favourable enthalpy contribution, the entropy contribution being small. Only in the case of the [16]aneN_4/3,3,3-tet comparison can the extra stability of the cyclic complex be assigned to a favourable entropy effect.

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3 Linear aliphatic tetra-amines of the type $H_2N(CH_2)_l$–NH-$(CH_2)_mNH(CH_2)_nNH_2$ may be denoted by the symbol l,m,n-tet.

ΔG°, ΔH°, and ΔS° Changes for the Formation of Thorium(IV)–Oxydiacetate, –Iminodiacetate, and –Thiodiacetate Complexes in Aqueous Solution

P. DI BERNARDO*, A. CASSOL, G. TOMAT, A. BISMONDO

Istituto di Chimica Generale ed Inorganica, Università di Padova and Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Padua, Italy

and L. MAGON

Istituto Chimico, Università di Ferrara, Ferrara, Italy

The changes in free energy, enthalpy, and entropy for the formation of thorium(IV)–oxydiacetate, –iminodiacetate, and –thioacetate complexes have been determined at 25.0 °C using aqueous 1.00 mol dm^{-3} $Na[ClO_4]$ as ionic medium.

The changes in free energy were computed from the stability constants determined by the potentiometric determination of the competitive H^+ ion concentration; the enthalpy changes by direct calorimetric titrations. Owing to the high stability of the first thorium(IV)–oxydiacetate complex it was not possible to determine his $\beta_{1,0,1}$ value by potentiometric measurements; from the calorimetric data, however, a $\log\beta_{1,0,1}$ value of about 7 could be inferred.

Thorium(IV) forms only chelate complexes with the oxydiacetate, while with the imino- and thio-diacetate ligands also mixed complexes were detected.

All the complexes are entropically stabilized, in fact the enthalpy changes, except in the second step of the thorium(IV)–oxydiacetate system, oppose to their formation (see Table I).

The basicity of the etheroatom in the ligand chain strongly affects the stability of the corresponding 1:1 metal–ligand complex: the stability increases on increasing the ligand basicity. Finally, it is remarkable the abrupt variation in the enthalpy and entropy values for the formation of the third thorium(IV)–oxydiacetate complex; such a trend, previously observed in the thorium(IV)–acetate system [1], may be ascribed to a probable coordination change around the metal ion.

References

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TABLE I. The Stepwise Stability Constants and the Corresponding ΔG°, ΔH°, and ΔS° Changes obtained at 25.0 °C and in 1.00 mol dm^{-3} $Na[ClO_4]$ Medium.

Reaction	logK	−ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
Th(IV)–oxydiacetate				
$M + L \rightleftarrows ML$	≈7	≈40	8.5 ± 0.1	≈160
$ML + L \rightleftarrows ML_2$	6.36 ± 0.09	36.3 ± 0.5	−12.1 ± 0.2	81
$ML_2 + L \rightleftarrows ML_3$	3.17 ± 0.04	18.1 ± 0.2	35.2 ± 0.2	179
Th(IV)–iminodiacetate				
$M + L \rightleftarrows ML$	9.69 ± 0.01	55.3 ± 0.2	6.5 ± 0.3	207
$M + HL \rightleftarrows MHL$	2.91 ± 0.01	16.6 ± 0.1	7.4 ± 0.2	80
Th(IV)–Thiodiacetate				
$M + L \rightleftarrows ML$	5.60 ± 0.01	32.0 ± 0.2	20.5 ± 0.4	176
$M + HL \rightleftarrows MHL$	3.79 ± 0.05	18.8 ± 0.2	12.4 ± 0.4	105
$ML + L \rightleftarrows ML_2$	4.25 ± 0.06	24.2 ± 0.4	14.8 ± 0.6	131