Molecular structure of [VO(sal-D,L-Asn)(py)(H_2O)] and reaction to produce coumarin-3-carboxamide

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The reaction of VO^{2+} with salicylaldehyde, asparagine and pyridine forms [VO(sal-D,L-Asn)(py)(H_2O)] 1; coumarine-3-carboxamide 2 is produced from the same system on ageing with di-oxygen. Both compounds are characterized by X-ray diffraction.

Complexes of metal ions with *N*-salicylideneamino acids serve as model systems for pyridoxal-potentiated enzymes.[1] Recently, several studies[2–4] have focused on vanadium in this context. Remarkably fast decarboxylation reactions of Cu^{III} tripeptide complexes[5] with terminal histidine residues, dioxygen-induced decarboxylations (and hydroxylations) activated by Ni^{II}[6] and stereoselective decarboxylations activated by Co^{III} centres[7] are known. We describe here the preparation and characterization by X-ray diffraction† of [VO(sal-D,L-Asn)(py)(H_2O)] **1** (sal-D,L-Asn = *N*-salicylidene-D,L-asparaginate) with a molecular structure as shown in Fig. 1. From these preparative solutions containing VO^{2+}, salicylaldehyde, D,L-asparagine and pyridine in H_2O/methanol, needle crystals of coumarin-3-carboxamide **2** were isolated and characterized by X-ray,† mass spectra and FTIR of individual microcrystals.‡ A mechanism involving an oxidative decarboxylation (possibly catalysed by vanadium) is discussed.

Aqueous $VOSO_4$ was slowly added to a stirred solution of salicylaldehyde and D,L-asparagine in H_2O/methanol. After 2 h, pyridine and $N(Me)_4NO_3$ were added. An aqueous solution of $N(Me)_4NO_3$ was slowly diffused into the mixture, in contact with air. One day later red–orange needle crystals of **1** were separated. After approximately one month, coumarin-3-carboxamide **2** formed as white needle crystals in the mother liquor. In similar experiments under an N_2 atmosphere or in the absence of vanadium **2** did not form.

The FTIR of **2** presents bands which agree with those reported.[8] The mass spectrum shows a fragmentation pattern that agrees with the process proposed for coumarin-3-carboxamides.[9]

The X-band EPR spectrum of a powdered frozen sample of **1** gave a broad signal centred at g = 1.978, typical of solid oxovanadium(IV) complexes. The EPR spectrum at 77 K of **1** dissolved in pyridine gave the spin-Hamiltonian parameters[10,11] $A_{\|} = 164 \times 10^{-4}$ cm^{-1}; $g_{\|} = 1.953$; $A_{\perp} = 59.3 \times 10^{-4}$ cm^{-1}; $g_{\perp} = 1.981$. Assuming that the structure of **1** is preserved in solution one can estimate[11] $A_{\|} = 164.8 \times 10^{-4}$ cm^{-1} if the contribution of the imine nitrogen is assumed to be[3] $\cong 170 \times 10^{-4}$ cm^{-1}. The magnetic susceptibility (χ_p) of **1** was measured as a function of temperature and the results can be fitted to $\chi = C/(T - \theta) + A$, a Curie–Weiss law, where $A = 5.39 \times 10^{-4}$ emu mol^{-1}: the Weiss constant θ is close to zero and μ_{eff} = 2.04 BM at 292.6 K.

Complex **1** exhibits essentially octahedral geometry, formed in the equatorial plane by the O, N, O, atoms of the Schiff-base ligand and the pyridyl nitrogen. The V=O distance of 1.592(4) Å is slightly shorter than the mean value for six coordinated complexes,[13] 1.615 Å: this stems from the very weak interaction to O(11) and from hydrogen-bonding between O(1) and H(52). Hydrogen-bonding distances are H(52)···O(1) 2.32(6), H(51)···O(31) 2.22(5), H(111)···O(5) 2.07(6), H(112)···O(32) 1.95(6). The vanadium atom is 0.334(1) Å away from the plane defined by the equatorial atoms, towards the vanadyl oxygen, a distance typical of other 6- and 5-coordinated complexes.[12,13] The configuration of the CH_2CONH_2 group is axial and parallel

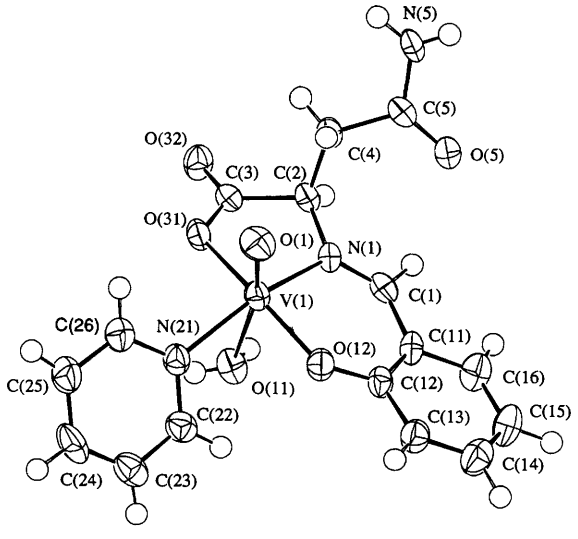


Fig. 1 ORTEP[25] diagram of [VO(sal-L-asn)(py)(H_2O)] **1** at 50% probability level, showing the atomic notation. The hydrogen atoms have been drawn with an arbitrary isotropic thermal parameter of 0.02 Å^2. Selected bond distances (Å) and angles (°): V(1)–O(1) 1.592(4), V(1)–O(12) 1.907(4), V(1)–O(31) 2.038(4), V(1)–O(11) 2.327(5), V(1)–N(1) 2.151(4), N(1)–C(1) 1.274(7), N(1)–C(2) 1.456(7).

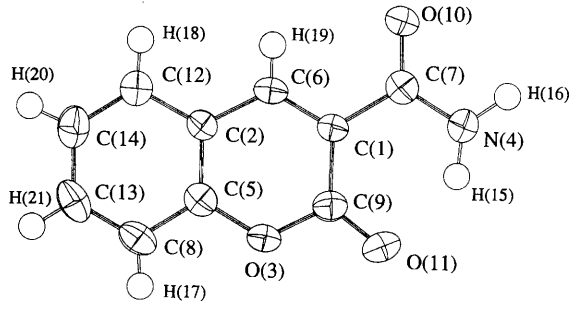
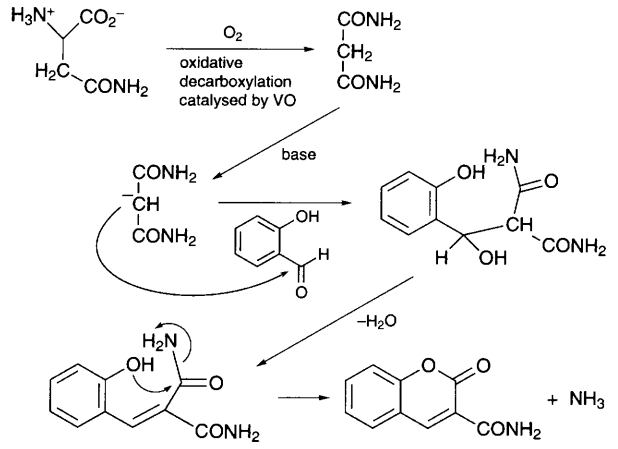


Fig. 2 ORTEP[25] diagram of coumarin-3-carboxamide **2** at 50% probability level, showing the atomic notation. The hydrogen atoms have been drawn with an arbitrary isotropic thermal motion parameter of 0.025 Å^2. Selected bond distances (Å) C(1)–C(6) 1.338(4), C(1)–C(7) 1.486(4), C(1)–C(9) 1.456(4), C(12)–C(14) 1.364(5), C(13)–C(14) 1.384(5), C(2)–C(12) 1.399(4), C(2)–C(5) 1.388(4), C(2)–C(6) 1.423(4), C(5)–C(8) 1.372(4), C(7)–N(4) 1.339(4), C(8)–C(13) 1.375(4), C(9)–O(3) 1.365(3), O(10)–C(7) 1.232(3), O(11)–C(9) 1.218(3), O(3)–C(5) 1.376(3).



Scheme 1 Possible mechanism for the production of coumarin-3-carboxamide from solutions containing VO^{2+}, salicylaldehyde and asparagine. The dehydration and cyclisation steps in the scheme could occur in either order, or as a concerted pair of processes.

to the VO group; the dihedral angle between V(1)=O(1) and C(2)–C(4) is 9.2(3).

Scheme 1 represents a possible mechanism for the formation of coumarin-3-carboxamide from solutions containing VO^{2+}, salicylaldehyde and asparagine. Biochemical and chemical oxidative decarboxylation of α-aminoacids are well documented reactions.[14] Oxidative decarboxylation reactions activated by V^V have been previously reported.[15,16,17] Vanadium (with salicylaldehyde) may catalyse the oxidative decarboxylation of asparagine, and possibly other steps of the reaction.

Reactions similar to those involved in the second and third steps included in Scheme 1 have been reported (*e.g.* refs. 18 and 19). The fact that **2** is not isolated in the absence of vanadium nor in N_2 atmosphere shows that the metal ion and oxygen must have some active role. The $[N(CH_3)_4](NO_3)$ is not necessary. Whether the ligand pyridine has a chemical role is not yet clear. Possibly oxidation of vanadium(IV) by atmospheric oxygen produces vanadate which catalyses the subsequent reactions. Vanadium complexes of *N*-salicylideneamino acids have now been found to catalyse several reactions, including the present formation of a coumarin, β-elimination from cysteines,[20] β-elimination from threonine derivatives,[21] deamination of aminoacids and peptides[4] and stereoselective oxidation[16,22] by hydroperoxides of sulfides to sulfoxides.

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Footnotes

† *Crystal data* for **1**: $C_{16}H_{17}N_3O_6V$, M_r = 398.27, monoclinic, space group $P2_1/c$, a = 14.314(4), b = 8.181(1), c = 15.260(1) Å, β = 106.96(1)°, V = 1709.3(7) Å^3, Z = 4, F_{000} = 820, D_c = 1.548 g cm^{-3}, μ(Mo-Kα) = 0.62 mm^{-1}, 4.5 ≤ 2θ ≤ 50°, ω-2θ scan, $R(F)[R_w(F^2)]$ = 0.097[0.124] for 303 parameters against 2575 reflections [$I > \sigma(I)$] out of 3009 unique reflections (program SHELXL-90[22]) corrected for absorption using ψ-scan technique, GOF = 1.072.

For **2**: $C_{10}H_7NO_3$, M_r = 189.17, monoclinic, space group $P2_1/c$, a = 4.764(2), b = 14.387(8), c = 12.379(2) Å, β = 95.75(2)°, V = 838.2(6) Å^3, Z = 4, F_{000} = 360, D_c = 1.499 g cm^{-3}, μ(Mo-Kα) = 0.11 mm^{-1}, 4.0 ≤ 2θ ≤ 60°, ω-2θ scan, $R(F)[R_w(F)]$ = 0.103[0.064] for 155 parameters against 1456 reflections [$F > 2\sigma(F)$] out of 2232 unique reflections (program SHELX-76[23]) corrected for absorption using ψ-scan technique. Atomic scattering factors for **1** and **2** were taken from International Tables.[24] 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 182/70.

‡ *Selected data* for **2**: FTIR ν/cm^{-1} 3395, 3155, 1735, 1715, 1685, 1610, 1565, 1450, 1390, 1200, 1165, 1009 and 769; mp 266 °C; ^{1}H NMR [300 MHz, $(CD_3)_2CO$] δ 8.90 (s, 1 H), 8.30 (br s, 1 H, NH), 7.96 (d, 1 H), 7.78 (t, 1 H), 7.47 (t, 1 H), 7.46 (d, 1 H) and 7.12 (br s, 1 H, NH); MS EI found: *m/z* 189.0426; fragmentation pattern: 189, 173, 145, 118, 89, 63 and 44.

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