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THERMODYNAMICS OF THE COMPLEXATION OF LANTHANIDES BY PYRAZINECARBOXYLATE

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ABSTRACT

The thermodynamic parameters of formation of 1 : 1 complexes between lanthanide cations and pyrazinecarboxylate have been determined by calorimetric titration in the ionic medium of 1.0 M $NaClO_4$ aqueous solution at 25° C. The thermodynamic parameters support the theory that the pyrazinecarboxylate acts as a bidentate ligand in the complexation and that the heterocyclic 1-nitrogen atom of the ligand is involved in chelate formation.

INTRODUCTION

The complexation reactions of various aminocarboxylate ligands [1–3] and heterocyclic carboxylate ligands [4–6] with trivalent lanthanide cations have been extensively studied. The results have shown that the ring nitrogen atom of α-picolinate is involved in the formation of a chelate ring [1,2], while the ring oxygen atom of furoate is not [4]. In the thermodynamic study of the complexation of trivalent lanthanide cations by a series of related aminocarboxylate ligands, Choppin and coworkers [1,2] have reported that the enthalpy of formation of the complexes includes a residual enthalpy, which is presumably a measure of the interaction between the lanthanide and the nitrogen donor atoms of the ligands, and which is a linear function of the total basicity of the nitrogen donors.

We have previously reported [7] on the stability constants of the lanthanide pyrazinecarboxylates in aqueous solution. It was noted that the stability constant of the lanthanide pyrazinecarboxylate deviates from the linear correlation of the stability constants log β_1 with the acidity constants pK_a of the monocarboxylate ligands. This suggests that the pyrazinecarboxylate

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ligand forms a chelate complex with the lanthanide ion. As an extension of the study, we have investigated the thermodynamic properties for the formation of the lanthanide pyrazinecarboxylates in order to confirm the bidentate nature of the pyrazinecarboxylate ligand. The thermodynamic parameters were obtained using the calorimetric titration method.

EXPERIMENTAL

Stock solutions of the lanthanide perchlorates and pyrazinecarboxylic acid were prepared and standardised by the methods described earlier [7]. All the working solutions were adjusted to give a total ionic strength of 1.0 M using $NaClO_4$. Sodium pyrazinecarboxylate buffer solutions were prepared by half-neutralisation of the pyrazinecarboxylic acid solutions with standard NaOH solution. Deionised water was used for the preparation of all solutions.

The calorimetric titrations were performed using a Tronac model 450 titration calorimeter. The accuracy of the calorimeter was tested by measuring the heat of protonation of THAM (tris-hydroxymethylaminomethane). The general procedure for the calorimetric titration has been described in the literature [8].

The heat of complexation was determined by titrating the neutralised pyrazinecarboxylic acid solution into the lanthanide solution. In a typical run, 50.0 ml of a lanthanide solution was titrated with incremental additions of 2.0 ml of the ligand solution. The enthalpy of protonation of pyrazinecarboxylic acid was determined by calorimetric titration of the ligand solution with a standard NaOH solution. The heat of dilution of the pyrazinecarboxylate buffer solution was measured by a blank titration of the solution into 1.0 M $NaClO_4$ solution.

RESULTS AND DISCUSSION

The acidity constant pK_a and the thermodynamic parameters for the protonation of pyrazinecarboxylic acid determined in an aqueous medium of 1.0 M ($NaClO_4$) ionic strength at 25°C are given in Table 1. Table 2 shows a typical set of calorimetric titration data for the europium(III)–monopyrazinecarboxylate system from which the thermodynamic parameters for the complexation are calculated. All the heats measured were corrected for the dilution and deprotonation of the ligand acid. Table 3 lists the thermodynamic parameters for the formation of some 1 : 1 lanthanide pyrazinecarboxylates in aqueous solution. The error limits indicate one standard deviation.

TABLE 1

Thermodynamic parameters of pyrazinecarboxylic acid ($\mu = 1.0$ M $NaClO_4$, $T = 25.0$ ° C)

pK_a	$-\Delta G_p$ (kJ mol^{-1})	ΔH_p (kJ mol^{-1})	ΔS_p (J mol^{-1} K^{-1})
2.76 ± 0.01	15.75 ± 0.03	2.53 ± 0.01	61.3 ± 0.1

TABLE 2

Enthalpy titration data for Eu^{III}-pyrazinecarboxylate (1 : 1) ($\mu = 1.0$ M $NaClO_4$, $T = 25.0$ ° C)

Volume of titrant (ml)	Q_{total} (mJ)	$Q_{corrected}$ (mJ)	$C_L \times 10^3$ (M)
0.80	151.7	102.4	1.063
1.00	189.6	128.0	1.324
1.20	227.5	153.6	1.582
1.40	265.5	179.2	1.839
1.60	303.4	204.8	2.093
1.80	341.3	230.4	2.346
2.00	379.2	256.0	2.596

Initial volume = 50.00 ml: $C_M = 1.034 \times 10^{-2}$ M; initial pH = 2.948; final pH = 2.693.

TABLE 3

Thermodynamic parameters for the formation of lanthanide monopyrazinecarboxylate (μ = 1.0 M $NaClO_4$, $T = 25.0$ ° C)

Metal	$-\Delta G_1$ (kJ mol^{-1})	ΔH_1 (kJ mol^{-1})	ΔS_1 (J K^{-1} mol^{-1})
La	13.12 ± 0.17	−0.72 ± 0.04	41.6 ± 0.1
Sm	16.26 ± 0.46	−0.30 ± 0.04	53.6 ± 1.7
Eu	16.09 ± 0.34	−0.29 ± 0.04	53.0 ± 1.3
Gd	14.26 ± 0.34	−0.12 ± 0.02	47.5 ± 1.2
Ho	16.60 ± 0.51	+0.28 ± 0.07	56.6 ± 2.0
Er	16.20 ± 0.17	+0.28 ± 0.02	55.3 ± 1.1
Lu	17.00 ± 0.29	+0.14 ± 0.02	57.5 ± 1.1

We noted previously [7] that the variation in log β_1 for the lanthanide pyrazinecarboxylates with increasing atomic number of the cations is similar to those observed for the α-picolinate and α-picolinate-*N*-oxide complexes. The similarity between the pyrazinecarboxylate and α-picolinate [2] is also found in the variations of ΔH_1 and ΔS_1 across the lanthanide series, see Table 3. This would mean that the hydration effect on the complexation of pyrazinecarboxylate is similar to that of α-picolinate The values of enthalpy of complexation of the pyrazinecarboxylate with the lanthanide ions are very small, indicating a weak interaction between the cation and the 1-nitrogen atom of the pyrazine ring of the ligand. This weak interaction is caused by

TABLE 4

Thermodynamic parameters of the europium complexes

Ligands	$-\Delta G_1$ (kJ mol^{-1})	ΔH_1 (kJ mol^{-1})	ΔS_1 (J K^{-1} mol^{-1})	Ref.
Pyrazinecarboxylate	16.09	−0.29	56.0	This work
α-Picolinate	20.58	−6.36	47.7	2
Anthranilate	24.31	4.60	97.0	3
Furoate	9.54	−6.32	53.1	4
Benzoate	12.33	7.9	68	9

the reduced basicity of the 1-nitrogen atom caused by the 4-nitrogen atom of the pyrazine ring of the ligand. It is clear that the driving force for the complexation of the pyrazinecarboxylate is an entropy effect.

The thermodynamic parameters for some europium(III) complexes are collected in Table 4. It can be seen from Table 4 that ΔS_1 for the pyrazinecarboxylate is comparable to that of the α-picolinate as well as that of the furoate. As mentioned above, the α-picolinate [2] is a bidentate ligand in which the ring nitrogen atom binds to the cation, and the furoate [4] is a monodentate ligand in which the ring oxygen atom is not involved in the chelation. Thus it seems that the type of complexation of pyrazinecarboxylate with lanthanide cations resembles that of α-picolinate. However, ΔH_1 for the pyrazinecarboxylate is about 6 kJ mol^{-1} less negative than ΔH_1 for the α-picolinate complex.

For the various aminocarboxylate ligands, the residual enthalpy $\delta\Delta H_1$, which is presumably a measure of the interaction between the lanthanide and the nitrogen donors of the ligands, is a linear function of the total basicity of the nitrogen donors, $\Sigma\mathrm{p}K_a(\mathrm{N})$, with a slope of about 3 [2]. The residual enthalpy was obtained by subtracting 6.5 kJ mol^{-1} from the measured value of ΔH_1 for the complexation of amino-monocarboxylate ligands: the estimated value of the enthalpy of complexation per carboxylate group of the carboxylate ligands is 6.5 kJ mol^{-1} [2,10]. As pyrazinecarboxylate and α-picolinate are both monocarboxylate ligands, the difference in the residual enthalpy is the difference in ΔH_1 for the complexation which is 6.07 kJ mol^{-1}. This difference in the residual enthalpy must be due to the difference in the basicity of the nitrogen donors of the two ligand systems. The difference in the basicity of the nitrogen donors of α-picolinate and pyrazinecarboxylate ligands is $\delta\Sigma\mathrm{p}K_a(\mathrm{N}) = 5.17 - 2.76 = 2.41$. Thus, the difference in the residual enthalpy between the two systems could be calculated as $3 \times 2.4 = 7.2$ kJ mol^{-1}, from Choppin's relationship [2], which is in approximate agreement with the difference in ΔH_1 for the complexation.

In conclusion, it seems likely that the pyrazinecarboxylate ligand forms quite stable chelate complexes with lanthanide cations in aqueous solution and that the driving force for the complexation is the entropy effect. The decreased stability in the pyrazinecarboxylate complex compared to the stability of the α-picolinate complex could be interpreted in terms of the weaker Ln–N interaction of the former because of the reduced basicity of the 1-nitrogen donor caused by the electron-withdrawing effect of the 4-nitrogen atom of the pyrazine ring. An identical phenomenon has been observed in the complexation of iron(II) with pyrazinecarboxylate in aqueous solution [11].

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