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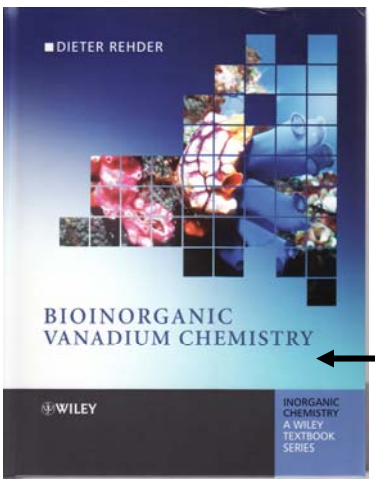
Winner of the Vanadis Award 2006

Awarded for outstanding research in the field of vanadium chemistry at the 5th "International Symposium on the Chemistry and Biochemistry of Vanadium" (IVS), St. Francisco 2006.

Biography

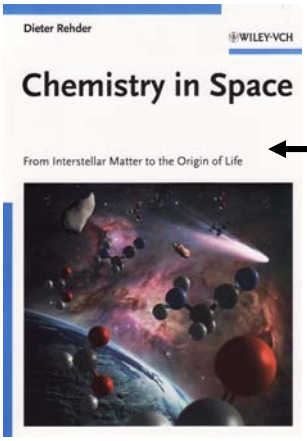
Born 1941 in Hamburg. Studies of Chemistry and Astronomy in Hamburg. Diploma in Chemistry 1967; Ph.D. (Dr. rer. nat.) 1970. Postdoctoral research and lecturing at the University of Hamburg and the "College for Tobacco Technology and Bio-Engineering" in Hamburg-Bergedorf; 1973-1975 Lecturer at the "College of Arts Science & Technology" and the "Institute for Sugar Technology" in Kingston/Jamaica. 1979 Habilitation in Hamburg. Since 1984 full Professor at the Institute of Inorganic and Applied Chemistry. 2008/2009 Guest lecturer at the University of Lund (Sweden).



Main fields of research: Organometallic, Bioinorganic and Medicinal Chemistry (of vanadium), oxido- and sulfidometal clusters, metal NMR.

Recent reviews and books:

- Vanadium enzyme models: D. Rehder, in: *Concepts and Models in Bioinorganic Chemistry*, Eds.: H.-B. Kraatz, N. Metzler-Nolte, Wiley-VCH, Weinheim **2006**, ch. 19.
- Vanadium-51 NMR: D. Rehder, T. Polenova, M. Bühl, Ann. Rep. NMR Spectrosc. **2007**, *62*, 49-114.
- Bioinorganic Vanadium Chemistry: D. Rehder, Wiley, Chichester **2008**.
- Is vanadium a more versatile target in the activity of primordial life forms than hitherto anticipated? D. Rehder**,** *Org. Biomol. Chem.*, **2008**, *6*, 957-964.



- Cellular cation transport studied by $^{6/7}$Li and ^{23}Na NMR in a porous Mo_{132} Keplerate. D. Rehder, E. T. K. Haupt, A. Müller, *Magn. Reson. Chem.* **2008**, *46*, 524-529.
- Chemistry in Space – From Interstellar Matter to the Origin of Life: D. Rehder, Wiley-VCH, Weinheim **2010**.
- Leben ohne Vanadium? - Bioanorganische Chemie des Vanadiums D. Rehder, *Chemie in Unserer Zeit* **2010**, in the press.

Research – General information

The main research activities focus on biological and medicinal aspects of vanadium, in part in cooperation with the group of Dr. Ebbe Nordlander, Lund University. Vanadium is a biologically relevant metal, employed by a variety of organisms (Fig. 1): It is in the active centre of two groups of enzymes, viz. vanadate-dependent haloperoxidases and vanadium-nitrogenases. In addition, vanadium is accumulated by certain life forms such as sea squirts (*Ascidiaceae*) and *Amanita* mushrooms, e.g., the fly agaric. More generally, vanadium appears to be involved in the regulation of phosphate-metabolising enzymes also in plants and animals; the insulin-mimetic potential of many vanadium compounds is related to this action.

Vanadium is also widely used to catalyse oxidation reactions; soluble "vanadium oxides" (polyoxidovanadates) are a more recent development in this field. Giant polyoxidomolybdates are presently investigated, by ^{7}Li and ^{23}Na NMR, in the context of their model character for the cellular cation (counter) transport (cooperation with Prof. Achim Müller, University of Bielefeld, and Dr. Erhard Haupt, Hamburg).

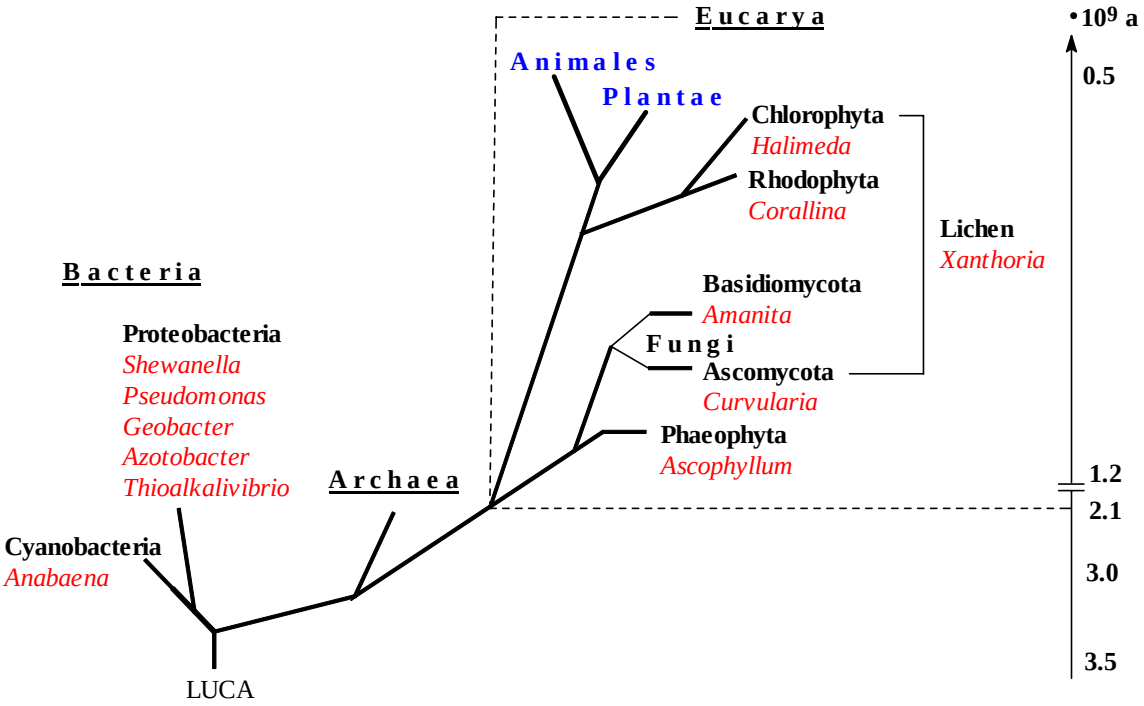


Figure 1. Phylogenetic tree, showing organisms, in red, which (can) use vanadium or depend (in blue) on trace amounts of vanadium. LUCA = last uniform common ancestor.

Specific Research Topics

(1) Vanadium in Biology and Catalysis

Our studies on the biological chemistry of vanadium are directed towards coordination compounds that model the active sites in vanadate-dependent haloperoxidases (present in marine algae, in fungi and lichen) and nitrogenases (in cyano- and proteobacteria), including investigations into the enzyme-substrate interaction. Fig. 2 shows reactions which are catalysed by haloperoxidases, *and* by structural/functional models of the active centre.

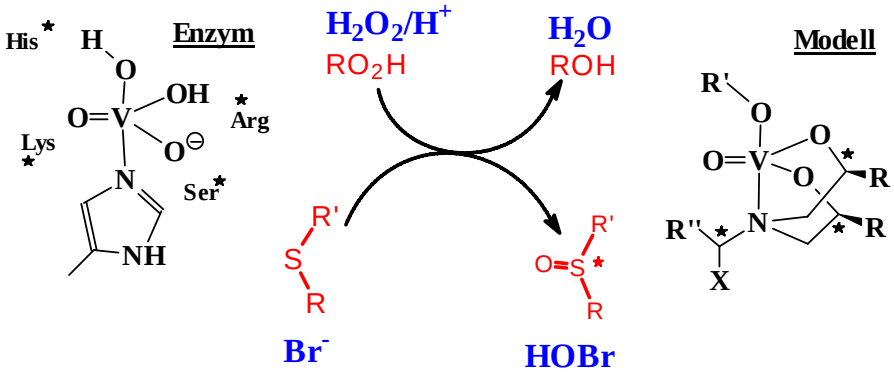


Figure 2. Modelling the enzymatic oxygenation of halide (blue) and sulfide (red). Asterisks indicate chiral centres.

Solution speciation studies of vanadate-ligand and vanadate-peroxide-ligand systems, carried out by multinuclear NMR plus potentiometry (co-operation with L. Pettersson, Umeå) or EPR plus potentiometry (cooperation with E. Garribba, Sassari, and T. Kiss, Szeged) complement investigations of the solid state structures, and help to elucidate the structure-function synergism.

Key publications

- Glycine- and sarcosine-based models of vanadate-dependent haloperoxidases in sulfoxygenation reactions: C. Wikete, P. Wu, G. Zampella, L. De Gioia, G. Licini, D. Rehder, *Inorg. Chem*. **2007**, *46*, 196-207.
- Sulfoxigenation catalysed by oxidovanadium complexes: P. Wu, C. Çelik, G. Santoni, J. Dallery and D. Rehder, *Eur. J. Inorg. Chem*. **2008**, 5203-5213.
- Modelling the sulfoxigenation activity of vanadate-dependent peroxidases, P. Wu, G. Santoni, M. Fröba, and D. Rehder, *Chemistry and Biodiversity* **2008**, *5*, 1913-1926.

(2) Medicinal Applications of Vanadium

The insulin-mimetic/enhancing behaviour of vanadium compounds, such as their ability to trigger glucose uptake by glucose-metabolising cells, or to inhibit lipolysis, has been investigated in the frame of a Europe-wide COST programme (COST D21-009-01) and in cooperation with the Pharmaceutical University in Kyoto (H. Sakurai). We synthesise vanadium compounds (Fig. 3, left) which minimise toxicity, optimise stability, intestinal absorption and cellular uptake, and mimic/enhance the anti-diabetic effects of insulin. – Vanadium complexes containing hydrazone-based ligands have been shown to exhibit antiamoebic activity and are thus potential drugs against amoebiasis (cooperation with M. Maurya, Roorkee, India); Fig. 3, centre and right.

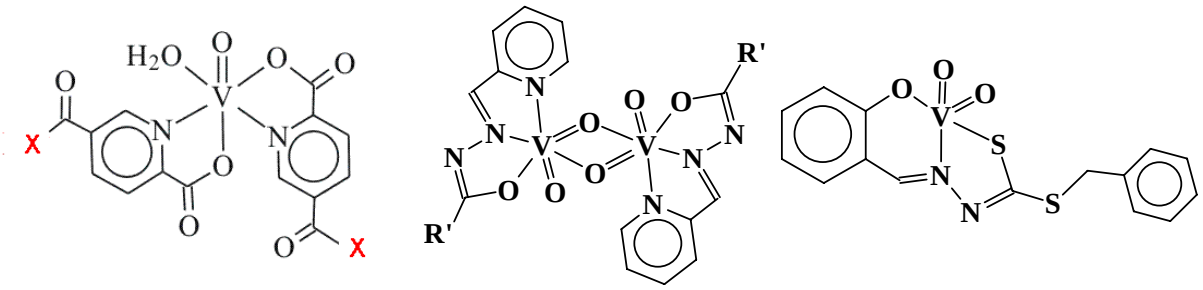


Figure 3. Left: A new family of effective insulin-mimetic vanadium compounds: *Bis*(1,5-dipicolinato)vanadium(IV). **X** can be OR (R= alkyl, galactosyl, inositolyl) or NHR (an amino acid residue). Centre and right: Compounds which exhibit *in vitro* anti-amoebic activity; R' = furanoyl or pridyl.

Key publications

- *In vitro* study of the insulin-mimetic behaviour of vanadium(IV, V) co-ordination compounds: D. Rehder, J. Costa Pessoa, C.F.G.C. Geraldes, T. Kabanos, T. Kiss, B. Meier, G. Micera, L. Pettersson, M. Rangel, A. Salifoglou, I. Turel, Dongren Wang; *J. Biol. Inorg. Chem*. **2002**, *7*, 384.
- Synthesis, characterisation, reactivity and *in vitro* antiamoebic activity of hydrazone based oxovanadium(IV), oxovanadium(V) and μ-*bis*(oxo)*bis*{oxovanadium(V)} complexes: M.R. Maurya, S. Agarwal, M. Abid, A. Azam, C. Bader, M. Ebel, D. Rehder, *Dalton Trans.* **2006**, 937.
- Aminoacid-derivatised picolinato-oxidovanadium(IV) complexes: Characterisation, speciation and *ex vivo* insulin-mimetic potential: H. Esbak, E. A. Enyedy, T. Kiss, Y. Yoshikawa, H. Sakurai, E. Garribba, D. Rehder, *J. Inorg. Biochem*. **2009**, *103*, 590-600.
- *Bis*- and *tris*(pyridyl)amine-oxidovanadium complexes: Characteristics and insulin-mimetic potential: J. Nilsson, E. Degerman, M. Haukka, G.C. Lisensky, E. Garribba, Y. Yoshikawa, H. Sakurai, E. A. Enyedy, T. Kiss, H. Esbak, D. Rehder, and E. Nordlander, *Dalton Trans*. 2009, 7902-7911.

(3) Clusters and Cell Models

The functionalisation, "shaping" and stabilisation of polyoxidometalate clusters by embedment into macro-cycles (such as the cryptand [212]-stabilised decavanadate in Fig. 4, left) allows for the design of “soluble oxides” as homogenous oxidation catalysts. Porous nano-capsules based on polyoxido-molybdates (Fig. 4, right) are models for the cellular transport of alkaline metal ions along ion channels. In cooperation with A. Müller (Bielefeld) and E. Haupt (Hamburg), these phenomena are investigated by multinuclear NMR (^{1}H, ^{7}Li, ^{14,15}N, ^{23}Na and ^{39}K NMR).

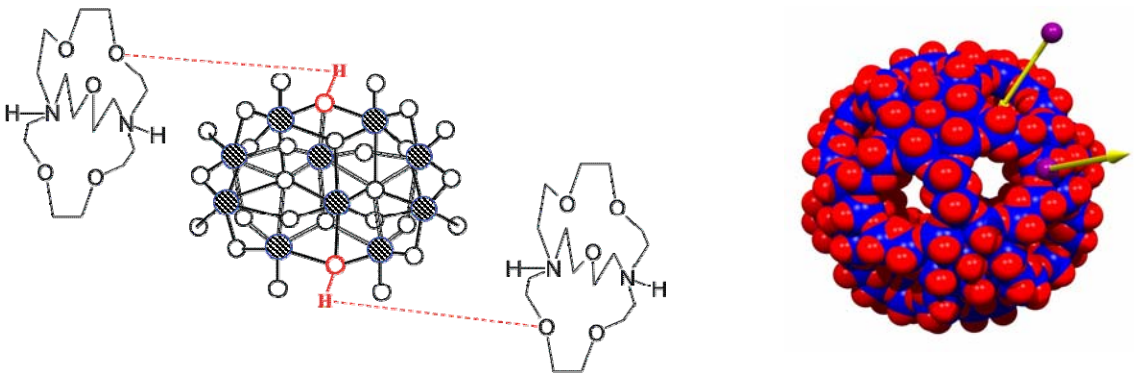


Figure 4. Left: Decavanadate $[H_2V_{10}O_{28}]^{4-}$ stabilised (through electrostatic and hydrogen bonds) by two cryptand cations $[C212H_2]^{2+}$. Right: Featuring Li^+ transport through the pores of a Mo_{132} polyoxidomolybdate.

Key publications

- Inorganic/organic hybrid salts derived from polyoxovanadates and macrocyclic (O_xN_2) cations: D. Wang, W. Zhang, C. Grüning, D. Rehder, *J. Molecul. Struct*. **2003**, *656*, 79-91.
- Counter cation transport modelled by porous spherical molybdenum-oxide based nano-capsules: D. Rehder, E.T.K. Haupt, H. Bögge, A. Müller, *Chem. Asian J*. **2006**, *1*, 76-81.
- Cellular cation transport studied by $^{6/7}$Li and ^{23}Na NMR in a porous Mo_{132} Keplerate type nano-capsule as model system: D. Rehder, E. T. K. Haupt and A. Müller, *Magn. Reson. Chem.* **2008**, *46*, 524-529.
- A spherical 24 butyrate aggregate with hydrophobic cavity in a capsule with flexible pores: Confinement effects and uptake-release equilibria at higher temperatures: C. Schäffer, H. Bögge, A. Merca, I. A. Weinstock, D. Rehder, E. T. K. Haupt and A. Müller, *Angew. Chem. Int. Ed*. **2009**, *48*, 8051-8056.

(4) Other Research Interests:

- (Transition) metal NMR, ^{51}V NMR in particular, as an analytical tool.
  [see, e.g.:Vanadium NMR spectroscopy, D. Rehder, T. Polenova and M. Bühl, *Ann. Rep. NMR Spectrosc*. **2007**, *62*, 49-114]
- Organometallic (vanadium and niobium) chemistry.
  [see, e.g.: Niobium-centered *C-C* Coupling of Isonitriles, C. Collazo, D. Rodewald, H. Schmidt, D. Rehder, *Organometallics* **15** (1996) 4884-4887; The unprecedented formation of molybdenum-centred 1,1,4,4,-tetrakis(phosphino)buta-1,3-diene from niobium-centred bis(phosphino)acetylene, D. Rodewald, D. Rehder, *Chem. Commun.* (1996), 1603-1604.]
- Chemical processes in interstellar gas and dust clouds, and their potential impact for the development of primordial life.
  [see: Chemistry in Space – From Interstellar Matter to the Origin of Life: D. Rehder, Wiley-VCH, Weinheim **2010**]

Main funding organisations:

German Research Society (DFG), EU (COST), German Academic Exchange Service (DAAD), Free und Hanseatic City of Hamburg.

Main current cooperations:

Hiromu Sakurai (Suzuka University, Japan), Achim Müller (Universität Bielefeld, Germany), Ebbe Nordlander (Lund Universitet, Sweden), Saroj Hazari and Tapashi Ghosh Roy (Chittagong University, Bangladesh), Eugenio Garribba (University of Sassari, Italy), Tamás Kiss (University of Szeged, Hungary), Tatyana Polenova (University of Delaware, Newark, USA).