



# 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  $\beta$ -cyclodextrin, the 6-deoxy-6-[(5-cyanoamidopropyl)(1,2-diamino)(*N,N'*-bis(salicylidene))]- $\beta$ -cyclodextrin and the 6-deoxy-6-[(5-cyanoamidopropyl)(1,2-diamino)(*N,N'*-bis(3-methoxysalicylidene))]- $\beta$ -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(II) complexes of [15]aneN<sub>5</sub> (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 (H<sub>2</sub>salen = *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 O<sub>2</sub><sup>•−</sup> involves the reduction of Mn(III) to Mn(II) by O<sub>2</sub><sup>•−</sup>, which is oxidized to O<sub>2</sub>. The Mn(II) is oxidized back to Mn(III) by another molecule of O<sub>2</sub><sup>•−</sup> yielding H<sub>2</sub>O<sub>2</sub> [10]:



The mechanism by which the Mn-salen acts as a catalase mimetic involves the oxidation of Mn(III) to oxomanganese by H<sub>2</sub>O<sub>2</sub>, 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<sup>−</sup> or CH<sub>3</sub>COO<sup>−</sup>, 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

**Zheng-Yu 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

## **Cyclodextrins:**

**Preparation And Application In Industry** Zhengyu Jin, 2018-01-10 Cyclodextrins 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

**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 *Cyclodextrin Technology* J. Szejtli, 1988-08-31 **Cyclodextrin Chemistry** Zheng-Yu Jin, 2013 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 Contents Introduction Jun Rong Huang Hai Ning Zhuang and Zheng Yu Jin Enzymes in Preparing Cyclodextrins Sheng Jun Wu Xiu Ting Hu Jin Moon Kim and Jing Chen Preparation and Analysis of Cyclodextrin An Wei Cheng Jin Peng Wang and Zheng Yu Jin Preparation of Branched Cyclodextrins Xing Zhou Yao Qi Tian and Zheng Yu Jin Preparation and Analysis of Cyclodextrin Derivatives Chao Yuan Yu Xiang Bai and Zheng Yu Jin Basic Application of Cyclodextrins in Supermolecule Chemistry Tao Feng Ai Quan Jiao and Zheng Yu Jin Use of Cyclodextrins in Food Pharmaceutical and Cosmetic Industries Yao Qi Tian Xing Zhou and Zheng Yu Jin Application of Cyclodextrins in Non industrial Areas Xue Hong Li and Zheng Yu Jin Readership Researchers and technicians in food pharmaceutical cosmetic and chemical industries as well as in non industry areas such as agriculture and environmental engineering supermolecule and analytical chemistry **Thin-layer Chromatography on Cyclodextrins** Nantana Sittichai, 1974 **Gas Chromatographic Enantiomer Separation with Modified Cyclodextrins** Wilfried A. König, 1992 **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 *Journal of Chromatography* ,2002 Proceedings of the Ninth International Symposium on Cyclodextrins Juan José Torres Labandeira, José Luis Vila-Jato, 1999-08-31 This volume contains the proceedings of the Ninth International Symposium on Cyclodextrins held in Santiago de Compostela Spain May 31 June 3 1998 The papers collected represent a summary of the last two years achievements in the application of cyclodextrins in such diverse fields as pharmaceuticals biotechnology textiles chromatography and environmental sciences Highlights Chiral selection of chemicals nuclear waste management cyclodextrins in nasal drug delivery cyclodextrins in pulmonary drug delivery cyclodextrins as pharmaceutical excipients pharmacokinetics stabilization of drugs by cyclodextrins structural characterization of cyclodextrin complexes by nuclear magnetic resonance and molecular modeling artificial receptors large cyclodextrins cyclodextrins as enzyme models new cyclodextrin derivatives and potentials Audience This book will be of interest to researchers whose work involves biotechnology pharmaceuticals food and chemicals and chromatographic methods as well as fundamental cyclodextrin research **Chiral Separations by Liquid Chromatography** Satinder Ahuja, 1991 A definitive reference for researchers working on problems involving chirality Presenting state of the art information this volume covers all the major modes of separation and offers contributions from the leading researchers who developed these techniques Four chapters provide a detailed review of the commonly used columns brush type cyclodextrin polysaccharide carbonate and protein Many of the papers focus on HPLC a technique which is also ideally suited for large scale preparation of optical isomers In addition the volume provides significant discussion on the use of chiral discriminators or selectors

**Cyclodextrins and Their Inclusion Complexes** József Szejtli, 1982 Chiral Chromatography Thomas E. Beesley, Raymond P. W. Scott, 1999-01-26 Chiral Chromatography Thomas E Beesley Advanced Separation Technologies Inc Whippany New Jersey USA Raymond P W Scott Chemistry Department Georgetown University Washington DC USA and Chemistry Department Birkbeck College University of London UK Analytical techniques based on separation processes such as chromatography and electrophoresis are finding a growing range of applications in chemical pharmaceutical and clinical laboratories The Wiley Separation Science Series provides the analyst in these laboratories with well focused books covering individual techniques so that they can be applied more efficiently and effectively to contemporary analytical problems The different enantiomers of a drug can exhibit widely different physiological activity in degree and nature As a result the separation and identification of enantiomers is now a very important analytical problem and chiral chromatography is the natural technique to apply to the resolution of such mixtures Chiral Chromatography provides the reader with a basic

understanding of the nature of chromatographic separations and relates the principles specifically to the separation of enantiomers The following information is included chiral separations involving both gas and liquid chromatography descriptions of the apparatus used for both techniques detailed discussion on the retention mechanism that results in chiral selectivity the structure and synthesis of a wide range of chirally active stationary phases used in both gas and liquid chromatography preparative applications for large scale purification of enantiomers applications of capillary electrophoresis and capillary electrochromatography In addition to the above a large number of examples of the separation of both commercially and physiologically interesting chiral mixtures are given as is a detailed discussion on the mechanism of selectivity of each example Thomas Beesley was founder and is the CEO for a leading manufacturer of chiral stationary phases and has published papers on TLC HPLC and chiral separations involving cyclodextrins He has also coauthored papers with Daniel W Armstrong an expert on modern cyclodextrin columns Raymond Scott has worked in the field of separation science for over 40 years and has contributed extensively to the development of both gas and liquid chromatography publishing over 160 papers on the subjects

**Chromatographic Analysis of Pharmaceuticals** John A. Adamovics, 1990

**Cyclodextrin Chemistry** Myron L. Bender, Makoto Komiyama, 1978 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

**Journal of Scientific and Industrial Research**, 1994 Planar Chromatography in the Life Sciences Joseph C.

Touchstone, 1990-02-08 Planar Chromatography in the Life Sciences Edited by Joseph C Touchstone This assemblage of studies from international researchers in planar or thin layer chromatography describes the many advances that have placed the technique so much in the vanguard of materials analysis research Chapters describe currents in planar chromatography use of bonded phases in planar chromatography immunostaining in TLC TLC in pharmaceutical research determination of

ascorbic acid by TLC densitometry isotope scanning in TLC and more This addition to the outstanding Wiley Series in Chemical Analysis is a reference staple for analytical chemists in academia and industry as well as scientists in related fields and students of chemistry and the life sciences 1990 0 471 50109 3 199 pp     *New Chromophores and Chromatography Methods for Protein Bioconjugation Reactions* Trung Nguyễn, 2006     **Proceedings of the Eighth International Symposium on Cyclodextrins** J. Szejtli, L. Szenté, 2012-12-06 This volume contains the proceedings of the Eighth International Symposium on Cyclodextrins held in Budapest Hungary March 31 April 2 1996 The 147 papers collected here are milestones in the exponentially increasing cyclodextrin literature and represent a summary of the last two years achievement in this field with applications in such diverse disciplines as pharmaceuticals food cosmetics textiles plastics and chromatography Some highlights lipophilicity profiles of cyclodextrins by computer molecular graphics recent toxicological studies on cyclodextrins Buckminsterfullerene cyclodextrin complexes hydroxypropyl beta cyclodextrin pharmacokinetics and toxicology peracylated cyclodextrins as drug carriers cyclodextrins in nasal drug delivery textile fibre surface modification by a reactive cyclodextrin cyclodextrin containing fabric care products drug targeting by cyclodextrin dimers for photodynamic cancer therapy cyclodextrins in ophthalmologic drugs new cyclodextrin derivatives and their potentials Audience This book will be of interest to researchers whose work involves pharmaceuticals food chemicals and flavours food additives chromatographic methods and biotechnology as well as fundamental cyclodextrin research

## Decoding **Cyclodestrins In Chromatography**: Revealing the Captivating Potential of Verbal Expression

In a period characterized by interconnectedness and an insatiable thirst for knowledge, the captivating potential of verbal expression has emerged as a formidable force. Its ability to evoke sentiments, stimulate introspection, and incite profound transformations is genuinely awe-inspiring. Within the pages of "**Cyclodestrins In Chromatography**," a mesmerizing literary creation penned by way of a celebrated wordsmith, readers set about an enlightening odyssey, unraveling the intricate significance of language and its enduring effect on our lives. In this appraisal, we shall explore the book's central themes, evaluate its distinctive writing style, and gauge its pervasive influence on the hearts and minds of its readership.

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