The spectroscopic study of Kinetic properties

of Pb(II) Complexes with Phosphonic Acid Derivative Ligands

Viktorie ŠIRŮČKOVÁ, Přemysl LUBAL1

*1Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*

*E-mail: siruckova.viki@gmail.com*

Pb(II) has been gaining popularity in various scientific fields – for example, in biomedicine for its potential to be a cancer-treating theranostic agent (in which 203Pb can be used for tumor visualization and 212Pb for tumor treatment) in the form of Pb(II) complexes of macrocyclic ligands. Macrocyclic ligands containing pendant arms with phosphonic/phosphinic acid-based groups enable greater structural variability of the macrocyclic complex as well as variability in the physico-chemical properties of the Pb(II) complex. In order to develop macrocyclic complexes with the desired properties for medicinal purposes, the kinetics and thermodynamics of the complexes must be well-understood. This poster presents a detailed kinetic and thermodynamic study of Pb(II) complexes with cyclen-based macrocycles containing one (DO3APABn, DO3APPrA, DO3AP) or four (DOTP, DOTPh, DOTPPh, DOTPOEt) phosphonic acid derivative pendant arms. The ligand DOTA, which contains four acetic acid pendant arms, is used as a comparison.

The kinetics of formation and dissociation of Pb(II) complexes in various pH conditions were monitored using conventional molecular absorption spectroscopy at λ = 260nm, while for very fast reactions (on the order of seconds), stopped-flow instrumentation was employed. The results for the formation kinetics indicated that complexes with ligands with one phosphonic-acid pendant arm had similar rate constants, while the formation of complexes with all four phosphonic-acid based ligands was slightly faster. The mechanism of formation was determined by doing studies with excess Pb(II) and is presented – in general, the complex is formed first as an out-of-cage complex with the pendant arms coordinating to the Pb(II) ion, which is then incorporated into the cavity through a second, slower step. The kinetic inertness of the complexes follows the order DOTA > DO3APABn ≈ DO3APPrA > DO3AP > complexes with all four phosphonic-acid derivative pendant arms. Preliminary computational studies were done to determine any relationship between structural parameters (such as bond length) and kinetic parameters. Overall, complexes with a longer Pb-N bond length had a faster rate of formation; those with a longer Pb-O bond length had a slower rate of dissociation.

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