

## Synthesis and Characterization of Vanadium(III) and Oxovanadium(IV/V) Species with Deprotonated Amide Ligands

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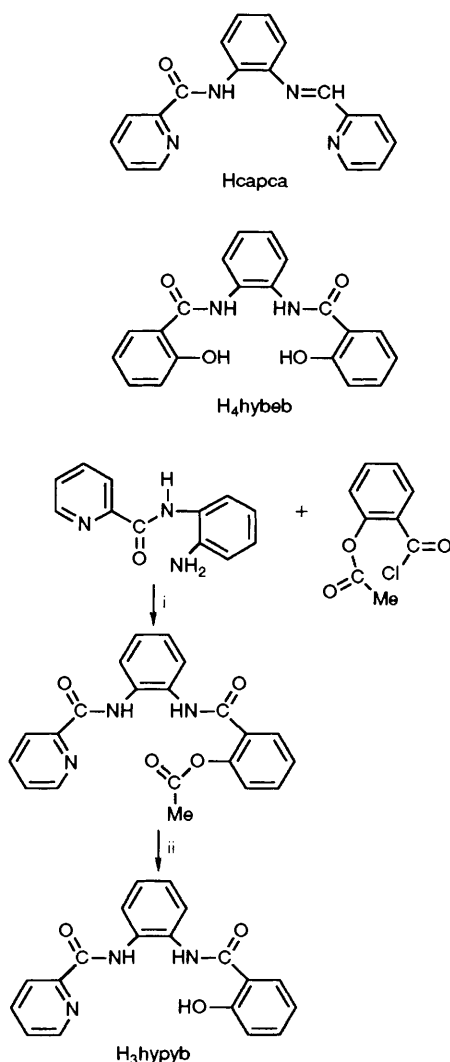
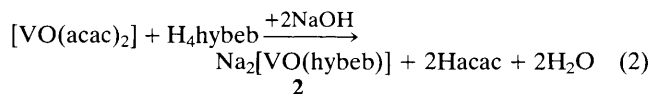
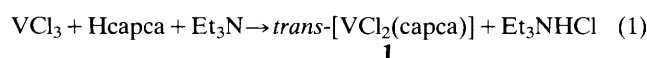
Reaction of the amide ligand *N*-[2-(2-pyridylmethyleneamino)phenyl]pyridine-2-carboxamide (Hcapca) with  $\text{VCl}_3$  affords the compound *trans*- $[\text{VCl}_2(\text{capca})]$  **1**, the first example of a vanadium(III) complex containing a vanadium–deprotonated amide nitrogen bond, while reaction of bis(pentane-2,4-dionato)oxovanadium(IV) with the related ligands 1,2-bis(2-hydroxybenzamido)benzene ( $\text{H}_4\text{hybeb}$ ) and 1-(2-hydroxybenzamido)-2-(2-pyridinecarboxamido)benzene ( $\text{H}_3\text{hypyb}$ ) yields the complexes  $\text{Na}_2[\text{V}^{\text{IV}}\text{O}(\text{hybeb})]$  **2** and  $\text{Na}[\text{V}^{\text{IV}}\text{O}(\text{hypyb})]$  **3** respectively; the X-ray crystal structures of **1** and **3** are reported.

Vanadium is a trace element in biological systems,<sup>1</sup> but our understanding of its biochemical role is still in its infancy.<sup>1</sup> In order to elucidate how vanadium might function in a complex biomolecule, it is first necessary to develop its basic coordination chemistry with biologically relevant ligands.

Interactions of vanadium with proteins may provide the key to our understanding of its biological role. Vanadium can potentially interact with amino ( $-\text{NH}_2$ ), carboxy ( $-\text{CO}_2^-$ ) and ligating atoms (N, O, S) of polar side chains, in addition to the peptide functionality on the surface of the protein. Little is known yet about the ligation of the deprotonated amide (peptide) group to vanadium.<sup>2–4</sup> Herein we report the first

structural characterization of such a vanadium(III) complex and also the preparation and characterization of rare examples of oxovanadium(IV)<sup>4</sup> and oxovanadium(V) species with deprotonated diamide polyanionic chelating ligands, as part of our programme for the preparation and characterization of vanadium compounds with amino acids and small oligopeptides (or peptide analogues).<sup>3</sup>

The ligand Hcapca was synthesized by condensing *N*-(2-aminophenyl)pyridine-2-carboxamide and pyridine-2-carbaldehyde under argon, while the ligand  $\text{H}_3\text{hypyb}$  was prepared by the route in Scheme 1. Refluxing a mixture of vanadium(III) chloride (1.90 mmol), Hcapca (1.92 mmol) and triethylamine (4.00 mmol) in dry toluene, under argon, for two days, yielded the mononuclear brown complex **1** [eqn. (1)]; yield 60%. Complex **2** was synthesized by refluxing a solution containing bis(pentane-2,4-dionato)oxovanadium(IV) (4.00 mmol), sodium hydroxide (8.00 mmol) and the ligand  $\text{H}_4\text{hybeb}$  in dry methanol, under argon, for three hours [eqn. (2)]; yield 77%. Complex **3** was prepared in a similar fashion to **2** and was obtained in 42% yield. Oxidation of **2** in MeCN with  $\text{AgClO}_4$  gave complex **4** [eqn. (3)]; yield 63%. Efforts to prepare the complex  $[\text{V}^{\text{VO}}(\text{hypyb})]$  have so far proved unsuccessful. Crystals of the complexes **1** and **3** suitable for X-ray structure analysis<sup>†</sup> were obtained by either cooling a hot concentrated solution of **1** in acetonitrile or by diffusion of diethyl ether into acetonitrile solution of **3**.

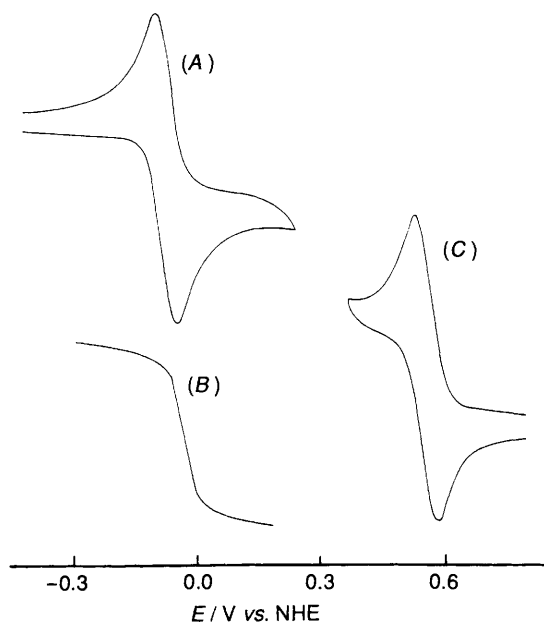


**Scheme 1** Synthesis of the ligand  $\text{H}_3\text{hypyb}$ . Conditions: i, dioxane, argon; ii, dioxane, aqueous  $\text{HCl}$  (15%).

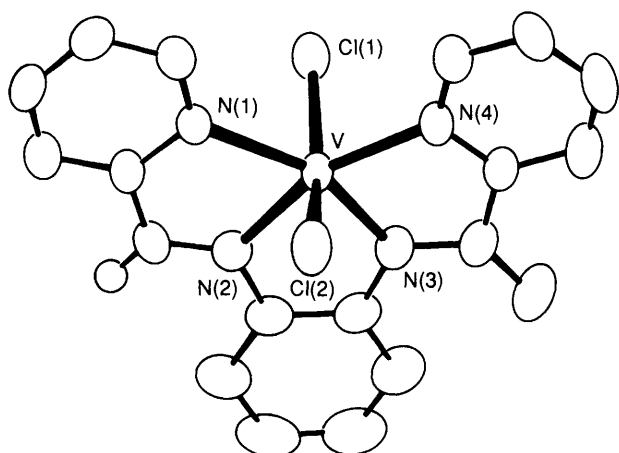
<sup>†</sup> Crystal data: **1**,  $\text{C}_{18}\text{H}_{13}\text{Cl}_2\text{N}_4\text{OV}$ ,  $M = 423.2$ , monoclinic, space group  $P2_1/m$ ,  $a = 10.599(1)$ ,  $b = 13.998(1)$ ,  $c = 14.402(1)$  Å,  $\beta = 98.65(1)^\circ$ ,  $U = 2112.5(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.32$ ,  $D_c = 1.330$  g cm<sup>-3</sup>, crystal dimensions  $0.11 \times 0.16 \times 0.40$  mm,  $\mu = 7.17$  cm<sup>-1</sup>, 4547 data collected, 4138 data unique, data used, 3063 with  $F_o \geq 5\sigma(F_o)$ ,  $\psi$ -scan absorption correction;  $F(000) = 856$  318 parameters,  $R(R_w) = 0.0323(0.0335)$  for 'observed' data, 0.0508(0.0467) for all data. Data collected on a Syntex  $P2_1$  four-circle diffractometer upgraded by Crystal Logic using Zr-filtered Mo radiation. The structure was solved by direct methods and refined anisotropically.

**2**,  $\text{C}_{10}\text{H}_2\text{N}_3\text{O}_4\text{NaV} \cdot \text{CH}_3\text{CN}$ ,  $M = 461.32$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.528(1)$ ,  $b = 11.210(1)$ ,  $c = 16.512(2)$  Å,  $\beta = 103.93(4)^\circ$ ,  $U = 2070.9(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.47$ ,  $D_c = 1.479$  g cm<sup>-3</sup>,  $\mu = 5.51$  cm<sup>-1</sup>, 2377 data collected, 2135 data unique, data used, 1774 with  $F_o \geq 3\sigma(F_o)$ ,  $\psi$ -scan absorption correction;  $F(000) = 940$  268 parameters,  $R(R_w) = 0.0649(0.0806)$  for 'observed' data, 0.0783(0.0828) for all data. The high final R values are a consequence of the small crystal size ( $0.04 \times 0.06 \times 0.17$  mm) and its poor quality. Data were measured as above and refined anisotropically.

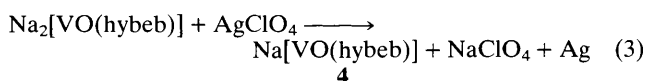
Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



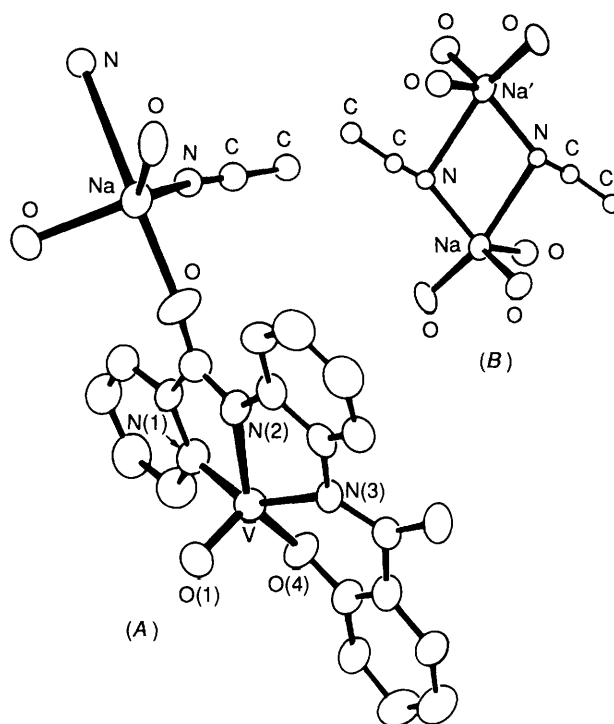
**Fig. 1** (A) DC cyclic voltammogram of  $\text{Na}_2[\text{VO}(\text{hybeb})]$  in MeCN with tetraethylammonium perchlorate ( $0.1 \text{ mol dm}^{-3}$ ) at a platinum electrode and a scan rate of  $100 \text{ mV s}^{-1}$ . (B) DC polarogram of the same solution as in A at a dropping mercury electrode. (C) DC cyclic voltammogram of  $\text{Na}[\text{VO}(\text{hybyb})]$  (conditions the same as in A).



**Fig. 2** ORTEP drawing of  $\text{trans}[\text{VCl}_2(\text{capca})]$  with 50% probability ellipsoids, giving atomic numbering. For clarity, hydrogen atoms are omitted. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): V-Cl(1) 2.340(1), V-Cl(2) 2.313(1), V-N(1) 2.175(2), V-N(2) 2.058(2), V-N(3) 1.982(2), V-N(4) 2.124(2); Cl(1)-V-Cl(2) 159.8, Cl(1)-V-N(1) 83.8, Cl(1)-V-N(2) 97.5, Cl(1)-V-N(3) 100.1(1), Cl(1)-V-N(4) 88.4(1), Cl(2)-V-N(1) 83.0(1), Cl(2)-V-N(2) 93.9(1), Cl(2)-V-N(3) 98.3(1), Cl(2)-V-N(4) 87.1(1), N(1)-V-N(3) 155.3(1), N(1)-V-N(2) 75.9(1), N(1)-V-N(4) 125.6(1), N(2)-V-N(4) 158.3(1), N(2)-V-N(3) 79.4(1), N(3)-V-N(4) 79.0(1).

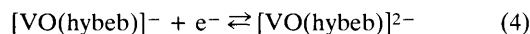


Complexes **1**, **2** and **3** are indefinitely stable in air in the solid state, but decompose in solution (especially **2** and **3**) in the presence of air. In contrast complex **4** is unstable in air even in the solid state. The decomposition products of all the complexes are under further investigation. The compounds were characterized by IR spectroscopy, cyclic voltammetry and polarography. Further characterization by magnetochemistry, EPR, UV-VIS and  $^{51}\text{V}$  NMR spectroscopy is underway.



**Fig. 3** (A) ORTEP drawing of  $\text{Na}[\text{VO}(\text{hybyb})] \cdot \text{CH}_3\text{CN}$  at 50% probability ellipsoids giving atomic numbering. For clarity, hydrogen atoms are omitted. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): V-O(1) 1.595(4), V-N(1) 2.107(5), V-N(2) 2.001(5), V-N(3) 2.016(5), V-O(4) 1.887(4), Na-O(2) 2.230(5); O(4)-V-O(1) 110.9(2), N(1)-V-O(1) 105.8(2), N(1)-V-O(4) 88.1(2), N(2)-V-O(1) 112.1(2), N(2)-V-O(4) 136.8(2), N(2)-V-N(1) 76.9(2), N(3)-V-O(1) 106.9(2), N(3)-V-O(4) 91.8(2), N(3)-V-N(1) 145.0(2), N(3)-V-N(2) 79.5(2). (B) Coordination environment of the sodium atom.

The redox properties of the complexes **2** and **3** in acetonitrile have been investigated by DC cyclic voltammetric and DC polarographic techniques (Fig. 1); both complexes display a reversible one-electron redox process [eqn. (4)] at  $-0.07$  and  $+0.56 \text{ V}$  (vs. NHE, normal hydrogen electrode) respectively. Cyclic voltammetry of **1** reveals a cathodic peak at  $-0.61 \text{ V}$  and an anodic peak at  $+1.04 \text{ V}$  vs. NHE. The cathodic peak may be assigned to reduction of  $\text{V}^{\text{III}}$  to  $\text{V}^{\text{II}}$  and the anodic peak to the oxidation of the chlorine ligand.



As shown in Fig. 2, the structure of the complex  $\text{trans}[\text{VCl}_2(\text{capca})]$  exhibits distorted octahedral coordination at the vanadium centre. The two chlorine atoms are *trans* and the angle Cl(1)-V-Cl(2) is bisected by the plane defined by the four nitrogen atoms of the ligand. Of the four V-N bonds, the bond to N(3), the deprotonated amide nitrogen, constitutes the shortest V-N distance [ $1.982(2) \text{ \AA}$ ] so far reported for octahedral vanadium(III) complexes. This is in agreement with the fact that the deprotonated amide nitrogen is a very strong  $\sigma$ -donor. The bond lengths to N(1) [ $2.175(2) \text{ \AA}$ ] and N(4) [ $2.124(2) \text{ \AA}$ ], the pyridine nitrogens, are substantially longer than the V-N(3) bond distance and different from each other as a consequence of the difference in the *trans* atoms [N(3) and N(2), respectively]. The bond length to N(2) [ $2.058(2) \text{ \AA}$ ], the imine nitrogen, agrees with other V-N bond distances reported for  $\text{V}^{\text{III}}$ -Schiff base complexes.<sup>5</sup> The V-Cl bond lengths [V-Cl(1)  $2.430(1)$  and V-Cl(2)  $2.313(1) \text{ \AA}$ ] are in the range expected for  $\text{V}^{\text{III}}$  complexes<sup>6</sup> and different from each other as a result of a hydrogen bond between H(6) and Cl(1) [C(6)-H(6)  $0.91(3) \text{ \AA}$ , H(6)⋯Cl(1)  $2.85(3) \text{ \AA}$  and C(6)-H(6)⋯Cl(1)  $153(2)^\circ$ ].

Fig. 3(A) shows a perspective view of **3**. The vanadium is in a distorted square pyramidal environment consisting of two deprotonated amide nitrogens, a pyridine nitrogen and a phenolate oxygen in the basal plane and an oxo ligand occupying the apical position. The vanadium atom is 0.642 Å above the mean plane defined by the basal atoms. The average V–N(2/3) bond distance of 2.009 Å is indicative of a strong bond of the deprotonated amide nitrogen to vanadium and is slightly longer than in the {*N*-[2-(4-oxopent-2-en-2-ylamino)phenyl]pyridine-2-carboxamido}oxovanadium(IV) [1.974(2) Å].<sup>3b</sup> The bond to O(4), the phenolate oxygen, constitutes the shortest V–O distance [1.887(4) Å] so far reported for oxovanadium(IV)<sup>3b</sup> species. The coordination environment of the sodium atom approximates to a trigonal bipyramid and the ligating atoms are two symmetry-related bridging [Fig. 3(B)] nitrogens (from acetonitrile solvent) and three oxygens, two amide ones and an oxo group, each one from a different anionic vanadium complex.

In summary, we have shown that vanadium(III) and oxovanadium(IV/V) interact with deprotonated amide groups and give compounds which are stable in the solid state

[vanadium(III) and oxovanadium(IV)] but unstable in solution in the presence of air; in particular the oxovanadium(V) species is unstable in air even in the solid state.

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