Inorganica Chimica Acta 450 (2016) 101–111

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Hyperbranched polyester poly(3-diethylaminepropionate)s and their copper(II) complexes: Synthesis, characterization and biological investigation

Marianna P. Kutyreva [a,*], Alfiya R. Gataulina [a], Gennadiy A. Kutyrev [b], Nikolay A. Ulakhovich [a], Tom Newman [c], Elvira M. Khasanova [a], Olga V. Bondar [a], Svetlana V. Yurtaeva [d], Sufia A. Ziganshina [d], Elena V. Khaldeeva [e]

[a] Kazan Federal University, 18 Kremlyovskaya St., 420008 Kazan, Russian Federation
[b] Kazan National Research Technological University, 68 K. Marx St., 420015 Kazan, Russian Federation
[c] Aurora Fine Chemicals LLC, 7929 Silverton Ave., Suite 609, San Diego, CA 92126, USA
[d] Zavoisky Physical-Technical Institute, Russian Academy of Sciences, 10/7 Sibirsky Tract St., 420029 Kazan, Russian Federation
[e] Kazan Research Institute of Epidemiology and Microbiology, 67 Bolshaya Krasnaya St., 420015 Kazan, Russian Federation

ARTICLE INFO

Article history:
Received 17 January 2016
Received in revised form 6 April 2016
Accepted 7 April 2016
Available online 20 May 2016

Keywords:
Hyperbranched polyesters
Poly-3-diethylaminepropionates
Cu(II) complex
EPR spectra
Ionization
Biological activity

ABSTRACT

New polydentate ligands based on hyperbranched second and third generation polyesters containing terminal (3-diethylamino)propionate fragments and their polynuclear copper(II) complexes were synthesized and characterized by spectroscopic methods. The acid-base properties spectroscopy determined that the functionalization degree of the diethylamine-modified hyperbranched polyesters ($\mathbf{L^I}$, $\mathbf{L^{II}}$) increases from the second (56%) to third (81%) generation. The polynuclear complexes Cu(II)–$\mathbf{L^I}$ and Cu(II)–$\mathbf{L^{II}}$ were observed. A coordination site of the complexes contains paramagnetic fragment $CuN_2O_2Solv_2$ where Solv is H_2O or DMSO. The hyperbranched poly(ester amine) of the third generation have strong antifungal activity against *Aspergillus fumigatus* culture, and its metal complex is active against *Candida albicans* culture.

1. Introduction

The chemistry of multinuclear coordination metal complexes, especially of coupled systems is of special interest in various fields of science. The main reason probably is due to the phenomenon of interaction between metal centers lying at the crossover point of two widely separated areas, namely the physics of the magnetic materials and the role of polynuclear reaction sites in biological processes [1–3].

Hyperbranched polymers (HBP) can be used for the production of new advanced materials based on polynuclear metal complexes demonstrating biological activity. HBP macromolecules are highly soluble in most organic solvents and exhibit high specific concentration of surface groups and a dimensionally unbound core (nucleus). It justifies the application of HBP as nanoplatforms and nanocontainers for various high- and low-molecular substances [4–6]. Non-toxic biodegradable hyperbranched polyester polyols (HBPO) can be used as a basic structure for the synthesis of new hybrid organic–inorganic materials with the use of an approach comprising sequential functionalization by organic coordinating fragments and metal ions [5,7–9].

The modification of an HBPO platform by nitrogen-containing fragments is more suitable for the production of water-soluble low-toxic biodegradable coordinately active macromolecular structures. The degradation capability of a polyester structure and terminal nitrogen-containing fragments can be provided by hydrolysis and aminolysis processes [10–15].

The primary amines are the most frequently used compounds for the amino-modification of HBP and dendrimers [2,3,16]. However, their presence results in a high cytotoxicity of derivatives for many cellular systems [17]. Functionalization by tertiary amines provides a significant toxicity reduction of HBPO amine derivatives [18]. Another toxicity reduction way is the addition of biophilic metal ions at the second stage of modification. This approach is rather well represented for Cu(II) and Zn(II) organometallic complexes with various generations polypropylenimine and poly(amidoamine) dendrimers [9,19,20]. Meanwhile, metal ions can

* Corresponding author.
E-mail address: mkutyreva@mail.ru (M.P. Kutyreva).

http://dx.doi.org/10.1016/j.ica.2016.04.013
0020-1693/