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THERMODYNAMICS AND KINETICS OF THE TRANSITION METAL COMPLEXES OF TRIPODAL AMINES

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CONTENTS

ABBREVIATIONS

tren	tris (2-aminoethyl)amine
Me_6tren	hexamethyltris(2-aminoethyl)amine
Et_6tren	hexaethyltris(2-aminoethyl)amine
trpn	tris(3-aminopropyl)amine
Me_6trpn	hexamethyltris(3-aminopropyl)amine
trbon	tris(4-aminobutyl)amine
TSN	1,1,1-tris(monomethylaminomethyl)ethane
TTN	1,1,1-tris(dimethylaminomethyl)ethane
ln	lanthanide
et	ethyl
alk	alkyl
DMF	dimethylformamide
NMF	monomethylformamide
DMSO	dimethylsulfoxide
FORM	formamide

A. INTRODUCTION

The coordination chemistry of tripodal amine ligands, such as tren, trpn, and their alkyl derivatives, has undergone rapid development in the past few years and several

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recent articles have reviewed various aspects of the chemistry of these compounds, such as their structure and magnetic properties[1], and the spectroscopy of the five-coordinate complexes[2,3]. Until now, however, there has been no summary of the many thermodynamic and kinetic studies which have been carried out on these complexes and this review will cover these areas.

B. THERMODYNAMIC CONSIDERATIONS

Although a large number of tripodal amine complexes have been isolated and characterized, studies suggest that an even greater variety exists in solution. Thus, in addition to five- and six-coordinate metal complexes, $M(\text{Amine})L^{n+}$ and $M(\text{Amine})L_2^{n+}$, solutions may contain hydroxo complexes, complexes in which the ligand is partially protonated, and binuclear complexes, even though the majority of these have not yet been isolated. This section of the review will be devoted to a discussion of the nature of these species in solution including their structures and equilibria, whereas the kinetic aspects of their behavior will be considered in the following section.

(i) Reactions with Protons

The presence of four amine-groups in tren and its analogs creates the possibility that reactions may occur with four protons per amine molecule. That such behavior does occur is shown by the isolation of tren · 4HCl[4] and trpn · 4HCl[5]. The basicity of the tertiary nitrogen is much lower than that of the primary amines, however, and tren · 3HCl is much more common. The lower basicity of the tertiary nitrogen has been verified by titrations of tren with HCl, which show only three neutralization reactions, the equilibrium constants for which are given in Table 1.

The decrease in each K with increasing temperature is quite normal, as is the increase in K with increasing ionic strength. Similarly the order $K_1 > K_2 > K_3$ is in accordance with expectations for a polyfunctional molecule, where the attraction for succeeding protons is decreased by electrostatic repulsion of those already bonded to the molecule. The small differences among these successive K values are

TABLE 1

Equilibrium constants for the reaction of tren with HCl[a]

Temperature (°C)	$\log K_1$	$\log K_2$	$\log K_3$	Ref.
10	10.45	9.55	8.28	6
20	10.15	9.26	7.98	6
20 (0.1N KCl)	10.29	9.59	8.56	7
20 (0.5N KCl)	10.29	9.84	8.79	7
25	10.14	9.43	8.41	8
30	9.91	9.00	7.71	6
40	9.63	8.65	7.48	6

[a] Unless otherwise noted, titrations were performed without supporting electrolyte.

TABLE 2

Thermodynamic functions for the tren–HCl reaction[a]

Reaction	$-\Delta G$ (kcal/mole)	$-\Delta H$ (kcal/mole)	ΔS (cal/moledeg)
$H^+ + tren \rightarrow Htren^+$	13.6	11.0	9
$H^+ + Htren \rightarrow H_2tren^{2+}$	12.3	12.3	0
$H^+ + Htren^{2+} \rightarrow H_3tren^{3+}$	10.7	10.3	2

[a] Reference (3)

quite notable, however, in comparison with those of other amines such as trien ($\log K_1 = 9.92$, $\log K_2 = 9.2$, $\log K_3 = 6.67$, $\log K_4 = 3.32$)[9]. The small $\Delta \log K$ values seen for tren most likely result from the fact that tertiary nitrogen is not protonated, and the primary amines which are protonated are widely separated and, therefore, not subject to the full impact of the electrostatic attraction mentioned above. [A similar result is also seen for the protonation of the first two (primary) amine groups of trien].

The temperature dependence of K found for tren[6] permits an evaluation of the thermodynamic functions for these protonation reactions (Table 2).

The free energies for these reactions decrease from 1 to 3, as expected from the values of K, but the enthalpies show more unusual behavior. Thus, $\Delta H_3 < \Delta H_1 < \Delta H_2$ (although there would seem to be no simple reason to expect, nor means to explain, the order $\Delta H_1 < \Delta H_2$) and this order clearly indicates the importance of the entropy term in establishing the order of the free energies. Indeed, the ΔS values also follow an irregular pattern. $\Delta S_1 > \Delta S_3 > \Delta S_2$, although the difference between the latter two values is rather small (2 cal/mole deg.) and may be approaching the limit of experimental error. The larger value for ΔS_1 (9 cal/mole deg.) is more pronounced and is probably the result of changes in solvation caused by placing a positive charge on the tren molecule for the first time.

Although the basicities of the many known tren analogs have not been measured as yet, equilibrium constants have been obtained for trpn[10]. These are $\log K_1 = 10.51$, $\log K_2 = 9.82$, $\log K_3 = 9.13$, $\log K_4 = 5.62$ (25°, 0.1 N KCl). The amine, trpn, is slightly more basic than tren.

The similarities in the basicities of the primary amine groups of tren and trpn lead to an inability to obtain solutions which contain exclusively mono- or di-protonated species of these molecules. In contrast, the larger difference between $\log K_3$ and K_4 for trpn makes the species H_3trpn^{3+} and H_4trpn^{4+} available by themselves, at pH ~ 7 and pH<4, respectively.

(ii) Reactions with metal ions—normal complexes

Many compounds with 1:1 metal–tren stoichiometry have been isolated and their continued existence in solution is indicated by evidence from several sources. Prue and Schwarzenbach[7] found these to be the only metal-containing species in solutions of Mn(II), Fe(II), Co(II), Cu(II), and Zn(II) and also suggested the presence of such species in solutions of Ni(II), Hg(II) and Ag(I) when they studied the neutralization of tren·3HCl with hydroxide in the presence of these metal ions.

Jonassen and several co-workers[11,12,13] verified the existence of Mtren^{2+} for M=Fe, Co, Ni, Cu, Zn and Cd through the use of conductance, potentiometry, and spectrophotometry. Surprisingly, under the conditions of their experiments, they found no evidence for the formation of a Mn(II) complex with tren.

These 1:1 complexes occur in solution for the most part, requiring addition of one or two molecules of water to become either five-or six-coordinate. Thus Mn, Fe, Ni and Cu acquire two molecules of water and become octahedral, as indicated by calorimetric measurements[14] and, in the case of Ni(II), visible spectroscopy[15]. The calorimetric measurements on Co(II) and Zn(II) tren complexes have been interpreted as indicating that these species coordinate only one molecule of water to become five-coordinate, a conclusion which is also supported by the excellent agreement between the spectra of aqueous Co(tren)$^{2+}$ and of Co(Me$_6$tren)Br^{2+} (which is known to be five-coordinate) in CH_2Cl_2[16].

The Hg(II)-tren complex has also been thought to be six-coordinate[7], although it is unclear whether this suggestion is based on any evidence stronger than analogy with other Hg(II) complexes whose structures are known to be octahedral in the solid state. In this study the two additional positions of the octahedron are thought to be occupied by chloride or bromide ions, known to bond strongly to Hg(II).

The complex of Ag(I) with tren seems to be a special case in that its geometry has not been determined and cannot be assumed to be octahedral. The tendency of Ag(I) to form linear complexes is well known, but difficulty is encountered in visualizing a species in which two of the primary amines of tren are the only groups occupying the two coordination sites of Ag(I). In marked contrast is the species Ag$_2$tren^{2+}, which has been proposed[7] (although of low stability) and which would seem to require coordination of the tertiary amine and one of the primary amines to the two coordination sites of Ag(I) [i.e. spanning of the "*trans*" positions of the

TABLE 3

Log K for $M^{n+} + L \rightarrow ML^{n+}$

Metal	L	Log K	Ref.
Mn^{2+}	tren	5.8	17
Fe^{2+}	tren	8.6	17
Co^{2+}	tren	12.8	17
Ni^{2+}	tren	14.6	17
Cu^{2+}	tren	18.8	17
Zn^{2+}	tren	18.7	17
Cd^{2+}	tren	12.3	17
Hg^{2+}	tren	~ 22.8	17
Ag^{+}	tren	7.8	7
Co^{2+}	trpn	6.36	10
Ni^{2+}	trpn	8.70	10
Cu^{2+}	trpn	13.1	10
Zn^{2+}	trpn	10.7	10

TABLE 4

Log K stability for metal–polyamine complexes

Complex	No. of chelate rings	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
M $(NH_3)_4$	0		~ 3.7	5.3	7.79	12.59	9.06
M $(en)_2$	2	4.9	7.7	10.9	14.5	20.2	11.2
M (trien)	3	4.9	7.8	11.0	14.1	20.5	12.1
M (tren)	3	5.8	8.8	12.8	14.0	18.8	14.6
M $(dien)_2$	4	7.0	10.4	14.1	18.9	21.3	14.4

Ag(I)]. The coordination of only the primary amines (with H_2O occupying the remaining position) would suggest the formation of Ag_3tren^{3+} species, for which no evidence has yet been obtained.

Of the many aspects of the behavior of M–tren complexes, the equilibria and thermodynamics of formation have been among the most controversial. This has been due in part to the geometrical constraints imposed by the tripodal nature of the tren ligand and the interest in determining how these constraints affect the stability of such complexes. Log K values for the complexation reactions of various metal ions with tren and trpn are given in Table 3. These log K values are uniformly lower for trpn than for tren ($\Delta \log K = 5.9$–8.0), which can be attributed to the larger chelate ring in the trpn cases.

For both of the ligands listed, the log K values follow the natural order[18], reaching a maximum with Cu^{2+}.

When these data are compared with those of several other ligands with four nitrogen donor groups (Table 4), it can be seen that the log of the stability constant generally increases with the number of chelate rings formed[19].

However, the behavior of Cu(II) (and to a lesser extent Ni(II)) deviates from this pattern. Thus, not only is the log K value for Cu–tren (18.8) less than that for Cu–trien (20.5), which has the same number of chelate rings, but it is also less than that for $Cu(en)_2$ (20.2), which contains only two rings.

This lower stability for the Cu–tren complex was originally attributed to the occurence of unique (for Cu^{2+}) tetrahedral distortion from the usual square-planar geometry of Cu(II). Now that the geometry of the $Cu(tren)^{2+}$ species has been shown to be *cis*-$[Cu(tren)(H_2O)_2]^{2+}$, the lower stability cannot be attributed to a difference in coordination number but rather must be due to the lower crystal field energy of this species compared to that of the *trans*-$Cu(trien)$-$(H_2O)_2^{2+}$ and to the possibly lower strength of a bond formed by a tertiary amine relative to a primary amine.

Some thermodynamic functions for the metal-tren systems are given in Table 5. The enthalpies of formation for metal–tren species are all negative and increase in magnitude with decreasing ionic radius or increasing tendency toward covalent bonding [Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)], an order which has already been seen for the stability constants. This identity in order and the absence of any distinct trend in the entropy values suggest that the free energies of forma-

TABLE 5

Thermodynamic functions for $M^{2+}_{(aq)} + L_{(aq)} \rightarrow ML^{2+}_{(aq)}$

Metal	L	$-\Delta H$ kcal/mole	ΔS cal/mole deg	Ref.
Mn^{2+}	tren	3.0 ±0.05	16.5 ±0.5	14
Fe^{2+}	tren	6.30 ±0.05	18.5 ±0.5	14
Co^{2+}	tren	10.65 ±0.15	22.0 ±1.0	14
Ni^{2+}	tren	15.15 ±0.05	16.0 ±0.5	14
Cu^{2+}	tren	20.4 ±0.1	18.0 ±1.0	14
Zn^{2+}	tren	13.85 ±0.2	19.5 ±1.0	14
Pr^{3+} [a]	tren	62.5 ±1.5		20
Gd^{3+} [a]	tren	60.3 ±1.5		20

[a] Calorimetric studies done in acetonitrile

tion and therefore the stability of the complexes are primarily the result of changes in the enthalpies. All values correspond to moderately or strongly exothermic reactions, although they are from 3–5 kcal $mole^{-1}$ smaller than the corresponding values obtained for the bis- ethylenediamine complexes $M(en)_2^{2+}$ (ref. 21). This difference has been attributed to the greater constraints imposed by the introduction of the third chelate ring, a suggestion which is supported by the close correspondence between the values for trien[22] and tren.

The values of the entropy changes are all positive, corresponding to the release of one or more coordinated water molecules, and range from 16–22 cal $mole^{-1}$ deg^{-1} making them comparable to values for $M(trien)^{2+}$ (ref. 21), and 9–20 cal $mole^{-1}$ deg^{-1} greater than those for $M(en)_2^{2+}$ (ref. 22). These results provide one more illustration of the 'chelate effect'[23]. (The value for $[Zn(tren)]^{2+}$ is less than those for $[Zn(trien)]^{2+}$ and $[Zn(en)_2]^{2+}$ and will be discussed further below.)

In comparing the entropies of the tren complexes among themselves, the values for Co^{2+} and Zn^{2+} are slightly higher than the others. This has been interpreted as being due to the release of a greater number of water molecules from $[Co(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$ to form the penta-coordinated $[Co(tren)(H_2O)]^{2+}$ and $[Zn(tren)(H_2O)]^{2+}$. Although these entropy differences are not large, the suggestion of a five-coordinate Co^{2+} species is supported by the greater ΔS value for $[Co(tren)]^{2+}$ than for $[Co(trien)]^{2+}$ (where octahedral $[Co(trien)(H_2O)_2]^{2+}$ is formed) as well as by spectroscopic evidence (vide supra). Similarly, the suggestion of $[Zn(tren)(H_2O)]^{2+}$ is based not only on the difference between its ΔS values (and those of other $[M(tren)]^{2+}$ species) but also on the comparison with the ΔS values for the trien and bis en complexes of Zn, both of which are larger due to the formation of tetrahedral $[Zn(trien)]^{2+}$ and $[Zn(en)_2]^{2+}$ by the expulsion of six water molecules from $[Zn(H_2O)_6]^{2+}$.

Recently, Rabenstein[24] determined the stability constants K (ML/MLX) for the complexation reaction $ML + X \rightleftharpoons MLX$ from PMR chemical shift measurements for complexes where M is cadmium or zinc, L is tren and X is glycine (gly) or ethylenediamine (en). The Log K (ML/MLX) values are as follows: $[Zn(tren)(en)]^{2+}$, 1.15;

TABLE 6

Enthalpy values between Me_6tren and the divalent transition metal ions

	$M\,Br_{2(aq)} + Me_6tren_{(aq)} \rightarrow M(Me_6tren)Br^+Br^-_{(s)}$
Metal	ΔH kcal/mole
Mn^{2+}	6.81 ±0.22
Fe^{2+}	2.53 ±0.22
Co^{2+}	– 3.15 ±0.24
Ni^{2+}	1.34 ±0.21
Cu^{2+}	–13.54 ±0.16
Zn^{2+}	– 6.56 ±0.15

$[Cd(tren)(en)]^{2+}$, 2.83; $[Zn(tren)(gly)]^{2+}$, 1.00; and $[Cd(tren)(gly)]^{2+}$, 2.59. The stability constant of the monohydroxy complex of $Zn(tren)^{2+}$ was also determined and found to be 2.90. These results, when compared with similar data for the nta (nitrilotetraacetic acid) system, suggest that $Zn(tren)^{2+}$ has less tendency to form mixed complexes with en and gly than the other complexes have, suggesting a possible difference in its structure and adding further support to the thermochemical results.

The reaction between Me_6tren and the divalent transition ions from manganese to zinc has also been studied calorimetrically (Table 6)[25].

The unusual heterogeneous reaction was used because the hydrolysis of the complexes in solution prevented a more direct investigation. The isomorphism of the solid compounds, however, suggests that the enthalpies of solution should be very similar to the enthalpy values in the table, and that the order should parallel those values. Thus, the order of the exothermicity of the reaction would be
$Mn < Fe < Ni < Co < Zn < Cu$, which (except Ni) parallels the order found for tren.

The enthalpies of complexation for Pr^{3+} and Gd^{3+} are approximately four times greater than those for the divalent ions discussed above. While the change of solvent from water to acetonitrile may be responsible for part of this difference it seems that these much larger values are primarily due to two other factors: (a) the higher charge of these rare earth ions, and (b) the coordination of two tren molecules per rare earth ion as compared with one tren per transition metal. The presence of two tren molecules is indicated both by the analysis of the complexes isolated and by the similarity between the enthalpies and those obtained for the formation of tetrakis (ethylenediamine) complexes ($\Delta H_{Pr} = -59.9$ kcal $mole^{-1}$; $\Delta H_{Gd} = -60.9$ kcal $mole^{-1}$)[20].

(iii) Protonated Complexes

A number of complexes with the tripodal ligand partially protonated have been proposed and are listed in Table 7.

The existence of the protonated tren complexes was proposed by Prue and

TABLE 7

Complexes with partially protonated ligands

Compound	$\log K_m \rightarrow MH_y^{x+2+}$	Ref.
$NiH\,tren^{3+}$	~ 9	7
NiH_2tren^{4+}	~ 4	7
$HgH\,tren^{3+}$		7
HgH_2tren^{4+}		7
$AgH\,tren^{2+}$	5.6 ± 0.15	7
AgH_2tren^{3+}	3.3 ± 0.3	7
$NiH\,trpn^{3+}$	5.27	10
$CuH\,trpn^{3+}$	10.76	10

Schwarzenbach[7] from an analysis of the shapes of the titration curves of tren·3HCl with NaOH in the presence of the metal ions. They calculated the maximum concentrations of the Hg(II) species to be 2(HgH_2tren^{4+}) and 17 ($HgH\,tren^{3+}$) percent of the total amine present while the amounts of the Ni(II) and Ag(I) species were described simply as small.

In contrast, the normal 1:1 tren complexes described[7] above were the only metal-containing species found in solutions of Mn, Fe, Co, Cu, and Zn, although these solutions also contained H_3tren^{3+}, H_2tren^{2+}, $H\,tren^+$ and tren, their relative amounts varying with the pH.

The titration curves of Jonassen and co-workers[11] clearly indicate breaks corresponding to the removal of one H^+ from H_3tren^{3+}, i.e., the formation of H_2tren^{2+} in solutions of Ni(II), Cu(II), and Zn(II), although it is unclear whether this species is complexedor free. Significantly, Co(II) and Fe(III) do not exhibit such breaks, while the data for Fe(II) are ambiguous and those for Mn(II) and Cd(II) are not given.

Paoletti, et al.[10], employed the species and stability constants as variables to obtain the best agreement between computer-generated and experimental titration curves of trpn.4HCl with hydroxide ion. Nickel and copper ions showed evidence of protonated species but cobalt and zinc ions did not.

Although stability constant data are very sparse for these protonated complexes, some generalizations can be made. First, for the metal ion which forms complexes with both tren and trpn, nickel, the former complex is the more stable, a result which is consistent with the smaller size of the chelate ring formed in this case. Secondly, for those metal ions which form both mono- and di-protonated complexes, log K is greater for the mono-protonated species, in keeping with the lower electrostatic repulsion in this case. Finally, the log K value for $[CuH\,trpn]^{3+}$ is greater than that for $[NiHtrpn]^{3+}$, which would be expected if these complexes followed the natural order of stability.

(iv) Hydroxo complexes

During their investigation of the neutralization of tren·3HCl with sodium hydroxide in the presence of various metal ions, Jonassen and co-workers[11,12,13] found

TABLE 8

Metal–ligand–hydroxo complexes with tripodal ligands

Metal	Ligand	1:1:1	2:2:1	2:2:2	2:2:3	Ref.
Mn^{2+}	tren	–	–	–	–	12
Fe^{2+}	tren	–	+	+	+	12
Fe^{3+}	tren	–	–	–	–	12
Co^{2+}	tren	–	–	+	+	11, 12
Ni^{2+}	tren		+	+	+	12, 13
Cu^{2+}	tren			+		12
Zn^{2+}	tren			+		12
Cd^{2+}	tren			+		12
Co^{2+}	trpn	+[a]				12
Cu^{2+}	trpn	+[b]				12

[a] $\log K = 2.990$

[b] $\log K = 3.991$

evidence for the formation of compounds at several hydroxide concentrations. These occurred at metal ion:tren:hydroxide ratios of 2:2:1, 2:2:2, and 2:2:3, although not all compounds were formed for all metal ions as shown in Table 8. Figure 1 shows the structures of the metal ion–trpn–hydroxo complexes suggested by the computer-analyzed titrations of Paoletti[10].

Clearly, the species in which the OH^-:metal:tren ratio is not an integral value require a hydroxo bridge in order to make sense chemically, and possible geometries of these species are shown below. Interestingly a dimer has been suggested as the species with 2:2:2 stoichiometry although there would seem to be nothing to preclude the formation of monomeric species (either five- or six-coordinate M(tren)(OH) or $M(tren)(OH)(H_2O)$, respectively, depending on the metal ion). Indeed, the species $[Co(tren)(OH)(H_2O)](ClO_4)_2$ has been isolated[26], and the analogous complex of

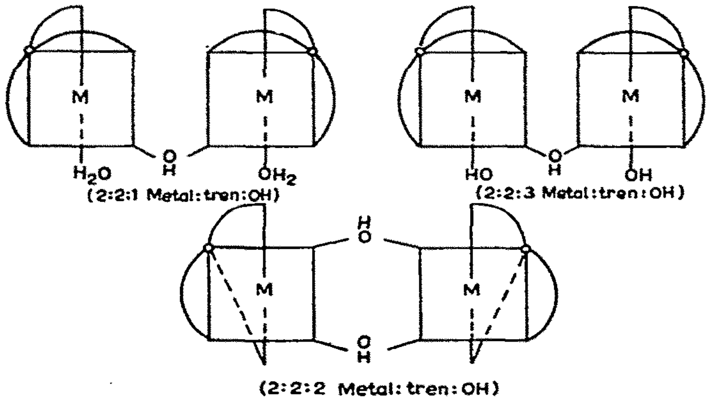

Fig. 1. Suggested structures of metal–ligand–hydroxo complexes with tripodal ligands.

cobalt(II) has been found in solution[27], in equilibrium with large amounts of Co(tren)OH$^+$.

Monomer formation seems especially likely in those cases where the formation of the 1:1:1 complex is not preceded by the appearance of a bridged entity, and even in those instances where a bridged species is formed first, (Fe(II) and Ni(II)) the hydroxo bridge could be easily broken to produce the simpler monomeric species. Clearly, further information, such as molecular weight data, for the 2:2:2 species, is needed to resolve this question.

The proposed hydroxo bridges are supported by magnetic susceptibility measurements which have been made for solutions of Ni(II) and Co(II)[11,13]. The susceptibilities of Ni(II)–tren solutions were found to decrease with the addition of hydroxide, becoming diamagnetic when the bridged $Ni_2(tren)_2(OH)_3^+$ was formed and then increasing to the normal weak field behavior as more hydroxide was added. A similar decrease was noted for solutions of Co(II)–tren, which showed a value corresponding to one unpaired electron at the neutralization of tren·3HCl, and then decreased still further to a plateau value as more hydroxide was added. These results, including the anomalously low values, can be explained by postulating spin exchange through the hydroxo bridges, as has been proposed for other systems[28].

The fact that the susceptibility remains low in the cobalt systems, but increases for nickel as the hydroxide concentration is increased, suggests that the additional hydroxide does not interfere with the spin-exchange pathway in cobalt, but does so for nickel. This provides evidence for the persistence of the bridged species in cobalt-tren solutions even at high pH values, but suggests that the nickel dimer is unstable relative to $Ni(tren)(OH)_2$ at such high pH's.

C. KINETICS

All of the kinetic data on tripodal amine transition metal complexes are for tren compounds, presumably because this amine is commercially available and can also be isolated from practical grade trien[13,20]. Further most of these data are for Co(III) complexes, because the reactions of these species can be followed by conventional techniques. With the advent of fast reaction methods, however, the behavior of other metal–tren complexes is beginning to be studied.

(i) Aquations

The acid hydrolyses of Co(III)–polyamine complexes have been studied extensively and much is known about the mechanisms of these reactions. It is known for instance, that in a series of similar polyamine complexes of the same charge, increased chelation slows down the rate of acid hydrolysis. In contrast, the first aquations of the Co(III)–tren complexes which have been studied so far show unusually rapid aquation rates for species containing three chelate rings. Table 9 gives the rate constants for some aquations of Co(III)–tren species, along with the corresponding values for the *cis*-bis(ethylenediamine) species, when available.

The aquation of both $Co(tren)Cl_2{}^+$ (ref. 29) and $Co(tren)Br_2{}^+$ (ref. 30) take place in two steps:

$$[Co(tren)X_2]^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(tren)XH_2O]^{2+} + X^-$$

$$[Co(tren)XH_2O]^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(tren)(H_2O)_2]^{3+} + X^-$$

The halo-aquo product has been isolated and characterized in both cases. Both processes are pseudo-first order, and unaffected by variation in the initial concentration of complex. The aquation rate for the dibromo complex is unaffected by pH(1–6) and by ionic strength.

The primary hydrolysis of $[Co(tren)F_2]^+$ (ref. 31) in acidic and neutral solutions proceeds by both an acid-independent and acid-catalyzed pathway involving an equilibrium between $[Co(tren)F_2]^+$ and $[Co(tren)FFH]^{2+}$ ions. The kinetics fit the rate law $-dC/dt = \{(k_o + k_H K_{eq} [H^+])/(1 + K_{eq} [H^+])\} C_t$, where C_t = total concentration of complex, k_o and k_H are the first-order rate constants for the acid hydrolysis of the nonprotonated and protonated complex, respectively, and K_{eq} is the equilibrium constant for the protonation reaction.

If one compares the rate of primary acid hydrolysis of the dichloro, dibromo, and difluoro (acid-independent path) tren species with the rates for the corresponding *cis*-bis(ethylenediamine) complexes (Table 9), the rate ratio $[Co(tren)X_2]^+/[Co(en)_2X_2]^+$ is 30 for the dibromo, 12 for the dichloro and 3 for the difluoro. This acceleration of the first aquation for the tren species has been attributed[40] to the combined effects of strain caused by the coordinated tren molecule and the peculiar geometric arrangement of tren, which causes steric crowding at the halide position *cis* to the tertiary nitrogen of tren. As a result, the *cis* ligand is unusually labile.

It was wondered if this acceleration in aquation rate was maintained in the release of the second halide ion (secondary aquation). Miller and Madan studied the aquation of both $[Co(tren)ClH_2O]^{2+}$ (ref. 37) and $[Co(tren)BrH_2O]^{2+}$ (ref. 36) and found them to be pseudo-first order and acid-inhibited over pH 1–3. This acid-inhibition has been attributed to an equilibrium in solution between the haloaquo complex and the more rapidly reacting halohydroxo complex. The chloroaquo complex is found to react only 1.5 times faster than the corresponding en complex. These results, along with similar indirect comparisons which can be made for the aquobromo compound, show that the second halide ion is considerably less labile than the first, due to the loss of some of the strain in the complex.

An investigation of the acid hydrolysis of $[Co(tren)ClBr]^+$ (ref. 40) seems to support the results above. Aquation of $[Co(tren)ClBr]^+$ proceeded via two parallel pseudo-first order reactions, one of which seemed to release chloride, and the other, bromide (as would be expected if a halide ion in one position is more labile than in the other).

The aquation of both $[Co(tren)ClH_2O]^{2+}$ and $[Co(tren)ClBr]^+$ show evidence

TABLE 9

Rates of aquation of some tren and related complexes

Substrate	Solvent	Temp. (°C)	k (sec^{-1})	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (cal/deg. mole)	Ref.
$[Co(tren)Cl_2]^+$	0.1 M $HClO_4$	25	2.96×10^{-3}	17.85	−10.4	39
cis-$[Co(en)_2Cl_2]^+$	0.1 M HNO_3	25	2.5×10^{-4}	22.2		32
cis-$[d\text{-}Co(tren)Cl_2]^+$	0.1 M HNO_3	25	1.5×10^{-4}			32
$[Co(tren)Cl_2]^+$	0.1 M PTSA[a] in D_2O	25	2.38×10^{-3}			33
$[Co(tren\text{-}d_6)Cl_2{}^+$	0.1 M PTSA[a]	25	2.11×10^{-3}			33
$[Co(tren\text{-}d_6)Cl_2]^+$	0.1 M PTSA[a]	25	1.70×10^{-3}			33
$[Co(tren)Br_2]^+$	0.1 M $HClO_4$	25	2.84×10^{-2}	15.1	−14.8	30
cis-$[Co(en)_2Br_2]^+$	0.1 M HNO_3	25	1.04×10^{-3}	23.8	+5	34
$[Co(tren)Br_2]^+$	DMSO	25	7.65×10^{-4}	17.9	−12	35
	Formamide	25	2.70×10^{-2}	10.1	−32	35
	DMF	25	4.28×10^{-4}	22.1	~0	35
	NMF	25	2.50×10^{-1}			35
$[Co(tren)F_2]^+$	b	25	3.5×10^{-3}[b]	22.3[b]	−6.5	31
$[Co(tren)H_2OBr]^{2+}$	1 M $HClO_4$	25	3.29×10^{-6}	24.4	−1.7	36
$[Co(tren)H_2OCl]^{2+}$	1 M $HClO_4$	25	2.38×10^{-6}	21.6	−11.0	37
cis-$[Co(en)_2H_2OCl]^{2+}$	0.1 M HNO_3	25	1.6×10^{-6}			38
$[Rh(tren)Cl_2]^+$	0.1 M $HClO_4$	25	1.97×10^{-5}	18.7		39
α-$[Co(tren)ClBr]^+$	0.1 M $HClO_4$	25	3.21×10^{-3}[c]	18.3	−13.5	40
β-$[Co(tren)ClBr]^+$	0.1 M $HClO_4$	25	3.38×10^{-2}[d]	16.2	− 9.0	40
$[Co(tren)CO_3]^+$		25	1.7×10^{-4}	15	−25	
		25	2.0[e]	11.1	−20	41

[a] PTSA = *p*-Toluene sulfonic acid
[b] acid ind. path
[c] release of Cl^-
[d] release of Br^-
[e] M^{-1} sec^{-1}

for the presence of geometrical isomers, which are theoretically possible in an octahedral tren complex. It was found[37] that the initial 10% of the first-order kinetics plot for the aquation of $[Co(tren)ClH_2O]^{2+}$ was noticeably curved and that spectral scans showed a slight shift in isosbestic points during the first part of the reaction. The kinetic data could be separated, however, into two first-order reactions and it was suggested that two isomers of $[Co(tren)ClH_2O]^{2+}$ were present and could be reacting in parallel. [Co (tren)ClBr] Br (ref. 40) was prepared from the chloro–aquo complex, and the first-order kinetic plot for its aquation also had initial curvature, but could be resolved into two first-order reactions. Bromide ion was released only during the initial part of the reaction, and it was assumed, but not confirmed, that chloride was released throughout the reaction. The two first-order rate constants obtained for the aquation of $[Co(tren)ClBr]^+$ ($k_\alpha = 3.21 \times 10^{-3}$ sec^{-1}, $k_\beta = 3.38 \times 10^{-2}$ sec^{-1}) agreed reasonably with the k_1 values for the aquation of $[Co(tren)Br_2]^+$ and $[Co(tren)Cl_2]^+$ ($k_{1Br} = 2.84 \times 10^{-2}$ sec^{-1}, $k_{1Cl} = 2.96 \times 10^{-3}$ sec^{-1}).

This evidence for isomerism seems to support the work of the Coliman[26], who reacted amino acids with $[Co(tren)(OH)(H_2O)]^{2+}$ to form $[Co(tren)(AA')]^{2+}$ (where A is the amino acid nitrogen and A′, the oxygen from carboxylate) and isolated isomeric glycinato and possibly malinato complexes. Geometrical isomers of $[Co(tren)ClNH_3]Cl_2$ have also been isolated[42] by the decomposition of a peroxo-bridged complex, $[NH_3(tren)CoO.OCo(tren)NH_3]Cl_4$ in concentrated aqueous NH_4Cl and fractional crystallization. A preliminary determination of the rates of acid hydrolysis of the two isomeric species (in 0.1 M $HClO_4$ at 26°C) gave pseudo first-order rate constants, of 15×10^{-5} and 7.4×10^{-5} min^{-1} for the α-isomer (NH_3 *trans* to tertiary amino nitrogen) and β-isomer, respectively.

The kinetics of acid hydrolysis of $[Rh(tren)Cl_2]^+$ (ref. 39) is pseudo-first order and unaffected by pH between 1–5. The single product formed was $[Rh(tren)H_2OCl]^{2+}$ and no evidence was found for any second aquation. The ratio $k_1$tren/$k_1(en)_2$ for the rhodium complexes at 80° is 6, while at 55° $k_1$tren/k_1 trien is approximately 5. Thus even with the larger central ion rhodium, the unusual effects of coordinated tren are still present.

The first aquation of $[Co(tren)Br_2]^+$ in several nonaqueous solvents has been examined by Madan and Peone[35] (Table 9). The rate constants observed seem to be typical of those seen for other Co(III) complexes. They vary by less than a factor of 1000 and there appears to be no simple relationship between the solvent dielectric constant and the rate constant.

Table 9 gives the pseudo-first order rate constants for the acid hydrolysis of $[Co(tren)Cl_2]^+$ and $[Co(tren\text{-}d_6)Cl_2]^+$ in H_2O and D_2O, which have been studied recently[33]. Both the solvent isotope effect (k_{H_2O}/k_{D_2O}) and the β-isotope effect (k_h/k_d) have been evaluated and compared with those for *cis* and *trans* $[Co(en)_2Cl_2]^+$ and $[Co(NH_3)_5Cl]^+$. For example, k_{H_2O}/k_{D_2O} for the tren complex is 1.26; but the ratio is 1.40–1.41 for the other species. The 10% lower value for the tren complex suggests that the nature of the complex itself can affect the ratio, contrary to previous opinions. This and other differences in the behavior of the tren complexes have been interpreted to mean that interactions between solvent molecules, β hydrogens of tren, and possibly the leaving chloride group may be more important in the distorted tren complexes than in regular octahedral cobalt amines.

Das Gupta and Harris[41] have studied the acid-catalyzed aquation of $[Co(tren)CO_3]^+$. The partial mechanism for this aquation is postulated to be the following:

$$[CoN_4CO_3]^+ + H_3O^+ \rightarrow [cis\text{-}CoN_4(OH_2)(CO_3H)]^{2+} \qquad k_1$$

$$[CoN_4(OH_2)(CO_3H)]^{2+} \rightarrow [cis\text{-}CoN_4(OH)(OH_2)]^{2+} + CO_2 \qquad k_2$$

with $k = k_0 + k_1 [H^+]$ ($k_2 \gg k_1 [H^+]$). The value of k_1 found for the tren complex (Table 9) does not differ substantially from that for the other amines studied. The lower value of $\Delta H^{\ddagger}$ (approximately 3–4 kcal/mole) is thought to be due to the increased strain of the O–Co–O linkage, caused by the geometrical requirements of tren. In addition, stopped-flow experiments show an initial increase in absorbance, followed by a decrease. This behavior, coupled with the levelling off of k at high acidities was interpreted as providing evidence for the existence of a dechelated intermediate $[Co(tren)(OH_2)(CO_2H)]^{2+}$. Such intermediates have been assumed to be present in the aquation of other amine carbonates which have been studied.

(ii) Exchange reactions

Margerum et al.[43] have studied the rate of replacement of bound water by NH_3 in $[Ni(tren)(OH_2)_2]^{2+}$ and other nickel-polyamine complexes by stopped-flow methods. For the following reaction

$$[Ni(tren)(H_2O_2)]^{2+} + NH_3 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [Ni(tren)(H_2O)(NH_3)]^{2+} + H_2O$$

at 6°, $k_{12} = 2.6 \times 10^5\ M^{-1}\ sec^{-1}$ and $k_{21} = 4.9 \times 10^3\ sec^{-1}$. The corresponding values for the analogous trien species are $1.2 \times 10^5\ M^{-1}\ sec^{-1}$ and $7.6 \times 10^2\ sec^{-1}$, and $k_{12}tren/k_{12}trien = 2.2$. This difference was attributed to the configuration of tren.

The water exchange behavior of Cu(II) and Ni(II) tren complexes has been studied by ^{17}O NMR[44]. Two different water exchange rates are found for the nickel complex at 25°, $k_1 = 8.2 \times 10^5$ and $\sim 9 \times 10^6\ sec^{-1}$, both with an activation energy of 8 kcal/mole. The reported substitutions in the Ni–tren complex by phen and bipy are slower than for NH_3 by ~20 and, because of the similarity in ratios, it has been suggested that the loss of the second water molecule (possibly rate-determining in phen and bipy substitution) is important here also. k_1 for $[Cu(tren)(OH_2)]^{2+}$ was $2.5 \times 10^5\ sec^{-1}$ with $\Delta H^{\ddagger} = 10.4$ kcal/mole.

Lincoln[45] studied the exchange of acetonitrile in $[Ni(tren)(CH_3CN)_2]^{2+}$, $[Co(tren)(CH_3CN)]^{2+}$, and their hexamethyl tren analogues. Two exchange rates were obtained for the nickel–tren species, $k_{1\alpha} = 165 \times 10^3 sec^{-1}$ at 25° and $k_{1\beta} > 2000 \times 10^3\ sec^{-1}$ at 40°, both of which are accelerated compared to $k_1 = 2 \times 10^3\ sec^{-1}$ at 25° for $[Ni(CH_3CN)_6]^{2+}$. The two exchange values suggest different environments for the two acetonitrile molecules, similar to the situation existing in $Ni(tren)(NCS)_2$[46]. The k_1 value for $(Co(tren)(CH_3CN)]^{2+}$ ($>2000 \times 10^3\ sec^{-1}$) is also much larger than the corresponding value for $[Co(CH_3CN)_6]^{2+}$ of $320 \times 10^3\ sec^{-1}$. In contrast to this labilization of the solvent by the polydentate amine ligand, the exchange rates for CH_3CN in $[Co(Me_6tren)(CH_3CN)]^{2+}$ and $[Ni(Me_6tren)(CH_3CN)]^{2+}$ are less than $0.1 \times 10^3\ sec^{-1}$, even at 80°. It is thought that the relative inflexibility of Me_6tren prevents close approach of the solvent to the metal ion, and therefore hinders rapid solvent exchange.

In a slightly different category are some exchanges of ligands other than solvent. Wilkins[47] compared the rate of replacement of water by NH_3 in $[Ni(tren)(H_2O)_2]^{+2}$ to that of replacement by some chelating nitrogen ligands. The k_f value for NH_3 ($260 \times 10^3\ M^{-1}\ sec^{-1}$) is approximately 25 times the same value for three bidentate ligands (phen – $13 \times 10^3\ M^{-1}\ sec^{-1}$, ornH$^+$ ($NH_3(CH_2)_3CH(NH_2)COO^-$ – $12 \times 10^3\ M^{-1} sec^{-1}$, bipy – $10 \times 10^3\ M^{-1}\ sec^{-1}$), while the value for gly was $90 \times 10^3\ M^{-1}\ sec^{-1}$. The reaction of terpy with $[Ni(tren)(H_2O)_2]^{2+}$ gave complex kinetic behavior.

Johnson and Forsberg[48] studied the exchange kinetics of tren with $[Nd(tren)_2]^{3+}$ in CH_3CN, from 20–80°, using the NMR line broadening technique. At the ligand–metal ion mole ratios studied [2:1 to 10:1], the reaction is first-order in both the complex and the ligand. The following mechanism was proposed:

$$[Nd(tren)_2]^{3+} + tren' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MN_3N' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MN_2N_2' \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MNN_3' \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Nd(tren)(tren)']^{3+} + tren$$

(N_x and N_y' represent the number of coordinated nitrogens for the departing and incoming ligand, respectively.) Transition state parameters at 25° are $\Delta H^{\ddagger} = 10.6 \pm 1.3$ kcal $mole^{-1}$, $\Delta S^{\ddagger} = -15.0$ cal deg^{-1} $mole^{-1}$ and $k = 58.2$ $mole^{-1}$ sec^{-1}.

(iii) Oxidation–reduction

In contrast to the interest which has been shown in other aspects of the chemistry of tertiary amines, their oxidation–reduction behavior has been studied very little. Taube et al.[49] have found that aqueous solutions of Cr(II) containing an excess of tren release H_2, ($2Cr(II) + 2H_2O \rightarrow 2Cr(III) + H_2 + 2OH^-$). The H_2 evolution was followed monometrically, and first-order rate constants were 4×10^{-4} sec^{-1} at pH 11 and lower by a factor of 10 at pH 9.5. The violet complex of Cr(III), which was also isolated, had a 1:1 Cr:tren ratio and its ion-exchange behavior was similar to that of *cis* $[Cr(en)_2(OH_2)_2]^{3+}$. Although the precise formula of the complex was not determined, it is thought to be $[Cr(tren)(OH_2)_2]^{3+}$.

The same authors also observed that Cr(II) added to a tren solution containing excess acrylamide is instantly oxidized to a different complex.

Bogdansky[27] has studied the interaction of molecular O_2 with Co(II)–tren species in solution from pH 7.8 to 12.8. Five complexes were present in solution over the pH range studied (3 octahedral, 2 5-coordinate) but only the 3 octahedral species reacted with O_2. All three were in rapid equilibrium and each reacted at a different rate with O_2.

$$\begin{tikzcd}
{[Co(tren)(H_2O)_2]^{2+}} \arrow[r, shift left, "K_{1A}"] \arrow[d, "1A"', "\begin{array}{l}1/2O_2\\ k_{1A}=1\text{–}3\times\\ 10^4 M^{-1} sec^{-1}\end{array}"] & {[Co(tren)(H_2O)(OH)]^+ + H^+} \arrow[l, shift left] \arrow[r, shift left, "K_{1B}"] \arrow[d, "1B"', "\begin{array}{l}1/2O_2\\ k_{1B}=2\text{–}5\times\\ 10^4 M^{-1} sec^{-1}\end{array}"] & {[Co(tren)(OH)_2] + H^+} \arrow[l, shift left] \arrow[d, "IC"', "\begin{array}{l}1/2O_2\\ k_{1C}=1\text{–}2\times\\ 10^4 M^{-1} sec^{-1}\end{array}"] \\
2 & 2 & 2
\end{tikzcd}$$

The reaction with O_2 was said to form bridged, binuclear peroxo intermediates from which molecular O_2 could be released by acidification below pH 4. After 2–3 days, irreversible oxidation to cherry-red $[Co(tren)(OH_2)_2]^{3+}$ occurred. The interconversions and proposed mechanisms are quite complex and the original thesis should be consulted for further details.

(iv) Anation

The bromide anation of $Co(tren)(OH_2)_2^{3+}$ has been studied spectrophotometrically by Kuo and Madan[50]. The kinetics fit a rate law $-d\,[complex]/dt = K_{AN}\,[Br^-][complex]$ with K_{AN} typically 10^{-4} sec^{-1} M^{-1}. At $\mu = 2.0$ M, $\Delta H^{\ddagger} = 25.2$ kcal mole^{-1} and $\Delta S^{\ddagger} = 0.19$ cal deg^{-1} mole^{-1}. The mechanism for the anation is believed to be an outer-sphere to inner-sphere interchange process (kinetically second-order).

D. CONCLUSION

The wealth of information which has been collected on the thermodynamics and kinetics of tripodal amine transition metal complexes might well stimulate one to find answers to several pertinent questions. Of primary importance is the influence of the chain length (and thereby ring size) of such amines on both the thermodynamic and kinetic behavior. Thus it would seem valuable to investigate the thermodynamics of formation of M^{2+} – trpn complexes. Similarly, studies of aquation rates of $Co(trpn)X_2^+$ as well as those of trpn and tren complexes of larger metal ions may be helpful in determining whether the anomalous aquation rates are due to distortion or to the presence of the tertiary nitrogen atom.

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