the basal plane. The four basal atoms are within 0.05 Å of this mean plane. The vanadium atom is 0.669 Å above the mean plane defined by the basal atoms. The ligand is not planar, the planarity being destroyed primarily by the torsional angles C(6)–N(2)–C(7)–C(12) and C(7)–C(12)–N(3)–C(13) which deviate from 180° by 17° and −34° respectively. Of the three V–N bonds, the bond to N(2), the amide nitrogen, constitutes the shortest V–N distance (1.984 Å) so far reported for vanadyl(IV). The longer bond lengths to N(1) (2.097 Å) and N(3) (2.052 Å) reflect the changes in donor strengths of the respective nitrogen atoms. It is interesting to note that the largest deviation from the best V(1)–N(2)–C(6)–C(7)–O(2) plane is 0.04 Å, which contrasts with other complexes of highly oxidised metal ions in which the amide function may be nonplanar.[9]

The redox properties of [VO(pycac)] in acetonitrile have been investigated by DC cyclic voltammetric and DC polarographic techniques (Fig. 2). The complex displays two reversible one-electron redox processes. These processes and their potentials (V *vs.* NHE, normal hydrogen electrode) are summarised in eqn. (2) and (3).

$$[\mathrm{V^{V}O(pycac)}]^{+} + \mathrm{e}^{-} \rightleftharpoons [\mathrm{V^{IV}O(pycac)}] \quad E_{\frac{1}{2}} = +0.82 \qquad (2)$$

$$[\mathrm{V^{IV}O(pycac)}] + \mathrm{e}^{-} \rightleftharpoons [\mathrm{V^{III}O(pycac)}]^{-} \quad E_{\frac{1}{2}} = -1.54 \qquad (3)$$

It is worth noting that to our knowledge [VO(pycac)] is the first example of a vanadyl(IV) complex showing a reversible one-electron reduction centred on vanadium.

Received, 25th July 1990; Com. 0/03372C

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