Bis(Zn^{II}-cyclen)錯体による水溶液中での バルビタールの認識

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Bis(ZnII-cyclen) Complex as a Novel Receptor of Barbiturates in Aqueous Solution

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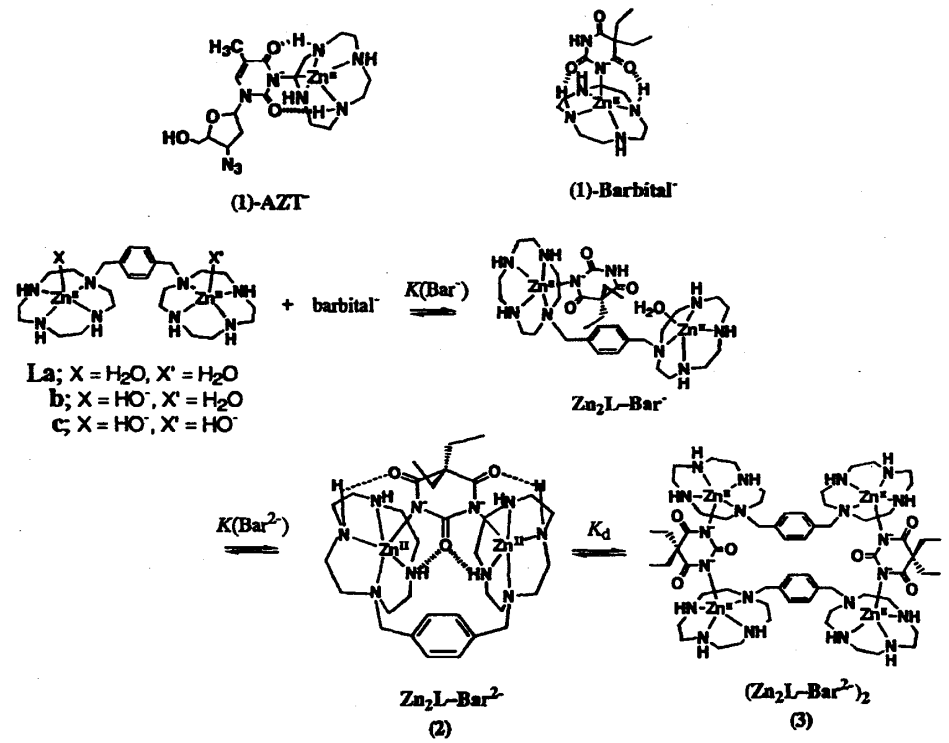
A new bis-zinc(II) receptor(Zn_2L), which has two macrocyclic 12-membered tetraamine (cyclen) Zn^{II} complexes connected through a *p*-xylenebridge, has been synthesized as a novel host molecule to recognize barubiturates (such as barbital (bar)) in aqueous solution. Each of the zinc(II) ions in the bis-zinc(II) receptor was originally intended to match the dianionic barbital anion (bar^{2-}) with supplementary hydrogen bonds between the cyclen NH's and the threee carbonyl oxygens in complementary positions to yield a 1:1 complex, Zn_2L-bar^{2-}. From an aqueous solution of equimolar Zn_2L and barbital at pH 8, however, a cyclic 2:2 complex, $(Zn_2L\text{-}bar^{2-})_2$, was isolated and characterized by X-ray crystal analysis. The NMR study in 10% (v/v) D_2O/H_2O has revealed dissociation of $(Zn_2L\text{-}bar^{2-})_2$ solely into the original target 1:1 complex Zn_2L-bar^{2-} and established the dimerization constant for $2Zn_2L\text{-}bar^{2-} \rightleftarrows (Zn_2L\text{-}bar^{2-})_2$, Kd(= $[(Zn_2L\text{-}bar^{2-})_2] / [Zn_2L\text{-}bar^{2-}]^2$) to be $10^{3.4}$ M^{-1}. The thermodynamic parameters were evaluated from the NMR measurements at 25, 35, 45, and 55℃: ΔG=-1.9 x 10^4 J mol^{-1}, ΔH=-3.3 x 10^4 J mol^{-1}, ΔS=-49 J mol^{-1} at 25℃. Potentiometric pH titration of Zn_2L (1mM) and barbital (1mM) disclosed extremely facile deprotonation of the two imido groups of barbital at pH less than 7 to form the dianionic barbital-bound Zn^{II} complexes Zn_2L-bar^{2-} and $(Zn_2L\text{-}bar^{2-})^2$, whereby the barbital binding affinity for

Zn_2L was estimated to be K_{bar} (= $[Zn_2L\text{-}bar^{2-}]/[\text{uncomplexed } Zn_2L][\text{uncomplexed barbital}])$ = $10^{5.8}M^{-1}$ at pH 8 and 25℃ with I = 0.10 ($NaNO_3$). The significance of the bis-zinc(II) receptor in stabilizing the dianionic barbital is evident by comparison with the interaction of Zn^{II}- cyclen complex (ZnL) with barbital, which yields only a 1:1 monoanionic barbital complex, ZnL - bar- (K_{bar} = [ZnL - bar-]/[uncomplexed ZnL][uncomplexed barbital] = $10^{4.2}$ M^{-1} at pH8 and 25℃ with I = 0.10 ($NaNO_3$).

抄録　Zn^{II}-cyclen（1）が含イミド化合物の受容体モデルとなることは既に見出されている。さらに優れたバルビタール受容体モデルを目指し、*p*-キシレンを架橋にして一分子内に二つのイミド認識部位を有する、新規化合物 bis-(Zn^{II}-cyclen)（L）を合成した。そして、バルビタールとの相互作用を検討した結果、（1）よりも強い相互作用を示した。新規化合物（L）が、バルビタールの2個のイミドNアニオンと、3個のカルボニルOを同時に認識する1：1錯体（2）の単離を目標としたが、pH8における（L）とバルビタールの溶液から2：2錯体（3）が得られ、X線構造解析で確認した。しかし、錯体（3）は水溶液中で解離して（2）⇄（3）の平衡関係にあることがNMR測定の結果から判った。



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