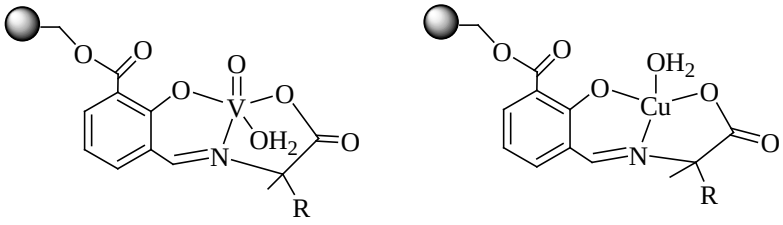
Publications – João Costa Pessoa - 2008

M. R. Maurya, M. Kumar, A. Kumar, J. Costa Pessoa
Oxidation of p-chlorotoluene and cyclohexene catalysed by polymer-anchored oxovanadium(IV) and copper(II) complexes of amino acid derived tridentate ligands, ***Dalton Trans***., 2008, 4220-4232.
http://www.rsc.org/Publishing/Journals/DT/article.asp?doi=b804823a

Short Abstract

3-Formylsalicylic acid (Hfsal) covalently bound to chloromethylated polystyrene (PS) cross-linked with 5% divinylbenzene reacts with DL-alanine and L-isoleucine to give the Schiff-base tridentate ligands PS-H_2fsal-DL-Ala and PS-H_2fsal-L-isoleu, respectively. These anchored ligands on reaction with $VOSO_4$ and $Cu(CH_3COO)_2.H_2O$ form complexes PS-[VO(fsal-DL-Ala)(H_2O)], PS-[Cu(fsal-DL-Ala)(H_2O)], PS-[VO(fsal-L-Ile)(H_2O)] and PS-[Cu(fsal-L-Ile)(H_2O)]. Structures of these immobilized complexes have been established on the basis of scanning electron micrographs, spectroscopic (Infrared, electronic and EPR), thermo gravimetric and elemental analyses studies. Oxidation of *p*-chlorotoluene and cyclohexene has been investigated using these complexes as catalyst in the presence of H_2O_2 as oxidant. Recycling studies indicate that these catalysts can be reused at least three times without any significant loss in their catalytic potential. However, EPR studies indicate that while the polymer supported $V^{IV}O$-complexes do not change upon use, the EPR spectra of the Cu-complexes show significant changes. The corresponding non-polymer-bound complexes [VO(fsal-DL-Ala)(H_2O)], [Cu(fsal-DL-Ala)(H_2O)], [VO(fsal-L-Ile)(H_2O)] and [Cu(fsal-L-Ile)(H_2O)] have also been prepared to compare their spectral properties and catalytic activities. Non-polymer-bound complexes exhibit lower conversion along with lower turn over frequency as compared to their polymer-bound analogues. Several EPR, ^{51}V NMR and UV-Vis studies have been undertaken to detect intermediate species, and outlines of the mechanisms of the catalytic reactions are proposed.



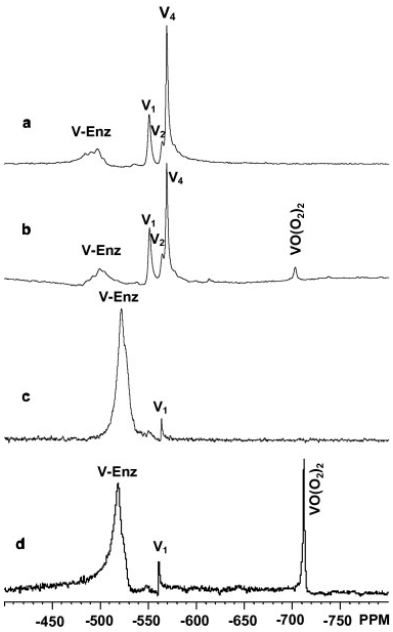
I. Correia, S. Aksu, P. Adão, J. Costa Pessoa, R. A. Sheldon, I. W. C. E. Arends

Vanadate substituted phytase: Immobilization, structural characterization and performance for sulfoxidations

J. Inorg. Biochem., 2008, 102, 318–329 http://dx.doi.org/10.1016/j.jinorgbio.2007.09.005

Short Abstract

A cross-linked enzyme aggregate (CLEA) of 3-phytase (EC 3.1.3.8) was synthesised, which was incubated with vanadate and tested as a biocatalyst in the asymmetric sulfoxidation of thioanisole using hydrogen peroxide as the oxidant. The results show that the 3-phytase-CLEA demonstrates a similar efficiency (*ca.* 95% conversion) and asymmetric induction (*ca.* 60%) as the free enzyme. Moreover, the 3-phytase-CLEA can be reused at least 3 times without significant loss of activity. The incorporation of vanadate in the active sites of two different phytases could be followed using ^{51}V NMR and circular dichroism (CD) spectroscopies. ^{51}V NMR spectra show the incorporation of vanadate into the active site at pH 5.0 and 7.6, and suggest coordination to oxygen functions at two different binding sites. CD studies showed that the α-helical content of the enzyme decreased upon coordination of vanadate, but in the concentration range used in the catalytic studies (<30 μM) the secondary conformation of the enzyme was unchanged. Acetonitrile decreases the α-helical content of both phytases from 59% to 51% and from 42% to 34%, in the 3- and 6-phytases, respectively, this being in agreement with the activity loss in the catalytic experiments.



^{51}V NMR spectra and assignment of the peaks for solutions containing 5 mM of vanadate and the phytases (2 mM) at pH 7.6:

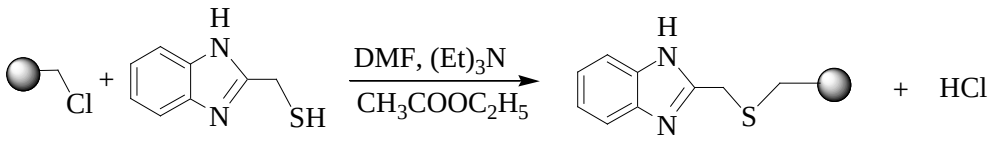
M. R. Maurya, A. Arya, P. Adão, J. Costa Pessoa,

Immobilisation of oxovanadium(IV), dioxomolybdenum(VI) and copper(II) complexes on polymer for the oxidation of styrene, cyclohexene and ethylbenzene,

Appl. Catal. A-Gen., 2008, 351, 239-252. doi:10.1016j.apcata.2008.09.021

Short Abstract

The reaction of 2-thiomethylbenzimidazole (Htmbmz) with chloromethylated polystyrene yielded a product designated by (PS-ligand). The PS-supported complexes PS-[VO(ligand)$_n$] (**1**), PS-[MoO_2(ligand)$_n$] (**2**) and PS-[Cu(ligand)$_n$] (**3**) (with n≈2), and the neat complexes [VO(tmbmz)$_2$] (**4**), [MoO_2(tmbmz)$_2$] (**5**) and [Cu(tmbmz)$_2$] (**6**) were prepared. EPR was particularly useful to characterize the binding modes in PS-[VO(ligand)$_n$] (**1**) and PS-[Cu(ligand)$_n$] (**3**). The catalytic potential of the complexes was tested for the oxidation of styrene, cyclohexene and ethylbenzene using 30 % H_2O_2 as an oxidant. Catalytic activities of the PS-supported complexes are higher than those of the corresponding neat complexes and the recycle ability of polymer-anchored metal complexes was checked confirming that they are not leached during the reaction/recovery procedures.



Htmbmz (**I**) PS-S-tmbmz

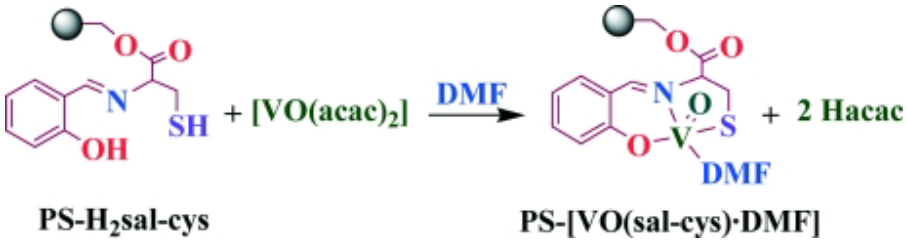
M. R. Maurya, U. Kumar, I. Correia, P. Adão, J. Costa Pessoa

A Polymer-Bound Oxidovanadium(IV) Complex Prepared from an L-Cysteine-Derived Ligand for the Oxidative Amination of Styrene

Eur. J. Inorg. Chem., 2008, 577-587. DOI: 10.1002/ejic.200700662

Short Abstract

The ligand H_2sal-cys (**I**) derived from salicylaldehyde and L-cysteine has been covalently bonded to chloromethylated polystyrene cross-linked with 5 % divinylbenzene. Upon treatment with [VO(acac)$_2$] in DMF the polystyrene-bound ligand PS-H_2sal-cys (**II**) gave the oxidovanadium(IV) complex, PS-[VO(sal-cys)·DMF] (**1**). The corresponding neat complex, [VO(sal-eta)]$_2$ (**2**), has also been prepared similarly in methanol. These complexes have been characterised by IR, electronic, EPR spectroscopic studies, magnetic susceptibility measurements and thermal as well as scanning electron micrographs studies. Both complexes catalyze the oxidative amination of styrene, in mild basic conditions, with secondary amines (diethylamine, imidazole, and benzimidazole) and gave a mixture of two aminated products in good yields. The polymer-anchored heterogeneous catalyst is free from leaching during catalytic action and recyclable



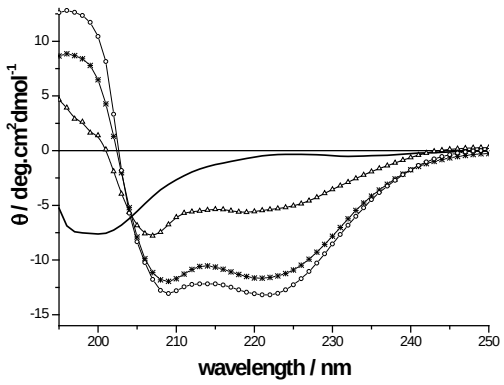
P. Adão, R. Seixas, R., P. Gomes, J. Costa Pessoa, M. Bastos

Membrane structure and interactions of a short Lycotoxin I analogue

J. Peptide Science, 2008, 14, 528-534 DOI: 10.1002/psc.984

Short Abstract

Lycotoxin I and Lycotoxin II are natural antimicrobial peptides that were identified in the venom of the Wolf Spider *Lycosa carolinensis*. These peptides were found to be potent growth inhibitors for bacteria (*Escherichia coli*) and yeast (*Candida glabrata*) at μM concentrations. The shorter Lyco-I analogue studied, LycoI 1-15 (H-IWLTALKFLGKHAAK-) was only active above 10 μM, but was also the least haemolytic of the set. The interaction of this peptide with liposomes of different composition was studied by microcalorimetry (DSC and ITC) and CD.



CD spectra (t = 35 °C) for Lyco I(1-15) 38 μM in aqueous buffer (solid line), and in the presence of LUVs of DMPC, with:

(-Δ-) - 1.25% peptide;

(-○-) - MPG, with 3.0% peptide

- MPC/DMPG (3:1) with 3.0% peptide.

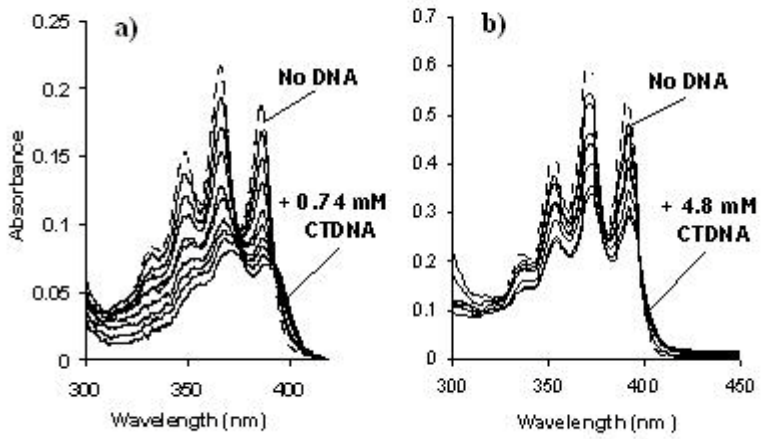
R. F. Vitor, I. Correia, M. Videira, F. Marques, A. Paulo, J. Costa Pessoa, G. Viola, G. Martins, I. Santos

Pyrazolyl-Diamine Ligands Bearing Anthracenyl Moieties and Their Rhenium(I) Tricarbonyl Complexes: Synthesis, Characterization and DNA-Binding Properties

ChemBioChem., 2008, 9, 131-142. DOI: 10.1002/cbic.200700433

Short Abstract

Two novel families of pyrazolyl-diamine ligands bearing an anthracen-9-yl group as a DNA seeking fragment, pz*$(CH_2)_2NH(CH_2)_2NHCH_2$-9-anthryl (pz* = pz (**L^1**), 3,5-Me_2pz (**L^2**)) and pz*$(CH_2)_2NH(CH_2)_2NH_2$ (pz* = 4-(9-anthrylmethyl)pz (**L^3**), 3,5-Me_2-4-(9-anthrylmethyl)pz (**L^4**)), have been prepared and fully characterized. In the case of **L^2**-**L^4**, the evaluation of their coordination capability towards the *fac*-$[Re(CO)_3]^+$ core led to the synthesis of the organometallic complexes *fac*-$[Re(CO)_3${3,5-Me_2pz$(CH_2)_2NH(CH_2)_2NHCH_2$-9-anthryl}] **(7)** and *fac*-$[Re(CO)_3${4-(9-anthrylmethyl)pz*$(CH_2)_2NH(CH_2)_2NH_2$}] (pz* = pz (**8**), 3,5-Me_2pz (**9**)). The interaction of the novel pyrazole-diamine ligands and their rhenium(I) complexes with calf thymus (CT) DNA has been investigated with a variety of spectroscopic techniques (UV-vis, fluorescence, circular dichroism and linear dichroism. Fluorescence microscopy studies have demonstrated that complexes **7** and **9** can target the nucleus of murine B16-F1 melanoma cells, appearing as promising platforms in the design of radiopharmaceuticals for targeted radiotherapy.



(a) Absorption spectra of **L^2** (4.0 x 10^{-5} M) and (**b**) Absorption spectra of complex **7** (8.0 x 10^{-5} M) in the presence of increasing concentrations of CT DNA.

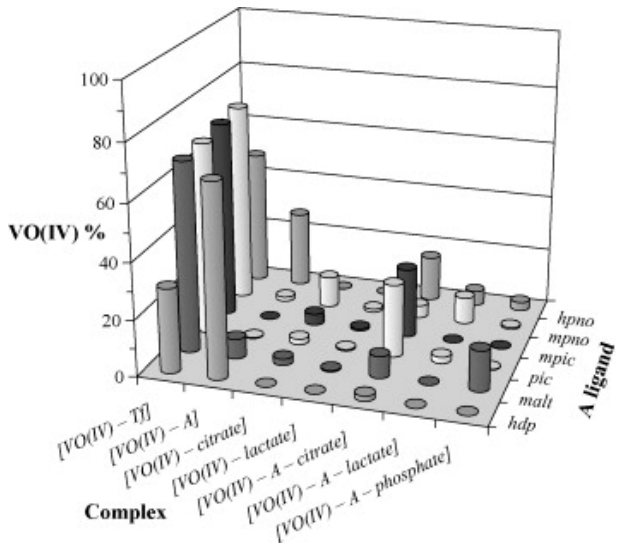
T. Kiss, T. Jakusch, D. Hollender, A. Dörnyei, E. A. Enyedy, J. Costa Pessoa, H. Sakurai, A. Sanz-Medel

Biospeciation of antidiabetic VO(IV) complexes

Coord. Chem. Rev., 2008, 252, 1153-1162. doi:10.1016/j.ccr.2007.09.011

Short Abstract

The possible transformations of antidiabetic vanadium(IV) complexes in the organism are discussed. These reactions involve absorption processes in the gastrointestinal tract, transport in the blood stream and interactions with endogenous binding molecules in the glucose-metabolizing cells. Modelling studies were mostly used to determine the actual chemical form of VO(IV) complexes in various biological environments. The results suggest that decomposition and subsequent ternary complex formation with endogenous or exogenous ligands in the organism affects the absorption efficacy of the originally neutral VO(IV) compounds considerably. During transport in the blood stream, transferrin displaces the carrier ligands from the VO(IV) compounds and plays an important role in transporting VO(IV) to the cell. In the cell, vanadium undergoes redox interaction with glutathione and complexation with adenosine 5′-triphosphate (the two important cell components present in mM concentration). In vitro and in vivo biological results confirmed some of the basic findings obtained from the modelling.



Distribution of various anti-diabetic VO(IV) compounds in serum at pH 7.4
$[V^{IV}O]_{tot}$ = 100 μM,
$[A_{ligand}]_{tot}$ = 200 μM