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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 dipyridylmethylamine 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, ¹H and ⁵¹V NMR, UV-Vis and IR measurements. (2-Hydroxybenzylidene)di(2-pyridin-2-yl)methylamine (HL) was prepared starting from dipyridin-2-yl-methylamine⁶ and salicylaldehyde (Scheme 1) in 93% yield.

Complexation of HL with triisopropoxyvanadium(v) oxide [VO(OⁱPr)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(OⁱPr)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(OⁱPr)₃ is performed in EtOH at 0 °C under an atmosphere of argon. Unfortunately, no crystals suitable for X-ray analysis were obtained.

The UV spectrum of **2** in acetonitrile exhibits three bands at

Scheme 1 Synthesis of HL and complexes **1** and **2**. Reagents and conditions: (i) salicylaldehyde, rt, MeOH, 93%; (ii) VO(OⁱPr)₃, MeOH, reflux, air, 5 min, 39%; (iii) VO(OⁱPr)₃, EtOH, 0 °C, argon, 2 h, 60%.

212 nm ($\epsilon = 1.89 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 266 (1.23) and 384 (0.23). The spectrum resembles the one recorded in acetonitrile of HL [213 nm ($\epsilon = 2.43 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 262 (1.95) and 319 (0.45)]. The UV spectrum of **1** in acetonitrile, however, exhibits four bands at 212 nm ($\epsilon = 0.89 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 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, ¹H and ⁵¹V NMR measurements. ES-MS spectra for **1** in acetonitrile show peaks at *m/z* 369.8 and 739.3 which can be attributed to

[†] Address correspondence concerning crystallography to this author.

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

{VO₂L' + 1H} and {2VO₂L' + 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 {VO₂L + H} and 743.4 {2VO₂L + 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). ⁵¹V 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*]pyridine¹¹ 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), imidazo-

Scheme 2 Proposed mechanism for the formation of complex **1** (R = H, CH₃).

pyridine type ligand L' is formed due to an oxidative cyclisation reaction. Catalytic oxidation experiments with these complexes are in progress.

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Notes and references

‡ Crystal data for **1**: C₁₈H₁₂N₃O₃V, *M_r* = 369.25, yellow needle (0.10 × 0.12 × 0.43 mm), monoclinic, space group *P*₂₁/*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) Å³, *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* > 2σ(*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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