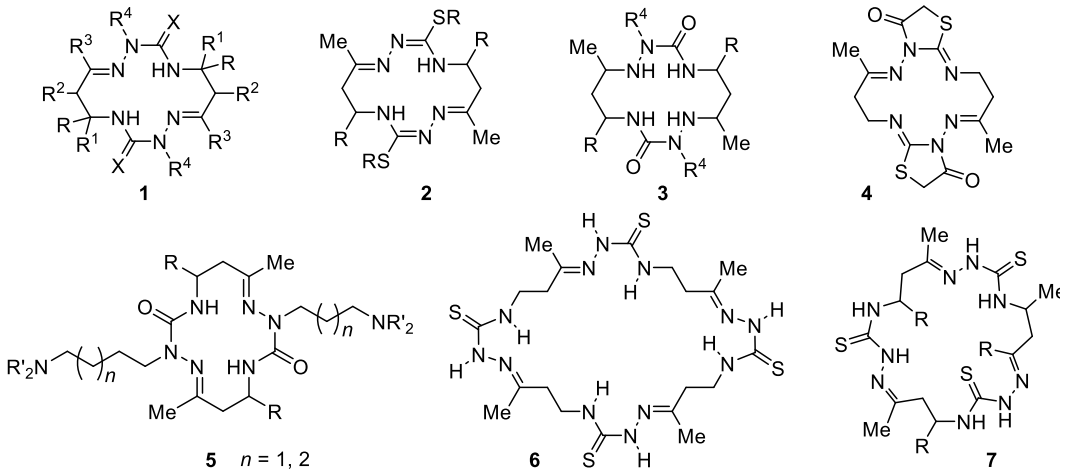
NOVEL (THIO)SEMICARBAZONE-BASED POLYAZA MACROCYCLES: SYNTHESIS, REACTIVITY, AND METAL-BINDING CAPACITY

Shutalev A. D., Fesenko A. A., Kuvakin A. S., Yankov A. N.

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow

e-mail: shad@ioc.ac.ru

Polyaza macrocycles (PAM) are of considerable importance in various fields of chemistry, biochemistry, medicine, and material science. A unique feature of PAM is their ability to bind different inorganic and organic cations, anions, and neutral molecules. Due to the great interest in the chemistry and applications of PAM, a huge number of these heterocycles have been synthesized to date. Among them, 14-membered polyaza macrocycles with the N_4 binding site are of special importance. At the same time, tetradentate 14-membered 1,2,4,8,9,11-hexaaza macrocycles remain unknown. The present work describes general preparative approaches from simple, readily available precursors to a wide range of these heterocycles, in particular, 14-membered cyclic bis-(thio)semicarbazones **1** (X = O, S) including scorpionands **5**, bis-isothiosemicarbazones **2**, **4**, and bis-semicarbazides **3**. Under certain conditions, 28- and 21-membered cyclic thiosemicarbazones **6** and **7** were also prepared.



Plausible pathways for the macrocyclizations to give **1**, **6**, and **7** were proposed based on our experimental data and DFT calculations. Reactivity of macrocycles **1**-**5** and their binding capacity towards various metal cations were studied.

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