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Vanadium(V) complexes based on a bis(pyridine)-imine ligand (HL); synthesis and crystal structure of a dioxovanadium(V) complex involving a ligand cyclisation

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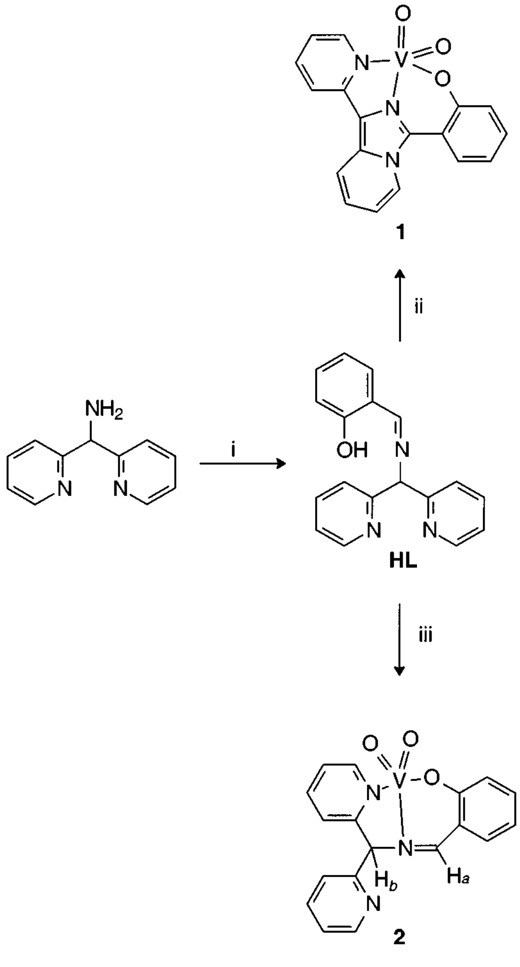
Synthesis and characterisation of two novel dioxovanadium(V) complexes based on (2-hydroxybenzylidene)di(2-pyridin-2-yl)methylamine (HL) and 3-(2-hydroxyphenyl)-1-pyridin-2-yl-imidazo-[1,5-*a*]-pyridine (HL′), which is the result of a vanadium-mediated oxidative cyclisation of HL, are reported.

The notion that vanadium plays an important role in various biological systems has invoked great interest in the coordination chemistry of vanadium.[1] Vanadium(V) complexes have been found to act as catalysts in oxidation reactions of various substrates using peroxides.[2] The catalytic oxidation by Schiff-base complexes of vanadium with dioxygen has also been reported.[3] During our investigation on the catalytic properties of V(V) complexes, we synthesised novel dipyridylmethyl amine Schiff base dioxovanadium(V) complexes and found a vanadium-mediated oxidative cyclisation.[4] In the course of this work, a related iron mediated oxidative cyclisation of a polypyridine ligand has been published by Meunier *et al.*[5] However, in our case the obtained cyclised product was not released from the metal, but remained coordinated resulting in a stable dioxovanadium(V) complex which was completely characterised by X-ray analysis, ES-MS spectrometry, ^{1}H and ^{51}V NMR, UV-Vis and IR measurements. (2-Hydroxybenzylidene)di(2-pyridin-2-yl)methylamine (HL) was prepared starting from dipyridin-2-yl-methylamine[6] and salicylaldehyde (Scheme 1) in 93% yield.

Complexation of HL with triisopropoxyvanadium(V) oxide [VO(O^{i}Pr)$_3$] in MeOH under reflux afforded complex **1** in 39% yield.[7] Yellow crystals suitable for X-ray analysis were obtained by evaporation of a MeOH–EtOH solution (1:1) of **1**.‡ An ORTEP plot is shown in Fig. 1. Complex **1** contains a dioxovanadium(V) moiety. The vanadium center is pentacoordinated by two nitrogen atoms [2.173(3) and 2.090(3) Å with a bond angle between N(1)–V(1)–N(3) of 72.87(12)°], one oxygen atom of the deprotonated phenolic moiety [1.888(3) Å and a bond angle between N(1)–V(1)–O(1) of 81.44°] and two oxo groups [1.610(4), 1.632(4) Å]. The V=O distances are nearly equal and typical for dioxovanadium(V) complexes in which the oxygens are not involved in hydrogen bonding.[8] The bond angle between the oxo groups and the vanadium center is 109.02(16)°.

We assumed that initially, upon addition of VO(O^{i}Pr)$_3$ to a solution of L in MeOH, complex **2** is formed. In fact, vanadium(V) complex **2** of the uncyclised Schiff base ligand can be obtained in 60% yield when the reaction of L with VO(O^{i}Pr)$_3$ is performed in EtOH at 0 °C under an atmosphere of argon. Unfortunately, no crystals suitable for X-ray analysis were obtained.



Scheme 1 Synthesis of HL and complexes **1** and **2**. *Reagents and conditions*: (i) salicylaldehyde, rt, MeOH, 93%; (ii) VO(O^{i}Pr)$_3$, MeOH, reflux, air, 5 min, 39%; (iii) VO(O^{i}Pr)$_3$, EtOH, 0 °C, argon, 2 h, 60%.

The UV spectrum of **2** in acetonitrile exhibits three bands at 212 nm ($\varepsilon = 1.89 \times 10^4$ M^{-1} cm^{-1}), 266 (1.23) and 384 (0.23). The spectrum resembles the one recorded in acetonitrile of HL [213 nm ($\varepsilon = 2.43 \times 10^4$ M^{-1} cm^{-1}), 262 (1.95) and 319 (0.45)]. The UV spectrum of **1** in acetonitrile, however, exhibits four bands at 212 nm ($\varepsilon = 0.89 \times 10^4$ M^{-1} cm^{-1}), 304 (0.25), 343 (0.36) and 417 (0.24). The distinction between complexes **1** and **2** was further corroborated using electron spray ionisation mass spectrometry (ES-MS), UV-Vis, IR, ^{1}H and ^{51}V NMR measurements. ES-MS spectra for **1** in acetonitrile show peaks at *m*/*z* 369.8 and 739.3 which can be attributed to

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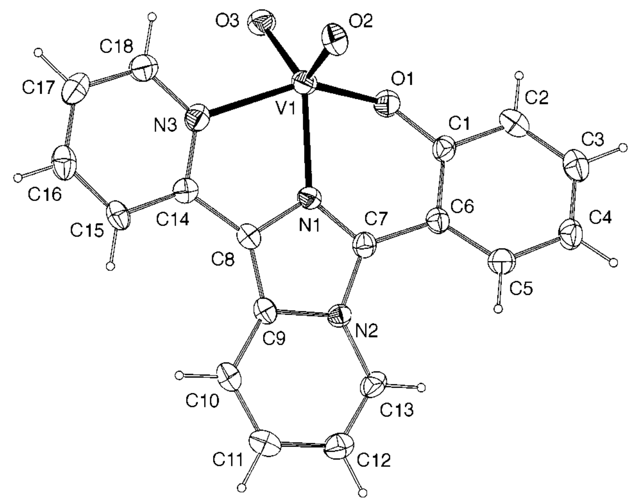
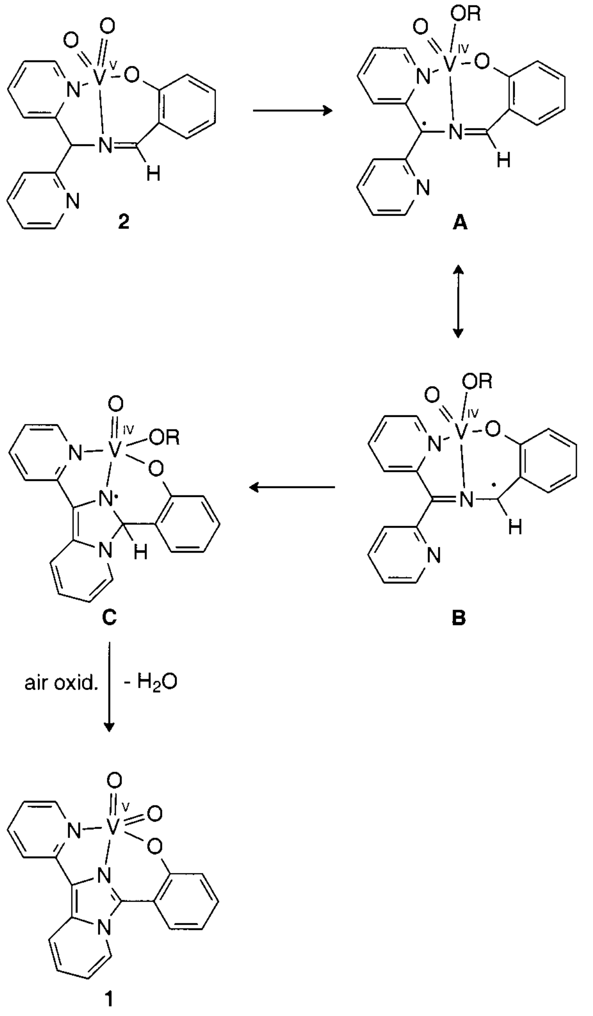


Fig. 1 An ORTEP plot of complex **1** (50% probability level).

{VO_2L' + 1H} and {$2VO_2L'$ + 1H}, respectively. In addition, electron ionisation mass spectrometry (EI-MS) measurements show, besides the parent peak at *m*/*z* 369, a peak at *m*/*z* 287 which corresponds to the mass of free HL′. In the ES-MS spectrum of **2** in acetonitrile peaks were observed at *m*/*z* 372.0 {VO_2L + H} and 743.4 {$2VO_2L$ + H}. Also the ^1H NMR spectra of complexes **1** and **2** clearly indicate the difference between the two ligand systems.§ Complex **1** lacks two protons compared with **2**, *i.e.* the characteristic imine hydrogen signal (H_a, Scheme 1) has disappeared as well as the signal for the double benzylic proton (H_b). ^{51}V NMR spectra of these two complexes, however, are very similar. Complex **1** dissolved in DMSO-d_6 has a single resonance at −543 ppm (band width, b.w. = 1303 Hz), whereas **2** shows a single resonance at −540 ppm (b.w. = 965 Hz). This is a strong indication that the coordination sphere around the vanadium(V) center is quite similar in both structures.[9] In the case of **2**, the vanadium ion is surrounded by one pyridine nitrogen, the imine nitrogen, the deprotonated phenolic oxygen and two oxo groups as depicted in Scheme 1. As a result, the second pyridine entity is non-coordinating. Heating of a solution of **2** in MeOH results in the formation of **1** as was also shown by ^1H NMR measurements. Infrared spectra reveal two V=O absorptions for both complexes, at 926 and 949 cm^{-1} for **1** and at 918 and 953 cm^{-1} for **2**, respectively. These observations correspond to the data known from the literature that stretching frequencies of V=O bonds with a length of 1.607–1.621 Å are found in the 930–960 cm^{-1} region.[10] The relatively low position of the V=O stretching band may indicate the existence of intermolecular interactions *via* O bridges, but no evidence for such interactions was found in the crystal structure.

The oxidative cyclisation of the coordinated Schiff base ligand L leads to the formation of an imidazo[1,5-*a*]pyridine[11] type of ligand (L′). Some imines of di(2-pyridyl)methylamine are known to cyclise spontaneously to imidazo[1,5-*a*]pyridines by air oxidation.[12] However, HL itself remained intact even after refluxing in MeOH solution in the air for 3 h. Therefore, the vanadium(V) ion is likely to play an active role in the cyclisation process. Based on these results, a reaction mechanism is proposed for the ligand cyclisation reaction resulting in the formation of **1** starting from **2** (Scheme 2).[13] First the Schiff base ligand is oxidised by vanadium(V) giving a vanadium(IV) species containing one oxo ligand and one hydroxy group (**A** and **B**). The radical in resonance structure **B** then attacks the non-coordinating pyridine nitrogen resulting in the formation of **C**, which is subsequently oxidised by air to form **1**. The involvement of a vanadium(IV) species is supported by results of EPR experiments with crude **1**. An EPR signal was observed (g = 1.97) which was attributed to a vanadium(IV) species by comparison with literature data.[14]

In conclusion, Schiff base ligand HL is found to be effective in the formation of a dioxovanadium(V) complex. However when HL is heated in the presence of vanadium(V), imidazopyridine type ligand L′ is formed due to an oxidative cyclisation reaction. Catalytic oxidation experiments with these complexes are in progress.



Scheme 2 Proposed mechanism for the formation of complex **1** (R = H, CH_3).

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Notes and references

‡ *Crystal data for* **1**: $C_{18}H_{12}N_3O_3V$, M_r = 369.25, yellow needle (0.10 × 0.12 × 0.43 mm), monoclinic, space group $P2_1/c$ (no. 14) with a = 7.0787(16), b = 16.833(5), c = 13.573(5) Å, β = 115.21(2)°, V = 1463.3(8) $Å^3$, Z = 4, D_c = 1.676 g cm^{-3}, $F(000)$ = 752, μ(Mo-Kα) = 7.0 cm^{-1}, 6346 reflections measured, 3006 independent, R(int) = 0.106, θ_{max} = 26.5°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromated, λ = 0.71073 Å, Enraf-Nonius CAD4T on rotating anode. Data were corrected for absorption (PLATON/DELABS). The structure was solved by direct methods (SHELXS86) and refined on F^2 using SHELXL97. Hydrogen atoms were taken into account at calculated positions. Convergence was reached at R = 0.0579 for 1984 reflections with $I > 2\sigma(I)$ and 226 parameters.

CCDC reference number 186/1318. See http://www.rsc.org/suppdata/dt/1999/659 for crystallographic files in .cif format.

§ ^1H NMR (300 MHz, DMSO-d_6) for **1**: δ 9.24 (m, 1H), 9.05 (m, 1H), 8.49 (m, 2H), 8.28 (m, 2H), 7.54 (m, 3H), 7.27 (m, 1H), 7.09 (m, 2H); and for **2**: 9.22 (s, 1H), 8.86 (s, 2H), 8.06 (m, 2H), 7.70 (m, 3H), 7.57 (m, 3H), 6.93 (m, 3H).

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