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Complexation of Yttrium, Lutetium, Actinium and Bismuth by new benzo-diaza-crown ether ligand in aqueous solutions

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The complexation of alpha- beta- and Auger- emitting radionuclides is under investigation for the target delivery of them to tumor cells. The search of new effective binding chelating molecules with fast kinetics of complex formation should be carried out among H4DOTA analogs as it is currently used for radiopharmaceuticals. Water soluble new azamacrocyclic compounds show not only thermodynamic affinity for metal cations but also demonstrate very fast complex formation. This work presents complexation study of Y(3+), Lu(3+), Ac(3+) and Bi(3+) by new benzo-diaza-crown ether ligand, L.

Stability constants of ML complexes (M= Y(3+), Lu(3+), Ac(3+) and Bi(3+)) are presented in the table. Potentiometric titration of aqueous solutions of ligand in the absence and presence of cations was performed in water-jacketed titration vessel maintained at 25.0±0.1°C. The formation of 1:1 ML complex was established. The protonation constants of the ligand L and the stability constants of the complexes were calculated from the electromotive force titration data applying Hyperquad software. Distribution of cation in solution shows that >50% of M(3+) are bound at pH>6.5. For complexation constant determination with Ac(3+), Bi(3+) and Y(3+) competitive complexation technique was used. Free Ac(3+) and Y(3+) are completely sorbed by cellulose and uncomplexed Bi(3+) is precipitated. Ligand sorption onto cellulose is negligible as determined in separate experiments.

Table. Stability constants of ML complexes determined in the present work and reference data

M(3+) Y(3+) Lu(3+) Ac(3+) Bi(3+)

Reaction $L + M(3+) \leftrightarrow L(M(3+))$

lgK(ML), potentiometrically 5.94(1) 5.87(1) - -

lgK(ML), competitive 6.90(1) - 7.02(2) 10.1(1)

lgK(MDOTA) [1] 24.3 25.5 - 30.3

R (CN6), A [2] 0.900 0.861 1.12 1.03

Addition of M(3+) to aqueous solution of ligand leads to hypsochromic shift of band in UV-vis absorption spectra. This could be the consequence of crown ether-fragment participation in complexation process. The observed spectral change proceeds within 1-2 minutes and is not changing within days that confirm fast complex formation.

Obtained stability constant values are still less than for M-DOTA complexes but complexation rate is quite fast. Larger values of Bi-L complexes are in agreement with M-DOTA complexes. This fact could be associated with smaller coordination number for Bi(3+) than for rare earths. That leads to deeper location of bismuth than yttrium in the cavity formed by carboxylate and macrocyclic oxygens and nitrogens of the ligand while rare earths usually have capping water molecule to complete coordination sphere.

Some deviation in stability constants calculated from different methods could be associated with different ionic media: KNO₃, NaNO₃ or NaClO₄

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Literature:

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[2] Shannon R.D. Acta Cryst A 32. 1976. P.751

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