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Journal of Inorganic Biochemistry 99 (2005) 1230–1237
JOURNAL OF Inorganic Biochemistry
www.elsevier.com/locate/jinorgbio

Biphenyl derived oxovanadium(IV) and copper(II) salen-type complexes – structure and redox tuning

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Received 8 October 2004; received in revised form 20 February 2005; accepted 21 February 2005
Available online 19 March 2005

Abstract

A series of vanadyl(IV) salen (*N*,*N*′-bis(salicylidene)ethylenediaminato)-type complexes (**1**–**4**) bearing phenyl or 2-hydroxyphenyl moieties have been prepared and characterized by means of mass spectrometry, infra-red, electron paramagnetic resonance (EPR), UV/Vis spectroscopy, cyclovoltammetry and X-ray crystallography. Their structures have been compared to their copper(II) analogs **5**–**8**. Hydrogen intralinkages have been observed in the crystral structure of **5**. The pendant hydroxy groups fine-tune the redox properties of the complexes. The catalytic activity in the oxygenation of ethyl phenyl sulfide to the corresponding sulfoxide was investigated. Results indicate that complex **1** bearing hydroxyphenyl subunits and a phenylene bridge is the most selective under these reaction conditions, with the smallest amount of the over-oxidized product, sulfone.

Keywords: Vanadium; Copper; Electrochemistry; Hydrogen bonding

1. Introduction

Both the catalytic abilities [1,2] and the important relation to biological problems [3] of vanadium coordination compounds lead to an increased interest in the chemistry of this early transition metal over the past decade. In the presence of hydrogen peroxide, organic hydroperoxides or molecular oxygen vanadium complexes are able to accelerate the oxygenation of aromatic and aliphatic substrates [4,5], promote the halogenation of organic compounds [6] and oxidize sulfides to the corresponding sulfoxides [7,8]. While vanadium dependent chloroperoxidases catalyze the oxidation of chloride, bromide and iodide, their bromoperoxidase analogs only catalyze the oxidation of the latter two halides. Since the vanadate(V) site in both metaloenzymes is the same, different catalytic activity must be tuned by the apoenzyme. In both enzymes the amino acid sequence and therefore the hydrogen bonding patterns vary [9].

The vanadium center in haloperoxidases of several sea-weed and lichen does not show any redox change during catalysis. However, for accumulation in the blood cells of some tunicates (ascidians or sea squirts) from sea water the metal ion is reduced from V(V) to V(IV) or V(III), probably by NADPH [10] or intracellular thiolates [11]. Cysteine methyl ester was found to reduce the metal ion from oxidation state +IV to +III [12].

Synthetic model complexes have contributed to the understanding of functional metal–functional group catalysis of phosphoryl-transfer enzymes [13,14] but this

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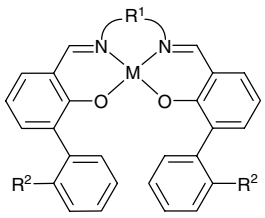
doi:10.1016/j.jinorgbio.2005.02.022



	M	R^1	R^2
1	VO	*o*-C_6H_4	OH
2	VO	*o*-C_6H_4	H
3	VO	CH_2CH_2	OH
4	VO	CH_2CH_2	H
5	Cu	*o*-C_6H_4	OH
6	Cu	*o*-C_6H_4	H
7	Cu	CH_2CH_2	OH
8	Cu	CH_2CH_2	H

Fig. 1. Schematic representation of the described complexes **1**–**8**.

feature is less well explored for artificial mimics of redox enzymes. Bifunctional zinc and titanium complexes [15] derived from biphenol or binaphthol have been described by Kozlowski and co-workers [16,17]. Molybdenum complexes with shifts of the redox potential caused by intramolecular hydrogen bonding have been described by Nakamura et al. [18].

In a previous work we demonstrated that tridentate Schiff base vanadium complexes with biphenyl subunits serve as suitable structural and functional models for vanadium dependent haloperoxidases. These complexes reveal intramolecular hydrogen bonding between non-coordinating hydroxyl groups and coordinated phenolate oxygen atoms. Improved activity of functionalized complexes compared to their unfunctionalized analogs has been observed for the oxygenation of sulfides [19]. Here we expand the study of the effect of second sphere hydroxyl groups on salen-type vanadium complexes which have been widely used in catalysis [20–22]. The secondary interactions affect the redox potentials of the metal site. A series of oxovanadium-(IV) and copper(II) salen- and salphen-type complexes derived from biphenyl were synthesized (Fig. 1; salen = *N*,*N*′-bis(salicylidene)ethylenediaminato; salphen = *N*,*N*′-bis(salicylidene)phenylenediaminato). As bridging diamine units, 1,2-diaminoethane and 1,2-diaminobenzene, were used. The compounds were characterized by mass spectrometry, IR and electron paramagnetic resonance (EPR) spectroscopy and their redox potentials were compared. Complexes **1**–**4** were applied as oxygenation catalysts in the reaction of ethyl phenyl sulfide with hydrogen peroxide to the corresponding sulfoxide.

2. Experimental

The starting materials were purchased from commercial sources (Acros, Aldrich, Fluka) and used without further purification. The precursor aldehydes 2,2′-dihydroxy-biphenyl-3-carbaldehyde and 2-hydroxy-biphenyl-3-carbaldehyde were prepared according to the literature procedures [23–25]. ^{1}H and ^{13}CN MR spectra were recorded on a Bruker DRX 200 instrument, chemical shifts are given in ppm referenced to the solvent peak of dimethyl sulfoxide (DMSO). Electrospray ionization (ESI) and high resolution mass spectra (HRMS) were recorded on a Waters ESI-Q-TOF Ultima API device, the sample concentration was 0.1 mM in acetonitrile (mobile phase: acetonitrile; flow rate: 50 μL min^{-1}). Infrared spectra (KBr pellets) were recorded on a BioRad Excalibur FTS 3000 spectrometer. Elemental analyses were conducted by the Microanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Heidelberg. The EPR spectra of frozen solutions were performed on a Bruker ESP 300E spectrometer at Xband (9.4 GHz) at 77 K. UV/Vis spectra were recorded on Specord S100 (Carl Zeiss Jena) in *N*,*N*-dimethylformamide (DMF). Cyclic voltammograms were obtained on a Perkin–Elmer 263A potentiostat at 25 °C in anhydrous DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH); scan speed 100 mV/s. Gas chromatographic and mass spectrometric (GC/MS) data were collected on an Agilent GC6890/MS5973 equipped with an HP-5MS capillary column (length: 30 m, inner diameter: 0.25 mm) with helium as carrier gas.

2.1. Preparations

The Schiff base ligands H_2L^1–H_2L^4 were prepared by addition of 1.0 mmol of the appropriate diamine to a stirred solution of 2.0 mmol of 2,2′-dihydroxy-biphenyl-3-carbaldehyde (H_2L^1, H_2L^2) or 2-hydroxy-biphenyl-3-carbaldehyde (H_2L^3, H_2L^4) in 10 mL of methanol. The resulting yellow solution was refluxed for 1 h and the solvent was removed under reduced pressure. The yellow-orange products were recrystallized from dichloromethane.

H_2L^1. Yield: 455 mg (91%). ^{1}H NMR (200 MHz, DMSO-d_6): $\delta = 6.76$–7.63 (m, 18H, H_{ar}), 9.00 (s, 2H, CHN), 9.26 (s, 2H, O′H), 13.41 (s, 2H, OH). Elemental analysis (%) calc. for $C_{32}H_{24}N_2O_4$: C, 76.78; H, 4.83; N, 5.60. Found: C, 76.95; H, 5.48; N, 5.30.

H_2L^2. Yield: 426 mg (91%). ^{1}H NMR (200 MHz, DMSO-d_6): $\delta = 6.65$–7.69 (m, 20H, H_{ar}), 9.05 (s, 2H, CHN), 13.93 (s, 2H, OH). High resolution mass spectra (HRMS) (ESI+): *m*/*z* calc. for $C_{32}H_{25}N_2O_2$ ($[M+H]^+$): 469.1916. Found: 469.1938.

H_2L^3. Yield: 348 mg (77%). ^{1}H NMR (200 MHz, DMSO-d_6): $\delta = 3.99$ (s, 4H, CH_2), 6.78–7.39 (m, 14H, H_{ar}), 8.66 (s, 2H, CHN), 9.87 (s, 2H, O′H), 13.71 (s, 2H, OH). ^{13}C{^{1}H} NMR (50 MHz, DMSO-d_6): $\delta = 58.12$, 118.40, 118.51, 126.83, 127.90, 128.61, 128.98, 131.33, 133.01, 137.29, 158.39, 167.48. HRMS