

ビス(サイクレン)・二核亜鉛(II)とマロン酸が 形成する錯体の構造解析

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Bull. Chem. Soc. Jpn. **83**(3), 267-272 (2010)

Dibridged Bis(Zn²⁺-cyclen): A Novel Host Molecule of Malonate Dianion in Aqueous Solution

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ABSTRACT: A dinuclear zinc(II) complex, *m,m*-bis(Zn²⁺-cyclen) was synthesized as a novel host molecule for a malonate dianion. The dizinc(II) complex has two zinc(II)-cyclen moieties (cyclen = 1,4,7,10-tetraazacyclododecane) connected through two *m*-xylene bridges. The 1:1 association constant of log *K* ($K = \{[\text{malonate-bound } m,m\text{-bis}(\text{Zn}^{2+}\text{-cyclen})]/[m,m\text{-bis}(\text{Zn}^{2+}\text{-cyclen})][\text{malonate}]\}/M^{-1}$) was determined to be 3.6 by potentiometric pH titration at 25 °C with *I* = 0.10 M (NaNO₃) in aqueous solution. The H/D exchange reaction of methylene hydrogen atoms of malonate dianion was accelerated by *m,m*-bis(Zn²⁺-cyclen) in D₂O. The half-life was determined to be 80 min for a 1:1 mixture (2 mM) of malonate and *m,m*-bis(Zn²⁺-cyclen) at 25 °C and pD 7. From an aqueous solution of equimolar malonate and *m,m*-bis(Zn²⁺-cyclen) however, a cyclic 2:2 malonate/*m,m*-bis(Zn²⁺-cyclen) complex was isolated. The structure was confirmed by X-ray crystallography.

抄録 サイクレン-亜鉛錯体の新規化合物を合成して、水溶液中でマロン酸と1:1の相互作用を示すことを、¹H-NMR、¹³C-NMRとpH滴定で確認した。そして、マロン酸のメチレンプロトンの重水置換が速くなることを見出した。そして、サイクレン-亜鉛錯体とマロン酸から得られる錯体のX線構造解析を行ったところ、2:2の組成であることが判った。

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