



New conjugates of superoxide dismutase/catalase mimetics with cyclodextrins

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ABSTRACT

Mimetics of antioxidant enzymes such as superoxide dismutases (SOD) or catalases are reported as potential new drugs able to reduce oxidative stress damage. In particular, manganese(III) complexes of salen-type ligands have been studied as both SOD and catalase mimetics. In this paper, we report the synthesis of two novel conjugates of salen-type ligands with the β -cyclodextrin, the 6-deoxy-6-[(5-cyanoamidopropyl)(1,2-diamino)(*N,N'*-bis(salicylidene))]- β -cyclodextrin and the 6-deoxy-6-[(5-cyanoamidopropyl)(1,2-diamino)(*N,N'*-bis(3-methoxysalicylidene))]- β -cyclodextrin, their spectroscopic characterization, and the synthesis and the characterization of their manganese(III) complexes. The SOD-like activity of the metal complexes was investigated by the indirect Fridovich method. The catalase like activity was tested using a Clark-type oxygen electrode. The peroxidase activity was tested using the ABTS (2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid)) assay. The glycoconjugation of salen-manganese(III) complexes yields compounds with enhanced SOD activity. These complexes also show catalase and peroxidase activities higher than the simple salen complexes (ELUK 113 and ELUK 108).

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1. Introduction

Antioxidant compounds have been considered as therapeutic agents for a variety of disorders associated with the oxidative stress. In fact, oxidative stress processes have been implicated in a variety of detrimental health conditions including ischemia-reperfusion injury [1], chronic inflammation [2], diabetes [3], neurodegenerative disease [4,5], cancer [6] and aging [7].

In this perspective, mimetics of antioxidant enzymes such as superoxide dismutases (SODs) or catalases are presented as potential new drugs to prevent oxidative stress damages [2,8,9]. Among these systems, metal complexes of manganese(II) or (III) seem to be among the most widely investigated molecules [10]. Particularly, the manganese(III) complexes of [15]aneN₅ (1,4,7,10,13-pentaza-cyclopentadecane) type ligands [10–13] are reported in the literature as SOD mimetics and the manganese (III) complexes of porphyrins [14,15] or salen (H₂salen = *N,N'*-bis(salicylidene)-ethylenediamine) type ligands [9,16–18] have been reported as both SOD and catalase mimetics.

The molecular mechanism by which the manganese complexes work is still not entirely understood, but a number of different hypotheses based on experiments *in vivo* have been made. The SOD and catalase activities of these molecules have been considered as the main reason for their tested pharmacological activity. Investigations have been carried out in order to understand the action mechanism [19].

As regards the salen-manganese(III) complexes, generally the SOD-like activity, investigated *in vitro*, is considered to be the operative mechanism *in vivo* [8,20,21]. It has been shown that salen complexes exert beneficial effects in several *in vitro* and *in vivo* animal models of human diseases which involve oxidative stress ranging from Alzheimer's [22,23], Parkinson's [24], Prion Disease [25] and motor neuron disease to multiple sclerosis and excitotoxic neuronal injury [26]. The flavonoid compounds have also been shown to afford protection from ischemia-reperfusion injury of the brain [20], heart [27] and kidney [28,29] in animal models.

In the case of Mn(III) to salen derivatives, the mechanism for the dismutation of O₂^{•−} involves the reduction of Mn(III) to Mn(II) by O₂^{•−}, which is oxidized to O₂. The Mn(II) is oxidized back to Mn(III) by another molecule of O₂^{•−} yielding H₂O₂ [10]:



The mechanism by which the Mn-salen acts as a catalase mimetic involves the oxidation of Mn(III) to oxomanganese by H₂O₂, releasing water [20]. The oxomanganese is then reduced to Mn(III) by another hydrogen peroxide molecule to form oxygen and water:



Starting from the most simple system [Mn(salen)(X)] (X = Cl[−] or CH₃COO[−], code name ELUK 8 and ELUK 108, respectively), other modified salen complexes have been investigated (Chart 1). The water solubility of this class of molecules is not very high, as has been reported by several authors [10].

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Cyclodextrins In Chromatography

Zhengyu Jin



Cyclodextrins In Chromatography:

Cyclodextrins in Chromatography Tibor Cserhádi, Esther Forgacs, 2007-10-31 Cyclodextrins can form complexes with a wide variety of organic and inorganic compounds a property which can prove useful when trying to separate complex mixtures This book provides an up to date and critical evaluation of the application of cyclodextrins in many fields of chromatography including thin layer gas liquid high performance liquid and supercritical fluid chromatography capillary electrophoresis and isotacophoresis Whilst mainly practical in nature the book also looks briefly at the theoretical background for the various techniques Any professional working with chromatography will welcome this unique book as both a practical compilation of methods and a source of reference to the literature regarding the use and impact of cyclodextrins in chromatography

Modified Cyclodextrins for Chiral Separation Weihua Tang, Siu-Choon Ng, Dongping Sun, 2013-05-24 Modified Cyclodextrins for Chiral Separation offers a review of the latest advances in developing modified cyclodextrins as chiral selectors for various chromatographic and electromigration techniques Over the years many descriptions of chiral separation have appeared in academic journals and books but most of them have been devoted to either the development of analytical methods and protocols or the summary of different chiral selectors including cyclodextrins for chiral separation applications This is in marked contrast to this volume which focuses on the research endeavors concerning the development of cyclodextrin derivatives specifically as either chiral mobile phases for capillary electrophoresis or chiral stationary phases for various chromatographic techniques including gas chromatography or high performance liquid chromatography and supercritical fluid chromatography The ongoing thread in this book is the synthesis of structurally defined cyclodextrin derivatives and their applications in enantiomer separation by means of different analytical techniques Modified Cyclodextrins for Chiral Separation is intended for those who are interested in expanding their knowledge of cyclodextrin chemistry and chiral separation and in what cyclodextrin modification can be made to suit the needs of chiral selectors for different analytical techniques It primarily focuses on the state of the art cyclodextrin chemistry which is the basis for all chiral selectors used in these chiral separation techniques Weihua Tang PhD is a professor at the Key Laboratory of Soft Chemistry and Functional Materials Ministry of Education Nanjing University of Science and Technology China Siu Choon Ng PhD is a professor at the Division of Chemical and Biomedical Engineering School of Chemical and Biomedical Engineering Nanyang Technological University Singapore Dongping Sun PhD is a professor at the Key Laboratory of Soft Chemistry and Functional Materials Ministry of Education Nanjing University of Science and Technology China

The History of Cyclodextrins Grégorio Crini, Sophie Fourmentin, Eric Lichtfouse, 2020-09-29 This book presents the historical development of Cyclodextrins by scientists who have made outstanding contribution to the field Cyclodextrins are safe cage like molecules that have found major applications in many industrial sectors such as medicine food agriculture environment and chemistry

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Cyclodextrin Fundamentals, Reactivity and Analysis Sophie Fourmentin, Grégorio Crini, Eric Lichtfouse, 2018-04-26 This book is the first volume of two volumes on cyclodextrins published in the series Environmental Chemistry for a Sustainable World After a brief description of the cyclodextrin fundamentals the first chapter by Grégorio Crini et al provides an overview of cyclodextrin research during the last 5 years The second chapter by Michal ezanka discusses the synthesis of novel cyclodextrin systems by selective modifications Then Eric Monflier et al describes the synthesis of nanostructured porous materials based on cyclodextrins and applications in heterogeneous catalysis and photocatalysis The use of thermal analyses for assessing cyclodextrin inclusion complexes is reviewed in chapter 4 by Daniel H d rug et al Experimental methods for measuring binding constants of cyclodextrin inclusion compounds are presented by David Landy The second volume reviews cyclodextrin applications in medicine food environment and liquid crystals

Encyclopedia of Chromatography Jack Cazes, 2009-10-12 Thoroughly revised and expanded this third edition offers illustrative tables and figures to clarify technical points in the articles and provides a valuable reader friendly reference for all those who employ chromatographic methods for analysis of complex mixtures of substances An authoritative source of information this introductory guide to specific chromatographic techniques and theory discusses the relevant science and technology offering key references for analyzing specific chemicals and applications in industry and focusing on emerging technologies and uses

Cyclodextrin Chemistry: Preparation And Application Zhengyu Jin, 2013-10-07 Cyclodextrin Chemistry covers the preparation of cyclodextrins and cyclodextrin derivatives CDs and their applications in industrial and non industrial areas An overall theme in the book is the screening of cyclodextrin glycosyltransferase CGTase the preparation of sugar branched cyclodextrins and CDs and the use of CDs for reconstructing various supermolecule systems The specific content also includes preparation methods spectroscopy techniques for CDs analysis and potential applications in food packaging nutrient fortification medicine cosmetics textiles chemicals feed agriculture and environment It summarizes the research merit of CDs in the past twenty years and also emphasizes hot topics and important areas of cyclodextrin chemistry in the future

Cyclodextrin Poonam Arora, Neelima Dhingra, 2018-04-18 The book is devoted to the highly versatile and potential ingredient Cyclodextrin a family of cyclic oligosaccharides composed of 1 4 linked glucopyranose subunits Its molecular complexation phenomena and negligible cytotoxic effects attribute toward its application such as in

pharmaceuticals cosmetics food agriculture textile separation process analytical methods catalysis environment protection and diagnostics Efforts have also been made to concentrate on recent research outcomes along with future prospects of cyclodextrins to attract the interest of scientists from the industry and academia The contributions of the authors are greatly acknowledged without which this compilation would not have been possible **Cyclodextrins and Their Complexes**

Helena Dodziuk,2006-08-21 Offering comprehensive and up to date know how in one compact book an experienced editor and top authors cover every aspect of these important molecules from molecular recognition to cyclodextrins as enzyme models Chapters include reactivity and chemistry chromatography X ray NMR plus other physicochemical methods as well as model calculations rotaxane and catenane structures and applications in the pharmaceutical industry The book also discusses other applications such as in the cosmetics toiletries textile and wrapping industries agrochemistry electrochemical sensors and devices A must for everyone working with these substances **Cyclodextrin Technology** J. Szejtli,2013-04-17

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are an extremely versatile class of chemicals highly prized for their ability to incorporate a plethora of organic inorganic and biologic guest molecules into their hydrophobic cavities and form host guest inclusion complexes As excellent molecular receptors they have long been exploited in many important industries such as food and agriculture pharmaceuticals cosmetics textiles analytical chemistry and enzyme mimics Researchers technicians and application specialists in many industries will appreciate this handy volume that systematically discusses how cyclodextrins are applied in their industries Special attention is devoted to the preparation of inclusion complexes novel properties of the resultant complexes and details on applying those properties to industry *Gas Chromatographic Enantiomer Separation with Modified Cyclodextrins*

Wilfried A. König,1992 *Encyclopedia of Chromatography (Print)* Jack Cazes,2001-06-29 This practical single volume source collects up to date information on chromatographic techniques and methodologies for the solution of analytical and preparative problems applicable across a broad spectrum of disciplines including biotechnology pharmaceuticals environmental sciences polymers food additives and nutrients pathology toxicology fossil fuels and nuclear chemistry It highlights real world applications easy to read fundamentals of problem solving and material identification methods and detailed references Written by over 180 esteemed international authorities and containing over 300 chapters 2600 works cited and 1000 drawings equations tables and photographs the *Encyclopedia of Chromatography* covers high performance liquid thin layer gas affinity countercurrent supercritical fluid gel permeation and size exclusion chromatographies as well as

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Komiyama, 2012-12-06 Chemistry was at one time completely described in terms of collision theory in which one molecule collided with another sometimes producing reaction Then came the realization that enzymes which are highly efficient catalysts work by way of prior complexation often stereospecific which is then followed by chemical reaction Thus systems that exhibit host guest relationships i.e. that show complexing are being looked at an ever increasing frequency The cyclodextrins are the first and probably the most important example of compounds that exhibit complex formation This is a book about the cyclodextrins There are of course other compounds that exhibit host guest relationships and thus bind other organic molecules but so far they have not achieved the importance of the cyclodextrins By their name it is obvious that cyclodextrins are cyclic compounds The complexes that they form are therefore cyclic inclusion complexes Because the complexes are cyclic in nature complexation can be very strong as opposed to 1:1 complex electrostatic or apolar complexes in which complex formation is two dimensional rather than three dimensional Cyclodextrins turn out to be excellent models of enzymes This is probably not fortuitous because they were first sought since it was discovered that the principal binding in the enzyme chymotrypsin was a cyclic inclusion complex Cyclodextrins can do more than form cyclic inclusion complexes they can catalyze as well But catalysis always occurs after complex formation **HPLC Method Development for**

Pharmaceuticals Satinder Ahuja, Henrik Rasmussen, 2011-09-21 High pressure or high performance liquid chromatography HPLC is the method of choice for checking purity of new drug candidates monitoring changes during scale up or revision of synthetic procedures evaluating new formulations and running control assurance of the final drug product HPLC Method Development for Pharmaceuticals provides an extensive overview of modern HPLC method development that addresses these unique concerns Includes a review and update of the current state of the art and science of HPLC including theory modes of HPLC column chemistry retention mechanisms chiral separations modern instrumentation including ultrahigh pressure systems and sample preparation Emphasis has been placed on implementation in a pharmaceutical setting and on providing a practical perspective HPLC Method Development for Pharmaceuticals is intended to be particularly useful for both novice and experienced HPLC method development chemists in the pharmaceutical industry and for managers who are seeking to update their knowledge Covers the requirements for HPLC in a pharmaceutical setting including strategies for software and hardware validation to allow for use in a regulated laboratory Provides an overview of the pharmaceutical development process clinical phases chemical and pharmaceutical development activities Discusses how HPLC is used in each phase of pharmaceutical development and how methods are developed to support activities in each phase **CRC Handbook of Basic Tables for Chemical Analysis** Thomas J. Bruno, Paris D.N. Svoronos, 2010-12-13 Winner of an Outstanding Academic Title Award for 2011 Researchers in organic chemistry chemical engineering pharmaceutical science forensics and

environmental science make routine use of chemical analysis but the information these researchers need is often scattered in different sources and difficult to access The CRC Handbook of Basic Tables **Chiral Separations By Liquid**

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