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Entropy-Controlled Formation of Metal Complexes with Hindered Ligands. The System Zinc(II)-1,3,5-*cis,cis*-Triaminocyclohexane

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Reactions in aqueous solution between linear multidentate amine ligands and metal ions have been thoroughly studied from the thermodynamic point of view.¹ The flexibility of the ligand and its ability to assume the preferred geometry of the metal ion both depend on the length of the aliphatic chain joining the nitrogen atoms. The pronounced stability in solution of metal complexes with linear polyamines is due to either a favorable enthalpy term, ΔH° , or a favorable entropy term, ΔS° . In practice, as far as the enthalpy term ΔH° is concerned, the endothermic effect of partial dehydration both of the metal ion and of the ligand is more than compensated by the exothermic effect of metal-nitrogen coordinate bond formation.² The strength of the coordinate bonds and hence the exothermicity of the reaction depend on the ability of the ligand to arrange its donor atoms at the corners of the coordination polyhedron in a stress-free configuration. The entropy contribution ΔS° is usually positive (10–20 cal K⁻¹ mol⁻¹) since the formation of the complex in solution leads to the release of water molecules of solvation and the resulting increase in translational entropy more than compensates for the loss of librational entropy by the ligand due to its increased rigidity on coordination (for a 1 M standard state). In the reactions of metal ions with linear polyamines the entropy change ΔS° contributes about 20–30% to the free energy change ΔG° .

In this work we report the thermodynamic functions ΔH° and ΔS° for the reactions of the hydrogen and zinc(II) ions at 25 °C in 0.1 M KCl with the ligand 1,3,5-*cis,cis*-tri-aminocyclohexane (tach). tach has three primary amine groups at the corners of an equilateral triangle of side 2.5 Å,³ and when it coordinates, it is forced to occupy the corners of one face of the coordination polyhedron. Since the nitrogen atoms are separated by propylenic chains, the metal complex formed contains six-membered chelate rings.

The equilibrium constants for the protonation of tach and for its interaction with the Zn^{II} ion have already been determined by means of pH titrations.⁴ We have measured the enthalpy changes associated with these reactions and the corresponding values of ΔS° have been calculated using the values of ΔG° and ΔH° .

Table I. Thermodynamic Functions for the Reactions of *cis,cis*-1,3,5-Triaminocyclohexane with Hydrogen and Zinc(II) Ions at 25 °C in 0.1 M KCl

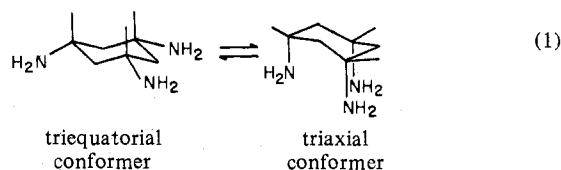
	ΔG° , ^a kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal K ⁻¹ mol ⁻¹
L + H ⁺ ⇌ LH ⁺	-13.86	-12.44 ± 0.20	4.7 ± 0.7
LH ⁺ + H ⁺ ⇌ LH ₂ ²⁺	-11.81	-11.69 ± 0.25	0.4 ± 0.8
LH ₂ ²⁺ + H ⁺ ⇌ LH ₃ ³⁺	-9.78	-11.02 ± 0.29	-4.2 ± 1.0
Zn ²⁺ + L ⇌ ZnL ²⁺	-9.41	-0.05 ± 0.64	31.0 ± 2.1
ZnL ²⁺ + OH ⁻ ⇌ ZnLOH ⁺	-7.98	-4.15 ± 0.76	13.0 ± 2.5

^a Calculated from the log *K* values reported in ref. 4.

The complex Zn(tach)²⁺ is less stable by nearly 2 log units than the corresponding complexes with linear triamines of general formula *m,n*-tri⁵ [*m,n*-tri = NH₂(CH₂)_{*m*}NH-(CH₂)_{*n*}NH₂]. The most appropriate comparison is with 3,3-tri⁶ since this ligand like tach forms six-membered chelate rings on complexation. Our calorimetric study shows that the enthalpy contribution is nil and that the stability in solution is due exclusively to an extremely favorable entropy change, viz., +30 cal K⁻¹ mol⁻¹ (Table I).

The stereochemistry of zinc complexes in aqueous solution is somewhat uncertain. The thermodynamic data relative to the formation in aqueous solution of complexes with polyamines have been variously interpreted in terms of tetrahedral,⁷ pentacoordinate,⁸ and, in a few cases, octahedral stereochemistry.⁵ From molecular models it is seen that, compared with linear ligands, tach has great difficulty in occupying the corners of the coordination polyhedron. This may well lead to weaker coordinate bonds and hence to a less marked heat change.

Another important point is that the free ligand tach exists as the triequatorial conformer.³ For coordination to a metal it is necessary that the ligand assume the triaxial conformation (see eq 1): the interconversion from the triequatorial to the



triaxial conformer is endothermic and leads to a heat loss by the ligand. It is somewhat difficult to establish the relative importance of these two negative contributions to the enthalpy change. In the gas phase the heat of the triequatorial-triaxial interconversion has been estimated to be 11 kcal mol⁻¹.³ In aqueous solution solvent interactions probably stabilize the triaxial species more because of its appreciably larger dipole moment and thus reduce considerably the interconversion energy. Thus, if we neglect the endothermic effects due to steric strain in the ligand and if we put the net energy change due to metal-ligand interaction equal to that ($\Delta H^\circ(\text{Zn}(3,3\text{-tri})^{2+}) = 5.5 \text{ kcal mol}^{-1}$) for the homologous ligand 3,3-tri, which like tach forms six-membered chelate rings, we arrive at a value of 5.5 kcal mol⁻¹ for the conformational interconversion of tach. This energy should be considered as the limiting value for the conversion of tach in aqueous solution.

The rigidity of this ligand explains the large entropy contribution which alone accounts for the stability of Zn(tach)²⁺. In fact coordination leads to no loss of freedom because the ligand is already nearly completely rigid. Since the entropy contribution to the triequatorial-triaxial interconversion can be considered small, the loss of librational entropy by the ligand is very small and this accounts for the fact that ΔS° for the entire reaction has an appreciable positive value. Such a favorable entropy change should be found whenever a rigid ligand forms complexes. A typical case is

that of the macrocyclic tetraamine ligands: these ligands have their donor atoms at the corners of a square. In fact it has been found that the reaction between the copper(II) ion and cyclen (cyclen = 1,4,8,12-tetraazadodecane) has an exceptionally large positive value of ΔS° , viz., 50 cal K⁻¹ mol⁻¹.¹⁰ cyclen unlike tach does not have to overcome a conformational energy barrier and therefore its reaction with the copper(II) ion is also accompanied by an appreciably exothermic heat change. Presumably the rigidity of the ligand is crucial to the comparatively high stability in solution of metal complexes with cyclic triamines.¹¹ The entropy contribution arising from the rigidity of the ligand has been completely ignored up to the present time in interpreting the high stabilities of complexes with macrocycles (the macrocyclic effect).¹²

The reaction of Zn(tach)²⁺ with the OH⁻ ion, i.e., hydrolysis, both is exothermic and is favored by the entropy change. The exothermicity probably reflects the formation of a stronger metal-oxygen bond following the removal of a proton. Furthermore the reaction leads to a decreased electric charge and this in turn leads to the release of some of the molecules of water of solvation. This clearly explains the positive value of ΔS° . Similar behavior is found in the case of the complex Zn(3,3-tri).⁹ Here the hydrolysis is ca. 10 times less favored than in the case of Zn(tach)²⁺ because both the enthalpy and entropy contributions are less favorable.

The thermodynamic behavior of tach toward the proton is also somewhat different from that of linear triamines. The stepwise basicity of tach is less than that of the triamine 3,3-tri which like tach has basic nitrogens separated by propylenic chains.⁶ This lower basicity is the result of different entropy and enthalpy contributions. What is more, unlike 2,2-tri¹³ and 3,3-tri,⁹ for both of which the second step in the protonation is more exothermic than the first, in the case of tach, $-\Delta H^\circ_1 > -\Delta H^\circ_2 > -\Delta H^\circ_3$. The entropy change ΔS° decreases for each successive step as in the case of the linear triamines and in general for all polyamines.

Experimental Section

cis,cis-tach was prepared and then purified by sublimation according to a method to be reported.¹⁴ The purity of the substance was checked by C, H, and N analyses and pH titrations. A standard KOH solution (~0.3 M) was prepared by washing KOH pellets repeatedly under nitrogen with carbon dioxide free water.

The solution from the third washing was collected. The normality and purity of the KOH solution were determined by pH titrations following the method of Gran.¹⁵ As the calorimetric apparatus requires more diluted reagents, two solutions of KOH (0.01 and 0.02 M) were obtained by diluting the standard KOH solution with carbon dioxide free water. The titer of the diluted solutions was checked calorimetrically against the neutralization (H⁺ + OH⁻) in 0.1 M KCl; the heat of this reaction (-13.395 ± 0.016 kcal mol⁻¹) has been determined in previous experiments and it is in good agreement with the reported values.¹⁶ An HCl solution was prepared by diluting the azeotropic mixture and the acidity was determined by titration against borax. A solution of ZnCl₂ was prepared and the zinc content determined gravimetrically as anthranilate. The tach solution (0.1 M) was prepared by dissolving the ligand in CO₂-free water and was kept under nitrogen. The ligand concentration was determined by pH titrations.

The calorimetric apparatus was an LKB 10700-1 Flow Micro-calorimeter. Reagents were injected into the mixing cell by LKB Perplex peristaltic pumps. The design of the experiment and the calibration of the apparatus have already been described in detail.¹⁷ In the protonation measurements a peristaltic pump (pump B) injected a solution of the free ligand tach into the calorimeter; the other pump (pump A) injected an HCl solution. The appropriate H⁺:tach ratios were obtained by changing the flow rates of the peristaltic pump and/or preparing solutions of different concentrations.

In the case of metal complex formation measurements, pump A injected a solution containing the ligand tach, an excess of hydrochloric acid, and an appropriate amount of a zinc(II) salt. Pump B was connected to the KOH solutions. All solutions used in the calorimetric experiments were adjusted to the 0.1 ionic strength by KCl, Erba CGS.

The method by which ΔH° is obtained from the calorimetric data has been described previously.¹⁷ The values of the equilibrium constants β_{pqr} used in the calculations were those reported in ref. 4. The ionic product of the water ($K_w = 1.63 \times 10^{-14}$) was taken from ref. 16. The calculations were performed with an IBM 360 computer.

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Registry No. tach, 26150-46-9; Zn, 7440-66-6.

Supplementary Material Available: Tables II and III listing the experimental details of the calorimetric measurements (analytical molar flow rates of the acid, metal ion and ligand, heat flow values, and percent of the species formed during the experiments) (2 pages). Ordering information is given on any current masthead page.

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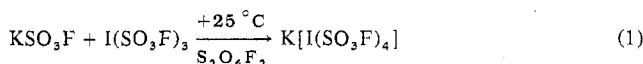
Bis(fluorosulfato)bromonium(III) and -iodonium(III) Cations [Br(SO₃F)₂]⁺ and [I(SO₃F)₂]⁺

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Iodine and bromine tris(fluorosulfate) have been known for some time¹ together with some of their physical and chemical properties^{2,3} and Raman spectra.⁴ Also known are the corresponding tetrakis(fluorosulfate) anions of iodine and bromine, e.g., as the potassium salts K[I(SO₃F)₄] and K[Br(SO₃F)₄].⁵ Fluorosulfate ion transfer according to



is not only a logical link between both types of compounds but also a useful synthetic route.⁴ In this reaction I(SO₃F)₃ is found to act as an SO₃F⁻ ion acceptor.

In analogy to the chemical behavior of some structurally related interhalogen compounds such as ICl₃ and BrF₃, both I(SO₃F)₃ and Br(SO₃F)₃ may also be expected to act as SO₃F⁻ ion donors toward suitable acceptors. However, no stable compounds of this type have been reported to date. The same applies to any other oxy acid derivative of trivalent iodine and bromine.