THE SPECTROSCOPIC STUDY OF KINETIC PROPERTIES OF Pb(II) COMPLEXES WITH PHOSPHONIC ACID DERIVATIVE LIGANDS

Viktorie ŠIRŮČKOVÁ, Přemysl LUBAL[1]

[1]*Department 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 ^{203}Pb can be used for tumor visualization and ^{212}Pb 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 (DO3AP^{ABn}, DO3AP^{PrA}, DO3AP) or four (DOTP, DOT^{Ph}, DOTP^{Ph}, DOTP^{OEt}) 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 $\lambda = 260$nm, 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 > DO3AP^{ABn} ≈ DO3AP^{PrA} > 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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