plexes are present in solution. We showed that ternary heterobinuclear complexes are present, of the type $[CuCd(car)]^{3+}$, $[CuCd(car)H_{-1}]^{2+}$, $[CuCd(car)H_{-2}]^{+}$.

It is noticeable that the deprotonated species are the most relevant both for binary and ternary systems, but they are dimeric for binary and monomeric for ternary systems. In the complex $[CuCd(car)H_{-2}]^{+}$ the second hydrogen ion displaced very probably comes from the pyrrole group of His-residue.

References

1 P. Amico, G. Arena, P. G. Daniele, G. Ostacoli, E. Rizzarelli and S. Sammartano, *Inorg. Chim. Acta, 35,* L383 (1979).
2 P. Amico, G. Arena, P. G. Daniele, G. Ostacoli, E. Rizzarelli and S. Sammartano, submitted to *Inorg. Chim. Acta* (1979).
3 M. L. D. Touche and D. R. Williams, *J. Chem. Soc. Dalton,* 1355 (1976).
4 R. P. Agarwal and D. D. Perrin, *J. Chem. Soc. Dalton,* 268 (1975).
5 G. Brookes and L. D. Pettit, *J. Chem. Soc. Dalton,* 2112 (1975).

Reactions Between Zinc(II) and Tetra-Azamacrocycles of Varying Sizes. $\Delta H°$ and $\Delta S°$ Contributions to the Macrocyclic Effect

E. GALLORI, E. MARTINI, M. MICHELONI and P. PAOLETTI

Istituto di Chimica Generale ed Inorganica, Università di Firenze, Via I. Nardi 39, 30132 Florence, Italy

Cyclic polyamines complexes with some first-row transition metal ions such as copper(II) and nickel(II) are, in general, more stable than the equivalent complexes formed by the same metals with the corresponding non-cyclic polyamine ligands: the Macrocyclic Effect [1]. Much published work exists on the thermodynamic interpretation of the Macrocyclic Effect [2].

In the case of Zn(II) complexes, the thermodynamic interpretation is made more difficult by both the relative ease with which zinc can change its coordination geometry and by the impossibility of making use of the spectroscopic techniques which have proved so useful for the other metals. In this communication we are reporting both the enthalpy and the entropy contributions to the reaction between the zinc(II) ion and saturated cyclic polyazamacrocycles (Fig. 1) and will be comparing these values with the existing values for the analogous non-cyclic polyamines (see Table I).

It can be likewise generally stated that the macrocyclic zinc complexes are more stable than the corresponding complexes with non-cyclic polyamines. This extra stability is almost entirely due to a very

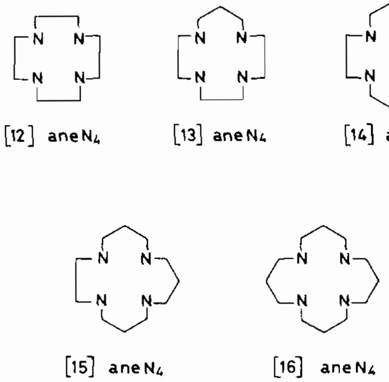

Fig. 1. Saturated tetra-azamacrocycles.

TABLE I. Thermodynamic Parameters for Macrocyclic and non-Cyclic Tetra-Aza Ligand Complexes of Zn(II).

Ligand	Log_{ML}	$-\Delta H°$ (kcal·mol^{-1})	$\Delta S°$ (cal·K^{-1}·mol^{-1})
[12]aneN$_4$	16.2	14.5	25.5
[13]aneN$_4$	15.6	15.3	20.1
[14]aneN$_4$	15.34	14.8	21.3
[15]aneN$_4$	15.35	16.5	13.3
[16]aneN$_4$	13.05	7.1	35.8
2,2,2-tet^3	12.02	8.9	25.0
2,3,2-tet^3	12.83	11.9	18.8
3,2,3-tet^3	11.25	10.6	15.9
3,3,3-tet^3	9.32	7.4	18.0

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.

References

1 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc., 91,* 6540 (1969).

2 A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *J. Chem. Soc. Dalton,* 577 (1978).

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.

$\Delta G°$, $\Delta H°$, and $\Delta S°$ 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

1 R. Portanova, P. Di Bernardo, O. Traverso, G. A. Mazzocchin and L. Magon, *J. Inorg. Nucl. Chem., 37,* 2177 (1975).

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

Reaction	logK	$-\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (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