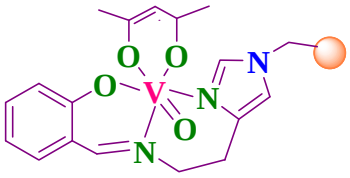
Publications – João Costa Pessoa - 2009

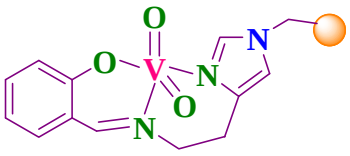
M.R. Maurya, A. Arya, A. Kumar, J. Costa Pessoa,
Polystyrene bound oxidovanadium(IV) and dioxidovanadium(V) complexes of histamine derived ligand for the oxidation of methyl phenyl sulfide, diphenyl sulfide and benzoin,
Dalton Trans., 2009, 2185-2195.
http://www.rsc.org/delivery/_ArticleLinking/ArticleLinking.cfm?JournalCode=DT&Year=2009&ManuscriptID=b814297a&Iss=12.

Short Abstract

Ligand Hsal–his (**I**) derived from salicylaldehyde and histamine has been covalently bound to chloromethylated polystyrene cross-linked with 5% divinylbenzene. Upon treatment with $[VO(acac)_2]$ in DMF, the polystyrene bound ligand gave the stable polystyrene bound oxidovanadium(IV) complex PS–$[V^{IV}O(sal–his)(acac)]$ **1**, which upon oxidation yielded the dioxidovanadium(V) PS–$[V^{V}O_2(sal–his)]$ **2** complex. The corresponding non-polymer bound complexes $[V^{IV}O(sal–his)(acac)]$ **3** and $[V^{V}O_2(sal–his)]$ **4** have also been obtained. These complexes have been characterised by IR, electronic, ^{51}V NMR and EPR spectral studies, and thermal as well as scanning electron micrograph studies. Complexes **1** and **2** have been used as catalyst for the oxidation of methyl phenyl sulfide, diphenyl sulfide and benzoin with 30% H_2O_2 as oxidant. These polymer-anchored heterogeneous catalysts do not leach during catalytic action, are recyclable and show higher catalytic activity and turn over frequency than the corresponding non-polymer bound complexes. EPR and ^{51}V NMR spectroscopy was used to characterise methanolic solutions of **3** and **4** and to identify species formed upon addition of H_2O_2 and/ or acid and/ or methyl phenyl sulfide.



PS-[VO(sal-his)(acac)] 1

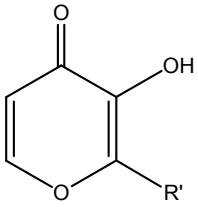


PS-[VO_2(sal-his)] 2

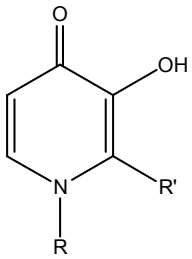
H. Faneca, V. A. Figueiredo, A. I. Tomaz, G. Gonçalves, F. Avecilla, M. C. Pedroso de Lima, C. F. G. C-Geraldes, J. Costa Pessoa, M. M. C. A. Castro
Vanadium Compounds as therapeutic agents: some chemical and biochemical studies, ***J. Inorg. Biochem.***, 2009, 103, 601-608.
http://dx.doi.org/10.1016/j.jinorgbio.2008.11.004

Short Abstract

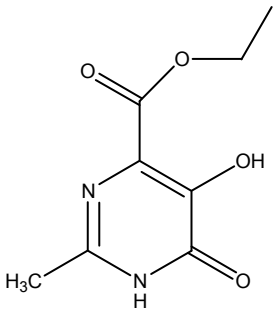
The behaviour of three vanadium(V) systems, namely the pyridinone V^{V}-dmpp, the salicylaldehyde derivative V^{V}-salDPA and the pyrimidinone V^{V}-MHCPE, is studied in aqueous solutions, under aerobic and physiological conditions using ^{51}V NMR, EPR and UV-Vis spectroscopies. The system V^{V}-MHCPE is studied by pH potentiometry and ^{51}V NMR, and the results indicate that, at pH ca 7, the main species present are $(V^{V}O_2)L_2$ and $(V^{V}O_2)LH_{-1}$ (L = $MHCPE^{-}$), and hydrolysis products, similar to those observed in aqueous solutions of V^{V}-dmpp, being the latter species protonated as the pH decreases originating $(V^{V}O_2)L$ and $(V^{V}O_2)LH$. All the V^{V}-species studied are stable in aqueous media with different compositions and at physiological pH, including the cell culture medium. The compounds were screened for their potential cytotoxic activity in two different cell lines. It was found that the toxic effects are incubation time and concentration dependent and specific for each compound and each type of cells. The HeLa tumor cells seem to be more sensitive to drug effects than the 3T3L1 fibroblasts. According to the IC50 values and to the results of reversibility to drug effects, the V^{V}-species resulting from the V^{V}-MHCPE system show higher toxicity in the tumor cells than in non-tumour cells, which may indicate potential antitumor activity.



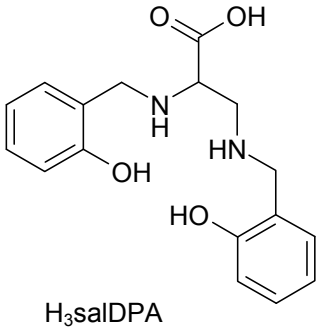
Maltol: R' = CH3-
Ethylmaltol:
R'= CH3CH2-



Hdmpp: R = CH3-
R' = CH3-



HMHCPE

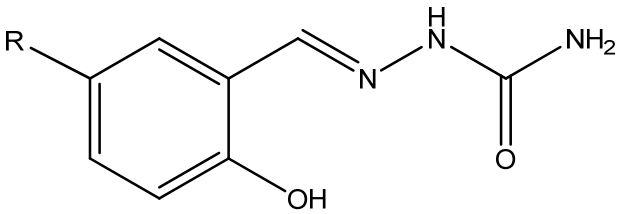


H_3salDPA

J. Benítez, L. Guggeri, I. Tomaz, G. Arrambide, M. Navarro, J. Costa Pessoa, B. Garat, D. Gambino,
Design of vanadium mixed-ligand complexes as potential anti-protozoa agents,
J. Inorg. Biochem., 2009, 103, 609-616.
http://dx.doi.org/10.1016/j.jinorgbio.2008.10.018

Short Abstract

In the search for new therapeutic tools against Chagas´disease (American Trypanosomiasis) four novel mixed-ligand vanadyl complexes, [$V^{IV}O(L^2\text{-}2H)(L^1)$], including a bidentate polypyridyl DNA intercalator (L^1) and a tridentate salycylaldehyde semicarbazone derivative (L^2) as ligands were synthesized, characterized by a combination of techniques, and *in vitro* evaluated. EPR suggest a distorted octahedral geometry with the tridentate semicarbazone occupying three equatorial positions and the polypyridyl ligand coordinated in an equatorial/axial mode. Both complexes including dipyrido[3,2-a: 2',3'-c]phenazine (dppz) as polypyridyl coligand showed IC_{50} values in the μM range against Dm28c strain (epimastigotes) of *Trypanosoma cruzi*, causative agent of the disease, being as active as the anti-trypanosomal reference drug Nifurtimox. To get an insight into the trypanocidal mechanism of action of these compounds, DNA was evaluated as a potential parasite target and EPR, and ^{51}V NMR experiments were also carried out upon aging aerated solutions of the complexes. Data obtained by electrophoretic analysis suggest that the mechanism of action of these complexes could include DNA interactions.

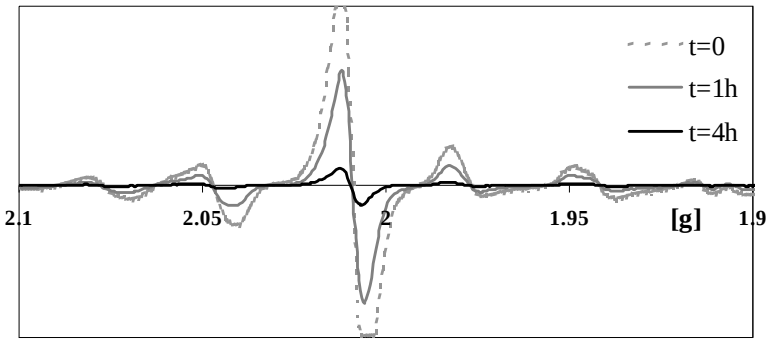


R = H salicyladehyde semicarbazone
R = Br 5-bromosalicylaldehyde semicarbazone

P. Adão, M.R. Maurya, U. Kumar, F. Avecilla, R.T. Henriques, M.L. Kusnetsov, J. Costa Pessoa, I. Correia,
Vanadium-salen and -salan complexes: characterization and application in oxygen transfer reactions,
Pure and Appl. Chem., 2009, 2009, 81, 1279-1296.
http://www.iupac.org/publications/pac/81/7/1279/

Short Abstract

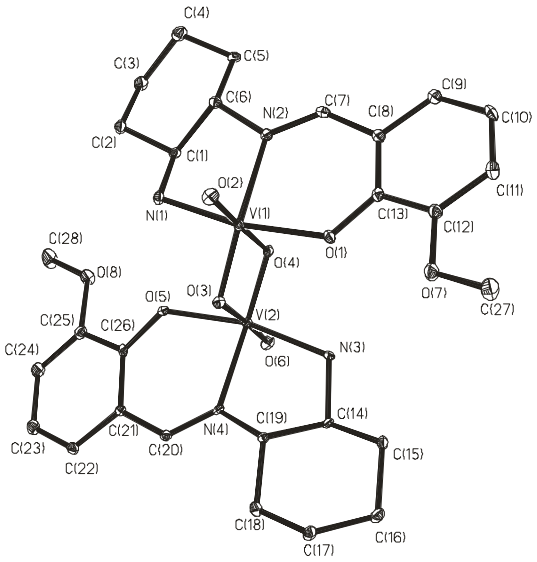
We report the synthesis and characterization of a group of new vanadium-salen and -salan complexes, their characterization and application in the oxidation of simple organic molecules with H_2O_2. The vanadium(IV) complexes were prepared and characterized in the solid state (FTIR and magnetic properties) and in solution by spectroscopic techniques: UV-Vis, circular dichroism, EPR and ^{51}V NMR, which provide information on the coordination geometry. Single crystals suitable for X-ray diffraction studies were obtained from solutions containing the vanadium(IV)-pyr(*S,S*-chan) complex: $[V^{V}O\{pyr(S,S\text{-chen})\}]_2(\mu\text{-}O)_2\cdot 2(CH_3)_2NCHO$, where the ligand is the "half" Schiff base formed by pyridoxal and 1*S*,2*S*-diaminocyclohexane. The dinuclear species shows a $OV^{V}(\mu\text{-}O)_2V^{V}O$ unit with tridentate ligands and two *μ*-oxo bridges. The vanadium(IV) complexes of the salan type ligands oxidize in organic solvents to a V(V) species and the process was studied by spectroscopic techniques. The complexes were tested as catalysts in the oxidation of styrene, cyclohexene and cumene with H_2O_2 as oxidant. Overall, the V-salan complexes show higher activity than the parent V-salen complexes and are an alternative ligand system for oxidation catalysis.



F. Avecilla, P. Adão, I. Correia, J. Costa Pessoa,
Influence of polidentate ligands in the stuctures of dinuclear vanadium(V) compounds,
Pure and Appl. Chem., **2009, 2009, 81,** 1297-1311.
http://www.iupac.org/publications/pac/81/7/1297/

Short Abstract

In this work we present a review discussing general structural features of oxygen-bridged dinuclear vanadium (IV and/or V) complexes covering only those that have been characterized by single crystal X-ray diffraction Many of these compounds contain functional Schiff bases and amines as ligands, this work illustrating the high propensity of the vanadium centre to increase its coordination number via dimerization of two tetra- or penta-coordinate monomers, if the steric and electronic control exerted by the ligands allows it. We also report the synthesis and characterization by single crystal X-ray diffraction of two new dinuclear complexes: [{V^{V}O[sal(*R*,*R*-chen)]}$_2$(μ_2-O)$_2$] **1** and [{V^{V}O[mvan(*S*,*S*-chen)]}$_2$(μ_2-O)$_2$] **2**. The complexes contain tridentate ligands with O-phenolate, N-imine and N-amine coordination to the V^{V}-centre. The molecular structures of these compounds demonstrate that they form dinuclear species in the solid state with a V_2O_4 core.

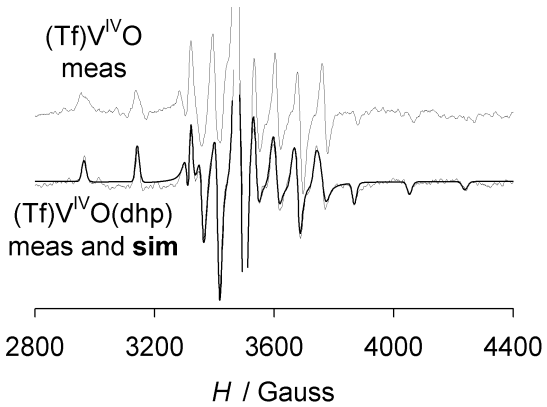


T. Jakusch, D. Hollender, É.A. Enyedy, C.S. González, M. Montes-Bayón, A. Sanz-Medel, J. Costa Pessoa, I. Tomaz, T. Kiss,
Dalton Trans., 2009, 2428-2437.

http://www.rsc.org/ej/DT/2009/b817748a.pdf

Short Abstract

The transport of different insulin mimetic oxovanadium(IV) compounds by serum proteins has been studied in model systems and in *in-vitro* samples. For the modeling study, an earlier fundamental *in situ* method was extended and applied to the ternary complex formation of apoTransferrin(apoTf) - $V^{IV}O$ - maltol or 1,2-dimethyl-3-hydroxy-4(1H)-pyridinone (dhp). Both systems were proved and evaluated in detail by simultaneous CD and EPR measurements. It has been found that the ligands studied (maltol, dhp and picolinic acid) and the synergistic carbonate are non-competitive binders. Based on the stability constants obtained for the species formed in the systems of $V^{IV}O$, carrier ligands and serum proteins (apoTf and HSA), modeling calculations were performed on the distribution of $V^{IV}O$ between the low and high molecular mass fractions of the blood serum. The results were confirmed on one hand by ultrafiltration and atomic absorption spectroscopic (AAS) measurements. Similarly, the interactions (in-vitro) of the $V^{IV}O$ complexes formed with maltol, picolinic acid and dhp with serum protein standards and also with human serum samples were evaluated. For this purpose, the proteins were firstly separated by liquid chromatography (HPLC), and the V containing fractions detected by inductively coupled plasma mass spectrometer, ICP-MS. The results were compared with those obtained by modelling calculations using the formation constants obtained by spectroscopic methods in this work and by pH-potentiometry in earlier publications. It has been observed that all the studied $V^{IV}O$ compounds showed similar chromatographic profiles after incubation with serum samples, being associated almost exclusively to transferrin as predicted by the modelling calculations. Interactions with human serum albumin of any of the species under study are practically negligible in the serum physiological conditions. Therefore, also as the present model calculations suggest, transferrin seems to be the main $V^{IV}O$ transporter in serum in *in-vitro* conditions, and this association is practically independent of the chemical form in which $V^{IV}O$ is administered.

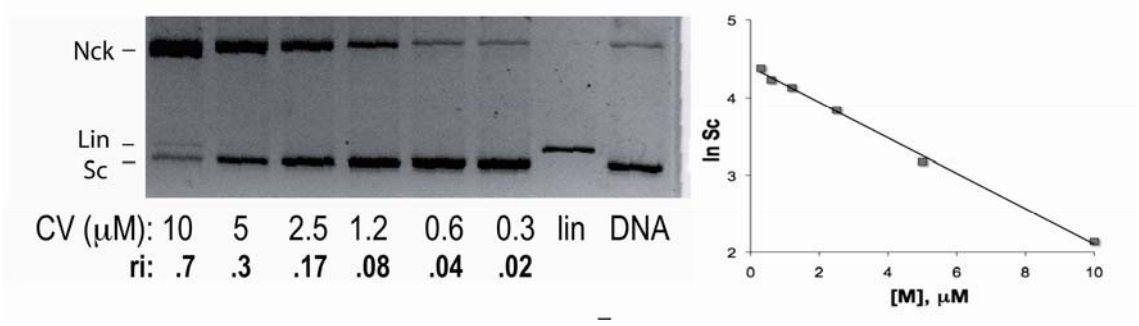


N. Butenko, I. Tomaz, O. Nouri, E. Escribano, V. Moreno, S. Gama, V. Ribeiro, J. P. Telo, J. Costa Pessoa, I. Cavaco
DNA cleavage activity of $V^{IV}O(acac)_2$ and derivatives,
J. Inorg. Biochem., 2009, 103, 622-632.

http://dx.doi.org/10.1016/j.jinorgbio.2009.01.003

Short Abstract

The DNA cleavage activity of several β-diketonate vanadyl complexes is examined. Vanadyl acetylacetonate, $V^{IV}O(acac)_2$, **1**, shows a remarkable activity in degrading plasmid DNA in the absence of any activating agents, air and photo-irradiation. The cleaving activity of several related complexes $V^{IV}O(hd)_2$ (**2**, Hhd=3,5-heptanedione), $V^{IV}O(acac\text{-}NH_2)_2$ (3, Hacac-NH_2=acetoacetamide) and $V^{IV}O(acac\text{-}NMe_2)_2$ (**4**, Hacac-NMe_2=N,N-dimethylacetoacetamide) is also evaluated. It is shown that **2** exhibits an activity similar to **1**, while **3** and **4** are much less efficient cleaving agents. The different activity of the complexes is related to their stability towards hydrolysis in aqueous solution, which follows the order **1~2** >> **3~4**. The nature of the pH buffer was also found to be determinant in the nuclease activity of **1** and **2**. In a phospate buffered medium DNA cleavage by these agents is much more efficient than in tris, hepes, mes or mops buffers. The reaction seems to take place through a mixed mechanism, involving the formation of reactive oxygen species (ROS), namely OH radicals, and possibly also direct cleavage at phosphodiester linkages induced by the vanadium complexes.

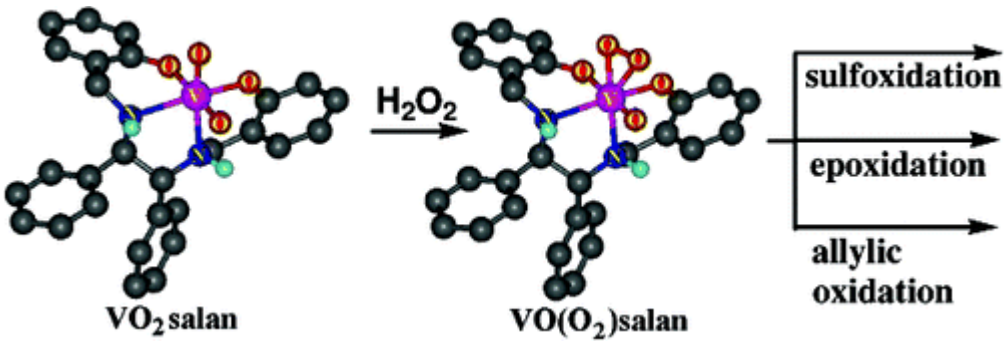


Effect of concentration of **1** on DNA cleavage. *Left*: Agarose gel electrophoresis evolution of plasmid pA1 degradation after incubation with **1**. *Right*: The same results, measured as logarithm of the percentage of the Sc form.

P. Adão, J. Costa Pessoa, R. T. Henriques, M. L. Kuznetsov, F. Avecilla, M. R. Maurya, U. Kumar, I. Correia,
Synthesis, characterization and application of vanadium-salan complexes in oxygen transfer reactions,
Inorg. Chem., 2009, 2009, 48, 3542-3561.
http://pubs.acs.org/doi/pdfplus/10.1021/ic8017985

Abstract

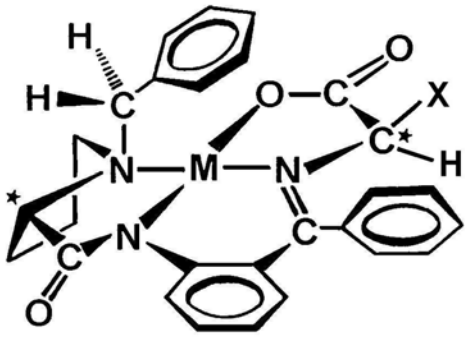
We report the synthesis and characterization of several chiral salen and salan type ligands and their vanadium complexes, which are derived from salicylaldehyde or salicylaldehyde derivatives and chiral diamines (1*R*,2*R*-diaminocyclohexane, 1*S*,2*S*-diaminocyclohexane and 1*S*,2*S*-diphenylethylenediamine). The structure of H_2sal(*R*,*R*-chan)$^{2+}\cdot 2Cl^-\cdot(CH_3)_2CHOH\cdot H_2O$ **1c** (H_2sal(*R*,*R*-chan) = N,N'-salicyl-*R*,*R*-cyclohexanediaminium), of Etvan(*S*,*S*-chen) **3c** (Etvan(*S*,*S*-chen) = N,N'-3-ethoxy-salicylidene-*S*,*S*-cyclohexanediiminato) and naph(*R*,*R*-chen) **6c** (naph(*R*,*R*-chen) = N,N'-naphthylidene-*R*,*R*-cyclohexanediiminato) were determined by single-crystal X-ray diffraction. The corresponding vanadium(IV) complexes and several other new complexes involving different salicylaldehyde-type precursors were prepared and characterized in the solid state and in solution by spectroscopic techniques: Single crystals suitable for x-ray diffraction were obtained for [{V^{V}O[sal(*S*,*S*-dpan)]}$_2$(μ-O)]·H_2O·2$(CH_3)_2$CHOH **14c** (sal(*S*,*S*-dpan) = N,N'-salicyl-*S*,*S*-diphenylethylenediaminato) and [{V^{V}O[*t*-Busal(*R*,*R*-chan)]}$_2$(μ-O)]·2$(CH_3)_2$CHOH **15c**, both containing a $OV^{V}(\mu\text{-}O)V^{V}O$ moiety ($V_2O_3^{4+}$ core) with tetradentate ligands and one *μ*-oxo bridge. Both structures are the first examples of dinuclear vanadium complexes involving the $V^{V}_2O_3^{4+}$ core with tetradentate ligands, the configuration of the V_2O_3 unit being twist-angular. The V-salen and V-salan complexes are tested as catalysts in the oxidation of styrene, cyclohexene, cumene and methyl phenyl sulfide with H_2O_2 and t-BuOOH as oxidants. Overall, the V-salan complexes show higher activity and normally better selectivity in alkene oxidation, and higher activity and enantioselectivity for sulfoxidation than their parent V-salen complexes, therefore being an advantageous alternative ligand system for oxidation catalysis. The better performance of V-salan complexes probably results form their significantly higher hydrolytic stability. Mechanisms for the alkene oxidation with these newly obtained V-salan compounds are discussed, including the use of DFT for the comparison of the several alternative mechanisms for epoxidation.



J. Costa Pessoa, I. Correia, G. Gonçalves, I. Tomaz,
Circular Dichroism in Coordination Compounds,
J. Arg. Chem. Soc., 2009, 2009, 97, 151-165.
(Special Issue dedicated to Professor E. Baran).

Short Abstract

Circular dichroism (CD) spectroscopy is widely used to study biological systems and non-biological systems, being an invaluable tool in inorganic chemistry, particularly in coordination chemistry. In this work it is described how CD may be used empirically to obtain structural and analytical information on transition metal complexes with optically active ligands, as well as relevant information on the interaction of metal ions with large bio-molecules such as proteins and DNA. Particular relevance is given to oxovanadium(IV) compounds.



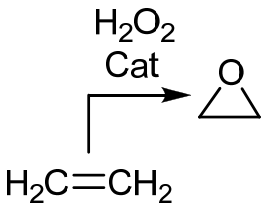
(a) [Ni^{II}(S-BBP-L-Ser)] (X = -CH_2OH)

M. L. Kuznetsov, J. Costa Pessoa,
Epoxidation of olefins catalysed by vanadium-salan complexes: a theoretical mechanistic study,
Dalton Trans., 2009, 5460-5468.

http://www.rsc.org/ej/DT/2009/b902424g.pdf

Short Abstract

Plausible mechanisms of olefin epoxidation catalysed by a V-salan model complex [V^{IV}(=O)(L)(H_2O)] (**1**, L = ($CH_2NHCH_2CH=CHO^-$)$_2$) in the presence of H_2O_2 are investigated and compared by theoretical methods using density functional theory. Three main routes, *i.e.* the Mimoun, Sharpless and biradical mechanisms, were examined in detail, and the Sharpless pathway is found to be the most favourable one. The reaction starts from the formation of an active catalytic species [V^{V}(=O)(OO)(LH)] (**3c**) upon interaction of **1** with H_2O_2, then concerted highly synchronous attack of olefin to **3c** occurs yielding epoxide and catalyst [V^{V}(=O)$_2$(LH)], the later being oxidized by H_2O_2 to **3c**. The activation barrier strongly depends on the proton location in the catalyst molecule and is the lowest when one of the oxygen atoms of salan ligand is protonated and the vanadium atom is penta-coordinated with one vacant coordination position (complex **3c**). Olefin in this reaction acts as an electron donor (nucleophile) rather than as an electron acceptor (electrophile).



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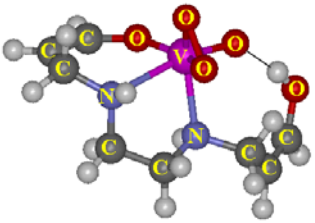
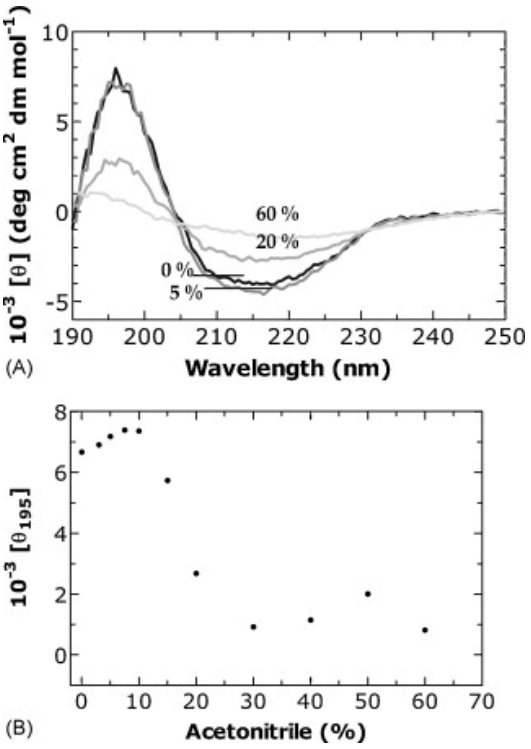


C. S. Oliveira, A. C. Sarmento, A. Pereira, I. Correia, J. Costa Pessoa, V. Esteves, H. Fonseca, E. Pires, M. T. Barros
Non-native states of cardosin A induced by acetonitrile: activity modulation via polypeptide chains rearrangements
J. Molec Cat B: Enzymatic, 2009, 61, 274-278.

http://dx.doi.org/10.1016/j.molcatb.2009.08.003

Short Abstract

Cardosin A is an enzyme containing two polypeptide chains, used for milk clotting in cheese making. It is a member of the aspartic proteinases (APs). Cardosin A is thought to be involved in many cellular events such as in pollen–pistil interaction and adhesion dependent recognition mechanisms. In the present study, the structural and activity effects of different amounts of acetonitrile (ACN) in cardosin A are presented. The results indicate that low ACN concentrations (up to 10% ACN) reversibly stimulate the enzyme activity accompanied by slight secondary structure induction. In light of the structural and stability studies performed so far, Cardosin A can adopt conformational alterations that can result in activity modulation via polypeptide chains rearrangements.



Cardosin A ACN induced effects monitored by CD. (A) Cardosin A far-UV CD spectra after 1 h incubation at 25 °C. (B) CD signal intensity observed at 195 nm upon change of the % (v/v) CAN.

J. Benítez, L. Guggeri, I. Tomaz, J. Costa Pessoa, V. Moreno Martínez, J. Lorenzo, F.X. Avilés, B. Garat, D. Gambino

A novel vanadyl complex with a polypyridyl DNA intercalator as ligand: a potential anti-protozoa and anti tumor agent

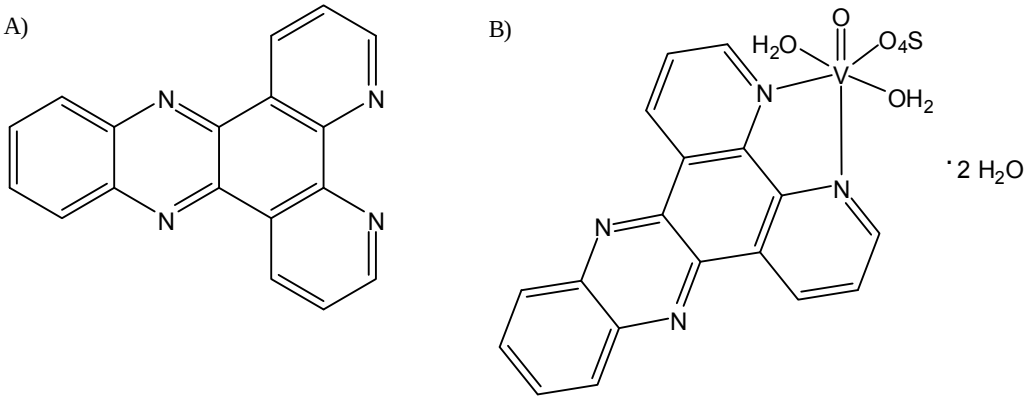
J. Inorg. Biochem., 2009, 103, 1386-1394.

http://www.sciencedirect.com/science?_ob=MImg&_imagekey=B6TGG-4WV77RM-1-H&_cdi=5254&_user=2459750&_orig=browse&_coverDate=10%2F31%2F2009&_sk=998969989&view=c&wchp=dGLbVzW-zSkzV&md5=4fff97fa23a84b34a763fab0a0ee872b&ie=/sdarticle.pdf

Short Abstract

In the search for new metal-based drugs for the treatment of tumoral and parasitic diseases a vanadyl complex, $[V^{IV}O(SO_4)(H_2O)_2(dppz)]\cdot 2H_2O$, that includes the bidentate polypyridyl DNA intercalator dppz, was synthesized, characterized by a combination of techniques, and *in vitro* evaluated on the human acute promyelocytic leukemia cell line HL-60 and against Dm28c strain epimastigotes of the parasite *Trypanosoma cruzi*, causative agent of Chagas´disease.

EPR spectroscopy suggests a distorted octahedral geometry for the complex with the dppz ligand acting as bidentate, binding through both N donor atoms in an axial-equatorial mode. An oxo group, two water molecules and a sulphate donor occupy the remainder coordination positions. The complex showed an IC_{50} value in the μM range against *T. cruzi*, being slightly more active than the anti-trypanosomal reference drug Nifurtimox. In addition it exhibited excellent *in vitro* antitumor activity against leukemia (HL-60 cell line) comparable to that of cisplatin, inducing cell death by apoptosis with IC_{50} values in the micromolar range. Data from gel electrophoresis and atomic force microscopy indicate that the complex interacts with DNA, suggesting that its mechanism of action may include DNA as a target. EPR and ^{51}V NMR experiments were also carried out with aged aerated solutions of the complex to get insight into the stability of the complex in solution and the species responsible for the *in vitro* activities observed.

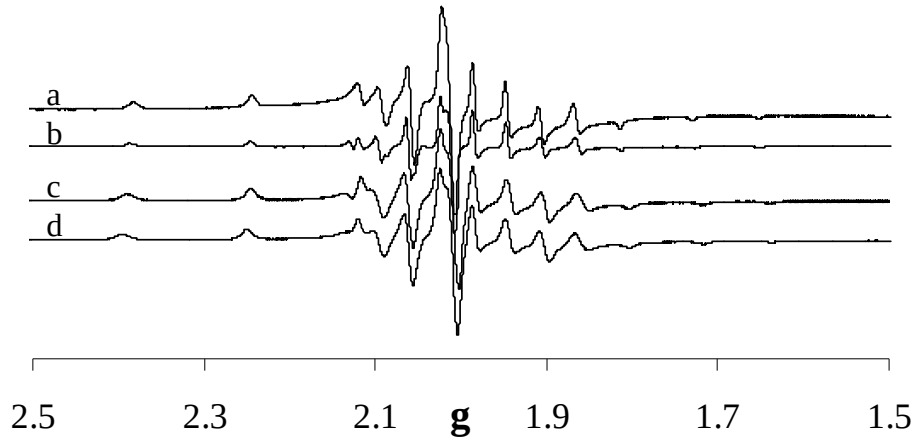


M.R. Maurya, A. Arya, U. Kumar, A. Kumar, J. Costa Pessoa
Polymer-bound oxidovanadium(IV) and dioxidovanadium(V) complexes: synthesis, characterization and catalytic application for the hydroamination of styrene and vinyl pyridine ***Dalton Trans***., 2009, 9555-9566.

http://www.rsc.org/ej/DT/2009/b912180c.pdf

Short Abstract

The Schiff base (Hfsal-aepy) derived from 3-formylsalicylic acid and 2-(2-aminoethyl)pyridine has been covalently bonded to Cl-polystyrene cross-linked with 5% divinylbenzene (PS-Hfsal-aepy). Treatment of [$V^{IV}O(acac)_2$] with PS-Hfsal-aepy in DMF gave complex PS-[$V^{IV}O$(fsal-aepy)(acac)] **1**, which on oxidation yielded the PS-[$V^{V}O_2$(fsal-aepy)] **2** complex. The corresponding neat complexes, [$V^{IV}O$(sal-aepy)(acac)] **3** and [$V^{V}O_2$(sal-aepy)] **4** have also been prepared. The compounds are characterized in solid state and in solution, by spectroscopic techniques (IR, UV-Vis, EPR, ^{1}H, ^{13}C and ^{51}V NMR), thermal as well as field-emission scanning electron micrographs (FE-SEM) studies. The crystal and molecular structure of [$V^{IV}O$(sal-aepy)(acac)] was solved by single-crystal X-ray diffraction. These complexes catalyze the hydroamination of styrene and vinyl pyridine with amines (aniline and diethylamine) yielding a mixture of two hydroaminated products in good yields. Amongst the two hydroaminated products, the anti-Markovnikov product is favored over the Markovnikov one. Plausible intermediates involved in these catalytic processes are established by UV-Vis, EPR and ^{51}V NMR studies, and an outline of the mechanism is proposed. The EPR spectrum of the polymer supported $V^{IV}O$-complex **1** is characteristic of a magnetically diluted $V^{IV}O$-complex, the resolved EPR pattern indicating that the oxidovanadium(IV) centers are well dispersed in the polymer matrix. Neat complexes exhibit lower conversion along with lower turn over frequency as compared to their polymer-anchored analogues. The polymer-anchored heterogeneous catalysts are free from leaching during catalytic action and are recyclable.



First derivative EPR spectra of frozen solutions of [$V^{IV}O$(sal-aepy)(acac)] **3** (**a**) in DMSO; (b) in MeOH. First derivative EPR spectra of (**c**) solid sample of PS-[$V^{IV}O$(fsal-aepy)(acac)] **1** at room temperature and (**d**) PS-[$V^{IV}O$(fsal-aepy)(acac)] **1** at 77 K after swelling in DMSO.

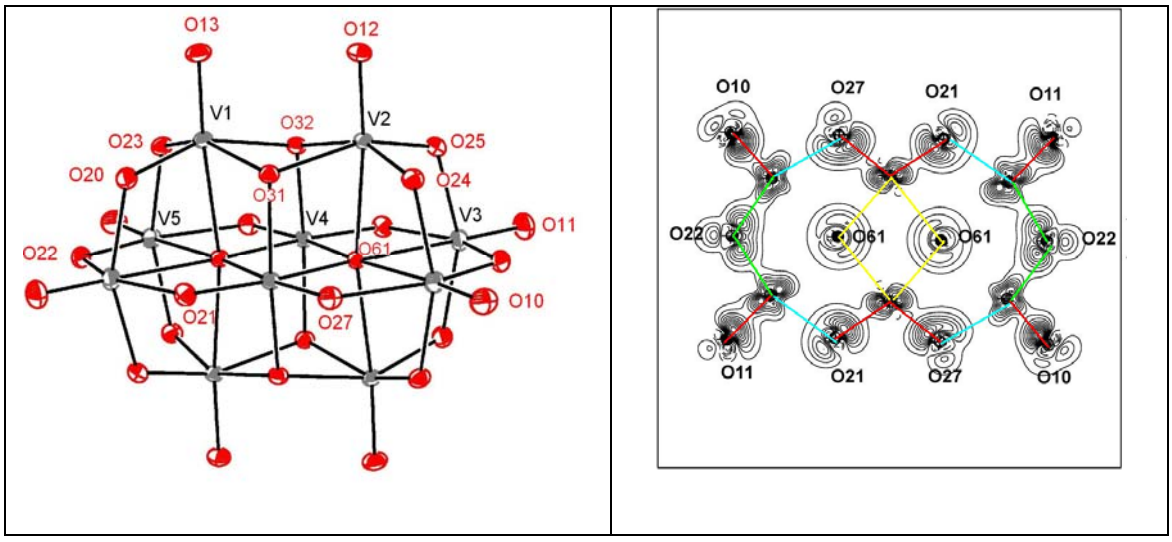
N. Bošnjakovic-Pavlović, A. Spasojević-de Biré, I. Tomaz, N. Bouhmaida, F. Avecilla, U. Mioč, J. Costa Pessoa, N. E. Ghermani
Electron and electrostatic properties of a cytosine decavanadate compound from high resolution X-ray diffraction: toward a better understanding of chemical and biological properties of decavanadates
Inorg. Chem., 2009, 48, 9742-9753.

http://pubs.acs.org/doi/pdf/10.1021/ic9008575

Short Abstract

We have synthesized and crystallized a cytosine-decavanadate compound, Na_3 $[V_{10}O_{28}]$ $(C_4N_3OH_5)_3(C_4N_3OH_6)3$ 3 $10H_2O$, and its crystal structure has been determined from a single-crystal X-ray diffraction. A high resolution X-ray diffraction experiment at 210 K was carried out. The data were refined using a pseudo-atom multipole model to get the electron density and the electrostatic properties of the decavanadate-cytosine complex.

Static deformation density maps and Atoms in Molecules (AIM) topological analysis were used for this purpose. To get insight into the reactivity of the decavanadate anion, we have determined the atomic net charges and the molecular electrostatic potential. Special attention was paid to the hydrogen bonding occurring in the solid state between the decavanadate anion and its environment. The comparison of the experimental electronic characteristics of the decavanadate anions to those found in literature reveals that this anion is a rigid entity conserving its intrinsic properties. This is of particular importance for the future investigations of the biological activities of the decavanadate anion.



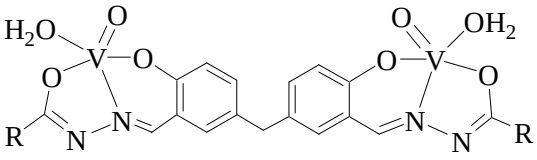
Static model deformation density in the cytosine-devanadate compound. Plane containing O10,O11,O21,O27,O22,O61,V3, V4, and V5 atoms. The longest V-O bonds (VI-Oa, VII-Oa, VIII-Oa) in the cage are in yellow, the medium bonds are in green (VII-Od) and blue (VII-Oe) color and shortest V-O bonds (VI-Oe, VIII-Of, VII-Og) are in red color.

M. R. Maurya, A. A. Khan, I. Irfan, A. Azam, A. Kumar, J. Costa Pessoa
Binuclear Oxidovanadium(IV) and Dioxidovanadium(V) Complexes of 5, 5'-Methylenebis(Dibasic Tridentate) Ligands: Synthesis, Spectral Characterisation, Reactivity, Catalytic and Antiamoebic Activities
Eur. J. Inorg. Chem., 2009, 5377-5390.

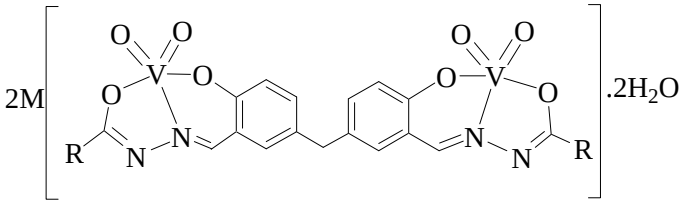
http://www3.interscience.wiley.com/cgi-bin/fulltext/122666953/PDFSTART

Short Abstract

The synthesis of dinuclear oxidovanadium(IV) and dioxidovanadium(V) complexes of two hydrazones {$CH_2(H_2$sal-nah$)_2$, **I**} and {$CH_2(H_2$sal-inh$)_2$, **II**} derived from 5,5'-methylenebis(salicylaldehyde) {$CH_2(Hsal)_2$} and nicotinic acid hydrazide (nah) or isonicotinic acid hydrazide (inh) is described. The compounds are characterized in the solid state and in solution, namely by spectroscopic techniques (IR, UV-Vis, EPR, ^1H, ^{13}C and ^{51}V NMR). It is demonstrated that the dioxidovanadium(V) complexes $K_2[CH_2\{V^VO_2$(sal-nah)$\}_2]\cdot 2H_2O$ (**3**), $Cs_2[CH_2\{V^VO_2$(sal-nah)$\}_2]\cdot 2H_2O$ (**4**) and $Cs_2[CH_2\{V^VO_2$(sal-inh)$\}_2]\cdot 2H_2O$ (**5**) of **I** and **II** are active in the oxidative bromination of salicylaldehyde, by H_2O_2, therefore acting as functional models of vanadium dependent haloperoxidases, and it is also shown that the corresponding oxidovanadium(IV) complexes $[CH_2\{V^{IV}O$(sal-nah)$(H_2O)\}_2]$ (**1**) and $[CH_2\{V^{IV}O$(sal-inh)$(H_2O)\}_2]$ (**2**) are catalyst precursors for the catalytic oxidation, by peroxide, of methyl phenyl sulfide and diphenyl sulfide, yielding the corresponding sulfoxide and sulfone. Plausible intermediates involved in these catalytic processes are established by UV-Vis, EPR and ^{51}V NMR studies. The dioxidovanadium(V) complexes along with ligands **I** and **II** were also screened against HM1:1MSS strains of *Entamoeba histolytica*, the results showed that the IC_{50} value of compound **3** and **5** are less than the IC_{50} value of metronidazole. The toxicity studies against human cervical (HeLa) cells line showed that the compounds **3** and **5** are toxic as compared to metronidazole.



R = 3-pyridyl: **1**; R = 4-pyridyl: **2**



For K^+: R = 3-pyridyl: **3**

For Cs^+ : R = 3-pyridyl: **4**; R = 4-pyridyl: **5**