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LETTERS TO THE EDITOR*

FACTORS AFFECTING THERMODYNAMIC STABILITY OF METAL COMPLEXES WITH TRIPODAL AMINES

Sir:

The thermodynamics of metal complexes with multidentate amines as ligands has been the subject of several books and reviews [1]. In particular, recent work by Madan et al. [2] deals with the thermodynamic and kinetic properties of metal complexes with tripodal amines. In our opinion the thermodynamic section is incomplete and some of the statements in it are questionable and unsubstantiated. The purpose of this communication is to emend inexactness, where evident, as well as to make some additional remarks.

The first comment concerns the reactions of hydrogen ions for which the ΔH values reported by Madan et al. are relative to the ligand tren only and moreover were derived on the basis of the temperature dependence of the equilibrium constants [3]. It has been clearly shown in the past that this procedure is inadequate and can lead to inaccurate results. Stepwise reactions with protons have been followed calorimetrically both for tris-(2 aminoethyl)-amine (tren) [4] and for tris-(3-aminopropyl)amine(trpn) [5]. Table 1 re-

TABLE 1

Enthalpy changes involved in the stepwise protonation of tris-(2-aminoethyl) amine (tren) and tris (3-aminopropyl)amine in aqueous solution at 25°C

Protonation step	$-\Delta H^0$ (kcal mole^{-1})	
	tren[a,b]	trpn[c]
$L + H^+ \rightleftharpoons HL^+$	11.70 (11.0)	12.31
$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	12.80 (12.3)	12.78
$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	12.15 (10.3)	12.39

[a] Values taken from ref. 4; 0.1 *M* KCl.
[b] Values in parentheses were obtained by temperature dependence of log k, ref. 3.
[c] Values taken from ref. 5.

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ports the enthalpy changes, ΔH^0, involved in the stepwise reactions at 25°C; the data obtained by the temperature dependence of log K of tren are also reported for comparative purposes. Madan underlines that the second step of the protonation is more exothermic than the first; this behaviour is not unusual, in fact it has been observed in the protonation of all the polyamines containing three or more nitrogen atoms, i.e. triamines [6], linear tetraamines [7] and pentaamines [8]. Moreover, in reactions involving hexaamines [9], both ΔH_2 and ΔH_3 have a more negative value than ΔH_1. Two different hypotheses have been advanced to explain this behaviour: the first involves a tautomeric equilibrium of the monoprotonated species of formula HL^* (L: amine ligand) [6]. The other explanation suggests a remarkable increase in the electrostriction of the water molecules around the ion itself due to the positive charge on the ion, HL^+. As a consequence the electrostatic contribution to the enthalpy change becomes exothermic [9,10].

Concerning the formation of metal complexes the only thermodynamic data reported by Madan et al. are relative to the tren ligand. A complete thermodynamic study (ΔG^0 obtained by pH measurements, ΔH^0 by calorimetric titration) has been reported for the homologous tripod-like ligand, trpn [5]. Metal complexes of tren consist of a system of three fused five membered chelate rings; on the other hand trpn complexes form a system of three fused six-membered rings. Thermochemical data of the corresponding reactions of the ligands, 1, 4, 7, 10-tetraazadecane(trien) [11] and 1, 5, 9, 13-tetraazatridecane(3, 3, 3-tet) [12] are also available. Therefore, it is possible to establish to what extent the length of the aliphatic chain affects the stability of metal complexes of both tripodal and linear tetraamine ligands. Table 2 reports ΔG^0, ΔH^0 and ΔS^0 values for the reactions of copper(II), nickel(II) and zinc(II) with the above ligands in aqueous solution at 25°C. The stability in solution

TABLE 2

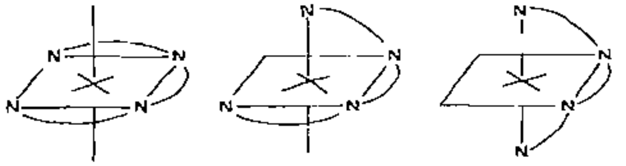
Thermodynamic functions for the reactions of copper(II), nickel(II) and zinc(II) ions with tripodal and linear tetraamines in aqueous solution at 25°C[a]

		tren[b]	trpn[c]	trien[d]	3,3,3-tet[e]
Cu^{II}	$-\Delta G^0$	25.8	17.9	27.4	23.3
	$-\Delta H^0$	20.4	14.7	21.6	19.5
	ΔS^0	18.0	10.8	19.5	12.8
Ni^{II}	$-\Delta G^0$	20.0	11.9	18.8	14.3
	$-\Delta H^0$	15.2	9.2	14.0	13.2
	ΔS^0	16.0	9.0	16.0	3.7
Zn^{II}	$-\Delta G^0$	19.7	14.6	16.4	12.7
	$-\Delta H^0$	13.9	8.9	8.9	7.4
	ΔS^0	19.5	19.1	25.0	18.0

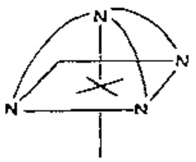
[a] ΔG^0 and ΔH^0 are expressed in kcal mole^{-1}; ΔS^0 in cal K^{-1} mole^{-1}; [b] ref. 16: 0.1 M KCl; [c] ref. 5: 0.1 M KCl; [d] ref. 11: 0.1 M KCl; [e] ref. 12: 0.1 M $NaNO_3$.

is dissected into the enthalpy and entropy terms. ΔH^0 is a relative measurement of the strength of the metal ligand interaction; ΔS^0 also provides information on the solute—solvent interactions.

The energy of the coordinate bond and the heat of formation in water of a metal complex with a multidentate chelating agent result from the balance of the geometrical requirements of the central ion and of the steric constraints of the ligand. When the complex has octahedral geometry (regular for nickel; tetragonally distorted for copper) the donor atoms of the linear tetraamine, trien, can be coplanar or not.



linear tetraamine



tripodal tetraamine

It can be shown easily that whatever the coordination, aliphatic chains do not exert any marked interrepulsion. On the contrary the tripod-like isomeric tetraamine tren is forced to adopt a non-coplanar coordination. Due to this type of configuration and to the geometry of the ligand steric repulsion between aliphatic chains are so strong that the positions of the amine groups are probably not those preferred by the metal ion; this causes weakening of the coordinate bonds. It is observed that nickel(II) and copper(II) complexes of tren have less negative ΔH^0 values than those of the corresponding complexes of trien (Table 2).

Longer aliphatic chains involve increase in the cumulative ring strain in metal complexes with linear tetraamines 3, 3, 3-tet and cause a small decrease in the exothermicity of the reaction. In the case of the tripodal ligand, trpn, the steric repulsions between the propylenic chains are much stronger. As a consequence the tripodal ligand is probably forced to change coordination (ligand field spectra of $[\mathrm{Cu\ trpn}]^{2+}$ in solution were interpreted in terms of trigonal bipyramid [5]) or to act as a terdentate ligand. Reactions of copper(II) and nickel(II) ions with trpn are markedly less exothermic than those with tren. It should be pointed out that the enthalpy change is less negative than that measured for the reactions of aliphatic triamines [1(c)].

In order to explain the large and positive values of the entropy changes, ΔS^0, for the reactions of zinc(II) ion with tetraamines, the formation of tetrahedral or five-coordinate complexes was postulated [1c]. The trend of ΔH^0 values is quite different from that seen in reactions of copper(II) and nickel-

TABLE 3

Thermodynamic functions for the reaction, $Cu^{2+} + HL^{+} \rightleftharpoons [CuHL]^{3+}$, in aqueous solution at 25°C

	$-\Delta G^0$ (kcal mole^{-1})	$-\Delta H^0$ (kcal mole^{-1})	ΔS^0 (cal K^{-1} . mole^{-1})
trien[a]	18.8	15.8	10.0
3, 2, 3-tet[b]	20.1	18.1	6.7
trpn[c]	14.7	12.8	6.1

[a] Ref. 11; 0.1 *M* KCl.

[b] 3, 2, 3-tet = 1, 5, 8, 12-tetraazatridecane, R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, J.Chem. Soc. Dalton, (1973) 1763, 0.5 *M* KNO_3.

[c] Ref. 5; 0.1 *M* KCl.

(II): tripod-like ligands show enthalpy changes larger than the isomeric linear tetraamines. This behaviour probably reflects the capability of the tripodal ligand to place its donor atoms at the corners of the coordination polyhedron.

Concerning complexes with protonated ligands, HL^+, it should be recalled that their solution stability depends not only on the atomicity of the chelate rings, but also on the position of the ammonium group. In Table 3 we report thermodynamic functions of the reactions of copper(II) ion with monoprotoated tetraamines. The complex [Cu H 3, 2, 3-tet]$^{3+}$ (3, 2, 3-tet: 1, 5, 8, 12-tetraazadodecane) is more stable than the complex (Cu H trien]$^{3+}$: in the former complex the ammonium group is situated at the end of a propylenic chain and, as a consequence, exerts a lower electrostatic repulsion.

The complex [Cu Htrpn]$^{3+}$ is considerably less stable than the above complexes [13]. Probably in the tripodal ligand the arm containing the ammonium group is hindered to a greater extent and exerts a stronger electrostatic repulsion than in linear tetraamines. This effect is more pronounced in the ligand tren, where the electrical charge is at the end of an ethylenic chain: the complex [Cu Htren]$^{3+}$ is not so stable as to be singled out during potentiometric titrations [14].

Copper(II) complexes with the tripodal ligands tren and trpn react with the hydroxide ion to give the species [CuOHL]$^+$. Their presence in aqueous solution has been proved by means of pH-metric titration [13,14]; furthermore the heat of the hydrolysis reaction, (CuL + OH), was calorimetrically determined [5,15]. The identification of polynuclear hydroxy-complexes was attributed to Paoletti and co-workers by Madan. This attribution is quite imaginary. Electronic spectra of the CuLOH species were interpreted in terms of trigonal bipyramid geometry of the chromophore [5,16]. This hypothesis has been endorsed by EPR studies [17].

Finally, it should be remembered that all the above reactions occur in aqueous solution. The measured heat results from two large contributions (hundreds of kcal. mole^{-1}) of opposite sign: (i) the exothermic formation of metal—nitrogen bond; (ii) the solvation terms (hydration of the product and dehydration of the reactants) which are on the whole endothermic. The extent and the intensity of the solvation terms are dramatically dependent on the properties of the solvent (dielectric constant, coordinating power, hydrogen bond formation, etc). In his review Madan compared the enthalpies of the reactions of 3*d* metal ions with tren in water with the corresponding ones of lanthanide ions in acetonitrile [18]. Changing the solvent from water to acetonitrile greatly reduces the weight of the solvation terms and unambiguously explains the lowest exothermicity of reaction of 3*d* metal ions. Preliminary studies of the reactions in acetonitrile between the $CuCl_4^{2-}$ ion and polyamines have been carried out by means of flow microcalorimetry: tetraamine ligands exhibit very large negative enthalpy changes (more than 60 kcal mole^{-1}) [19].

A comparison of the results in water is not possible, in fact 4*f* metal ions do not react with polyamines in water. In view of the strong "a" [20] (or "hard") [21] character of rare earths, nitrogen ligands cannot compete with the "harder" oxygen ligand water. However these ions are able to react in aqueous solution with the ligand ethylenediaminetetraacetate (EDTA) which contains both nitrogen and oxygen donor atoms. Calorimetric investigations have shown that reactions of trivalent 4*f* metal ions are slightly exothermic (1—3 kcal mole^{-1}) [22]. On the other hand reactions of divalent 3*d* metal ions with EDTA show more negative enthalpy changes (5—10 kcal mole^{-1}) [23].

All this experimental evidence emphasizes the importance of the solvation terms in the thermodynamics of metal complex formation in polar media.

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