Novel vanadium(iii/iv) compounds with the diamidate ligand 1,2-bis(2-pyridinecarboxamide)benzene (H_2bpb)

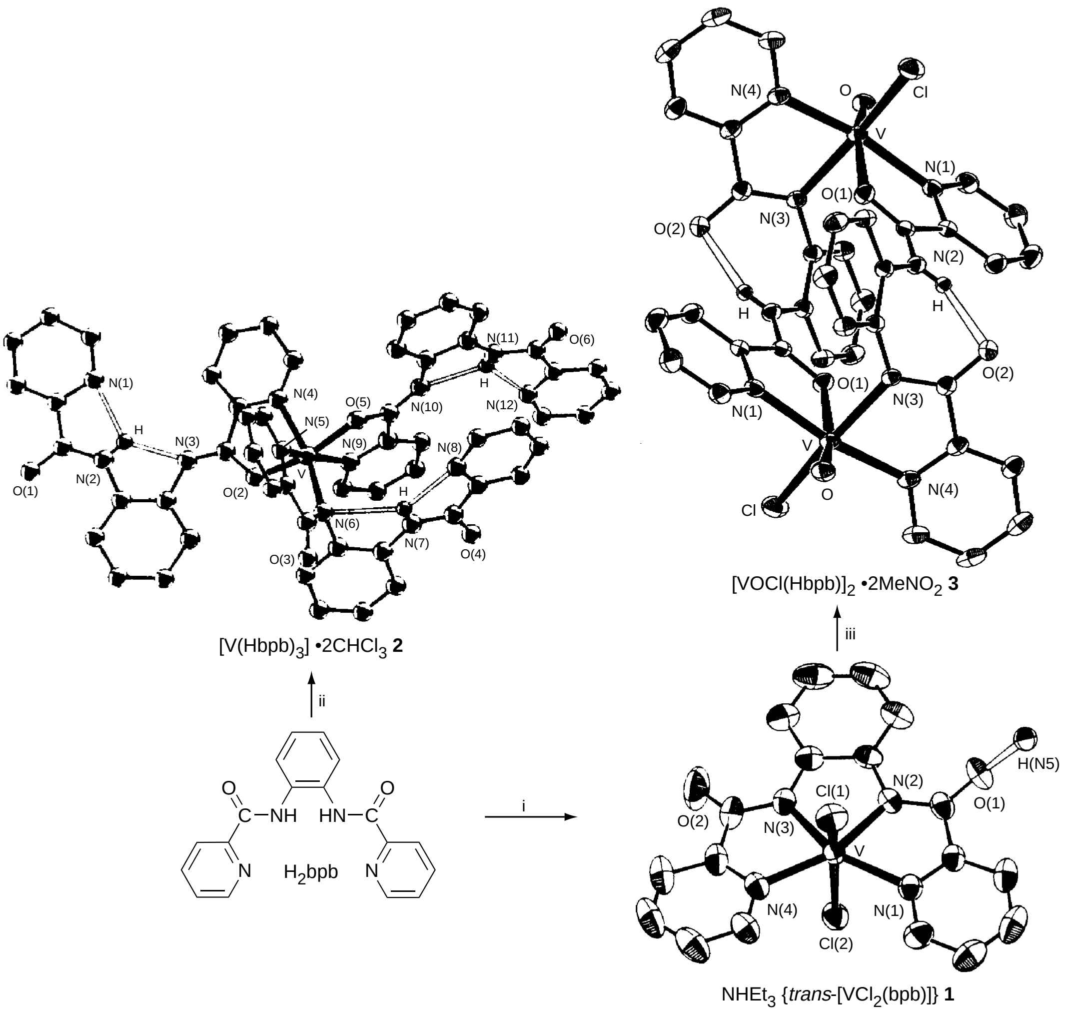
Antonis T. Vlahos,[a] Themistoklis A. Kabanos,*[a] Catherine P. Raptopoulou[b] and Aris Terzis[b]

[a] *Department of Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45 110 Ioannina, Greece*
[b] *NRPCS Demokritos, Institute of Materials Science, 15 310 Agia Paraskevi Attikis, Greece*

Reaction of the diamidate ligand H_2bpb with VCl_3 depending on the base affords either the compound $NHEt_3${*trans*-[$V^{III}Cl_2$(bpb)]} 1 or [$V^{III}(Hbpb)_3$]·$2CHCl_3$ 2; aerial oxidation–hydrolysis of 1 gives the dimeric species [VOCl(Hbpb)]$_2$·$2MeNO_2$ 3; the X-ray crystal structures of 1, 2 and 3 are reported.

Vanadium is a bioessential element,[1] but its role in biological systems is not yet well understood. The synthesis as well as the structural and spectroscopic characterization of low molecular mass model complexes of the biologically important oxidation states (+II to +V) of vanadium will help in making further progress in the elucidation of the biological role of vanadium.

Currently our group[2a] in parallel with others[2b] have embarked on a study of the interaction of vanadium with the amide(peptide) functionality, –NHCO–, which is a potential metal-ion binding site in biomolecules. Herein we wish to report the synthesis and structural characterization of vanadium(iii) and oxovanadium(iv) compounds, $NHEt_3${*trans*[$V^{III}Cl_2$(bpb)]} **1**, [$V^{III}(Hbpb)_3$]·$2CHCl_3$ **2** and [V^{IV}OCl(Hbpb)]$_2$·$2MeNO_2$ **3** (Scheme 1). The structure of **1** is the first example of a vanadium(iii) centre that is bound by two deprotonated amidate nitrogens, while the structures of **2** and **3** are the first examples of vanadium(iii/iv) centres with simultaneous ligation of a deprotonated amide nitrogen and of an amide oxygen from two different amide functionalities.



Scheme 1 Synthesis and X-ray crystal structures of complexes **1**, **2** and **3**. *Conditions*: i, VCl_3, NEt_3, toluene; ii, VCl_3, NH_3, toluene; iii, CH_3NO_2, air. Selected interatomic distances (Å): for **1**, V–N(3) 1.996(2), V–N(2) 2.016(2), V–N(4) 2.136(2), V–N(1) 2.141(2), V–Cl(1) 2.350(1), V–Cl(2) 2.357(1). For **2**, V–O(5) 1.936(3), V–O(2) 1.974(3), V–N(6) 2.011(4), V–N(9) 2.114(4), V–N(5) 2.118(4), V–N(4) 2.186(4). For **3**, V–Cl 2.355(1), V–O 1.587(2), V–N(3) 2.086(2), V–N(4) 2.115(2), V–N(1) 2.145(2), V–O(1) 2.217(2).

Refluxing a mixture of vanadium(III) chloride (1.30 mmol), H_2bpb (1.30 mmol) and triethylamine (6.50 mmol) in dry toluene under argon for 14 h yielded the mononuclear brick red complex **1** and $NHEt_3Cl$ [eqn. (1)].

$$VCl_3 + H_2bpb + 2NEt_3 \rightarrow \underbrace{NHEt_3\{trans[VCl_2(bpb)]\}}_{\mathbf{1}} + NHEt_3Cl \quad (1)$$

By layering diethyl ether into a chloroform solution of **1** and $NHEt_3Cl$ brick-red crystals of complex **1** (yield 20%) suitable for X-ray structure analysis† were obtained. Because the solubilities of complex **1** and $NHEt_3Cl$ were almost identical in various organic solvents **1** could not be separated from $NHEt_3Cl$ and so gaseous ammonia (bubbling) was substituted for triethylamine whereupon crystals of **2** were obtained in a very low yield (5%) (this is under further investigation). When a nitromethane solution of **1** was exposed to the atmosphere the dimeric species **3** is formed as green crystals (yield 80%).

As shown in Scheme 1, the structure of complex **1** 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 bpb^{2-}. The mean $V–N_{amide}$ bond length [2.006(2) Å] is slightly longer (0.024 Å) than the only other known vanadium(III)–amidate distance[2a] and this might be due to the stronger, dianionic ligand set in complex **1**, which results in a lower effective charge on the vanadium(III) centre and therefore longer V–N distances. The bond lengths to N(1) [2.141(2) Å] and N(4) [2.136(2) Å] the pyridine nitrogens lie at the lower limit of $V–N_{py}$ distances seen in the literature.[2a,3] The V–Cl bond lengths [V–Cl(1) 2.350(1), V–Cl(2) 2.357(1) Å] are in the range expected for vanadium(III) complexes.[2a,4] Comparison of the structure of complex **1** described herein with its iron analogue,[5] *i.e.* $NHEt_3\{trans\text{-}[FeCl_2(bpb)]\}\cdot MeCN$, reveals a close similarity, except that there is a small reduction in the average V–N bond length (*ca.* 0.04 Å) [V–N (av.) 2.07(8), Fe–N (av.) 2.11(1) Å] that results in a slight increase of the *cis*-bite angles of the vanadium complex.

The structure of complex **3** (Scheme 1) consists of discrete dimers. The vanadium(IV) centres are related by a centre of symmetry. In this dimeric species, each vanadium has a distorted octahedral environment and is bonded to two pyridine nitrogens, one amidic oxygen, one amidic nitrogen (from two bridging μ_2-η^4-$Hbpb^-$ ligands), to a chlorine atom and to an oxo group. The ligated pyridine nitrogens are *trans* to each other and the amidic oxygen is *trans* to the oxo ligand. The V=O and the V–Cl (the chlorine atom is *cis* to the oxo group) bond lengths of 1.587(2) A and 2.355(1) Å, respectively, are in good agreement with those reported in the literature for octahedral oxovanadium(IV) compounds.[6,7] The $V–O_{amide}$ bond distance [2.217(2) Å] is almost identical with the only other known vanadium(IV)–amidate O distance[6] [2.206(1) Å], while the $V–N_{amide}$ bond [2.086(2) Å] is substantially longer (*ca.* 0.09 Å) than the mean $V–N_{amide}$ distance [2.00(1) Å] for various oxovanadium(IV)–amidate compounds,[2] and this might be due to the substantial deviation from planarity of the bridging ligand $Hbpb^-$. Compound **3**, unlike the double-helical complexes of Constable *et al.*,[8] resembles instead the non-helical dimer of Williams and coworkers.[9]

While the formation of **1** is straightforward, the reasons for the preferential formation of **2** when ammonia is substituted for triethylamine are not at all clear. The vanadium atom in **2** is coordinated to three singly deprotonated chelated rings (η^2-$Hbpb^-$) in a distorted octahedral coordination, environment with two different modes of coordination, *i.e.* N_{py},O_{am} (two chelate rings) and N_{py},N_{am} (one chelate ring). One might expect a tris-chelate vanadium(III) complex through pyridine and deprotonated amide nitrogen atoms, since the deprotonated amides normally coordinate *via* N.[10] To this general trend there are only two other exceptions.[11,12] Steric hindrance, or strong preference of the vanadium(III) centre for oxygen ligation might be an explanation for amidate-O ligation and not deprotonated amidate-N ligation in two chelate rings of **2** (theoretical calculations are under way).

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Footnotes

† *Crystal data*: for **1**, $C_{24}H_{28}Cl_2N_5O_2V$, M = 540.37, monoclinic, space group $P2_1/n$, a = 10.501(1), b = 20.958(3), c = 11.781(2) Å, β = 90.340(4)°, U = 2592.7(6) Å^3, Z = 4, $D_c(D_m)$ = 1.384(1.36) g cm^{-3}, T = 298 K, no. of unique reflections = 5086, no. of parameters 372, $R1$ = 0.0359, $wR2$ = 0.0935 with $I > 2\sigma(I)$.

For **2**, $C_{56}H_{41}Cl_6N_{12}O_6V$, M = 1241.65, monoclinic, space group $P2_1/c$, a = 16.380(2), b = 26.182(3), c = 14.573(1) Å, β = 113.568(3)°, U = 5728.6(10) Å^3, Z = 4, $D_c(D_m)$ = 1.440(1.42) g cm^{-3}, T = 293 K, no. of unique reflections = 7313, no. of parameters = 840, $R1$ = 0.0461, $wR2$ = 0.1076 with $I > 2\sigma(I)$.

For **3**, $C_{38}H_{32}Cl_2N_{10}V_2$, M = 961.63, triclinic, space group $P\bar{1}$, a = 12.672(3), b = 10.961(2), c = 8.950(2) Å, α = 112.069(6), β = 99.993(8), γ = 109.705(8)°, U = 1018.35 Å^3, Z = 1, $D_c(D_m)$ = 1.567(1.55) g cm^{-3}, T = 296 K, no. of unique reflections = 3890, no. of parameters = 333, $R(R_w)$ = 0.0362(0.0377) with $F > 6\sigma(F)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/341.

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