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Potentiometric Determination of Stepwise Formation Constants of Mn(II), Fe(II), Fe(III), Co(II), Co(III) and Cu(II) Chelates with 1,4,7-Triazacyclononane

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Proton-ligand dissociation constant of 1,4,7-triazacyclononane $(H_3[9]aneN_3)^{3+}$ and the stability constants of its chelates with Mn(II), Fe(II), Fe(III), Co(II), Co(III) and Cu(II) have been determined pH-metrically in aqueous solution in the presence of 0.1 M $NaNO_3$ at 20°–32°C. The thermodynamic parameters for the mono- and bis- complexes under investigation are also evaluated.

The formation constants for the mono complexes of $(H_3[9]aneN_3)^{3+}$ were determined by spectrophotometric[1], X-ray and cyclic voltammetric methods[2]. The few studies of complexes containing cyclic triamines indicate that these complexes exhibit thermodynamic and kinetic stability normally associated with macrocyclic complexes[3,4]. The recent studies reveal that these types of ligands are δ-donors and good π-donors but weak acceptors. A survey of literature reveals that the study of transition metal complexes with $(H_3[9]aneN_3)^{3+}$ using pH-metric technique is scarce. The present work represents more data on the complexing strength of cyclic tridentate amine. The formation constants of the complexes of 1,4,7-triazacyclononane $H_3[9]aneN_3)^{3+}$ with Mn(II), Fe(II), Fe(III), Co(II), Co(III) and Cu(II) in aqueous solution and at an ionic strength of 0.1 M $NaNO_3$ at 20° and 32°C have been determined employing Calvin-Bjerrum pH-titration technique.

The ligand $\{(H_3[9]aneN_3)^{3+}\cdot 3Cl^-\}$ was prepared as described previously[1]. The structure and purity of the compound were checked by IR spectra and microanalysis. A solution of 1×10^{-2} M of $\{(H_3[9]aneN_3)^{3+}\cdot 3Cl^-\}$ was prepared and standardized by standard NaOH solution. A solution of 1×10^{-2} M of $([9]aneN_3)$ was prepared by neutralizing $\{(H_3[9]aneN_3)^{3+}\cdot 3Cl^-\}$ with NaOH. Standard aqueous solutions of Mn(II), Fe(III), Co(II) and Cu(II) as chlorides and Fe(II) as sulphate were prepared and standardized complexometrically by EDTA titration[5]. Carbonate-free NaOH sticks were washed with boiling water and finally dissolved in CO_2-free bidistilled water. The solution was standardized against potassium hydrogen phthalate. The standard solution of NaOH was then used to standardize HNO_3 solution potentiometrically. Conductance measurements were carried out

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at 20°C with a CM 25 conductivity meter, using immersion cell. The pH-measurements were performed at 20° and 32°C ± 1°C using digital pH-meter DRLONDE with combined glass electrode with sensitivity of 0.1 pH unit. Calvin-Bjerrum[6] titration technique was used to determine the dissociation constants of the ligand and the formation constants of their metal chelate at 20° and 32°C in aqueous solution at 0.1 M ionic strength. The following mixtures were prepared and the total volume in each case was made up to 50 ml:

mixture (A): 5 ml 0.1 M HNO_3 + 5 ml 0.1 M $NaNO_3$

mixture (B): mixture (A) + 20 ml 1×10^{-2} M $(H_3[9]aneN_3)\cdot 3HCl$

mixture (C): mixture (B) + 20 ml 1×10^{-2} M metal ion

These mixture were individually titrated potentiometrically against 3×10^{-2} M NaOH solution in the atmosphere of N_2 gas. All steps were repeated three times at 20° and 32°C.

The conductometric titration at 20°C (Fig. 1) shows formation of ML and ML_2 complexes between the ligand $(H_3[9]aneN_3)$ and Fe(III), Fe(II), Co(III), Co(II) and Cu(II), while in the case of Mn(II) only 1 ML species is observed.

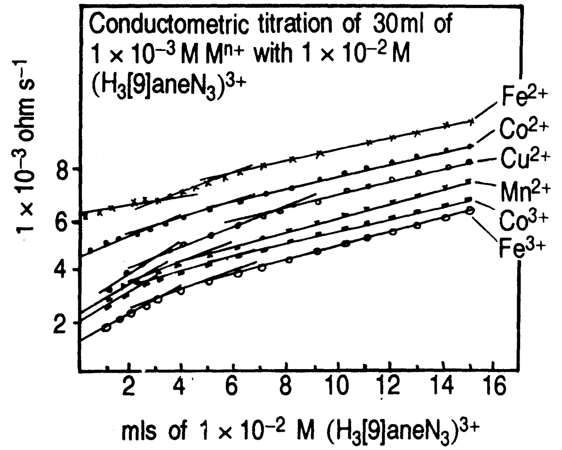

Fig. 1

The conductance value of chelates is little increased with increase in the ligand concentration. This may be attributed to the non-liberation of H^+ ions. Thus, chelation can take place through a coordination bond between the metal ion and three nitrogen atoms.

The potentiometric titration curve of free ligand $\{(H_3[9]aneN_3)^{3+}\cdot 3Cl^-\}$ gives two separate buffer regions. The first one is between a = 1 and a = 2 (a = number of moles of base added per mole of ligand). The second one is located at higher pH values between a = 2 and a = 3. This indicates the liberation of two protons during titration. Curves A and B are used to calculate $n_{\bar{H}}$ (average number of protons associated with the ligand) using the relation:

$$\bar{n}_H = y + \frac{(V_1 + V_2)(N^0 + E^0)}{(V^0 + V_1)Tc_l^0}$$

(where y is the total number of dissociable protons attached with the reagent molecule, V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curves A and B, respectively, N^0 is the normality of NaOH, E^0 is the initial concentration of free acid and Tc_l^0 is the total concentration of free ligand).

Interpolation of plots of $n_{\bar{H}}$ values against pH at half $n_{\bar{H}}$ values gave the values of log K^H for the ligand. The proton-ligand formation curve shows two pK^H values (Table 1). These values correspond to stepwise dissociation of the second and third protons of the ligand. The first proton dissociation is very fast and thus not detected. This is because the ligand can be considered as strong acid. The suggested equilibrium of the ligand and the pK^H values obtained at 20° and 32°C are shown in Table 1. The results are in agreement with the pK^H values reported earlier[1].

TABLE 1

ACID DISSOCIATION CONSTANTS OF $(H_3[9]aneN_3)^{3+}$ IN 0.1 M $NaNO_3$ AT 20° AND 32°C.

Reaction	pK_a at 20°C	pK_a at 32°C
$H_3L^{3+} \xrightarrow{K_{a1}} H_2L^{2+} + H^+$	pK_{a_1} = (strong)	pK_{a_1} = (strong)
$H_3L^{2+} \xrightarrow{K_{a2}} H_2L^{+} + H^+$	$pK_{a_2} = 6.8$	$pK_{a_2} = 6.3$
$H_3L^{+} \xrightarrow{K_{a3}} L + H^+$	$pK_{a_3} = 10.5$	$pK_{a_3} = 10.2$

The strong acid behaviour of $(H_3[9]aneN_3)^{3+}$ may be explained by the close proximity of the NH_2^+ groups which results from the cyclic nature of the amine. The second acid dissociation is also at least an order of magnitude more acidic than that of some tridentate amines such as {*cis*-1,2,5-tris[pyridine-2-carbaldiaminol] cyclohexane)[7],1,2,3-propanetriamine[8] and diethylenetriamine[9]} probably because the species groups.

The titration curves of the (1 : 2) metal-ligand solutions C are well separated from the ligand solution B in the pH range 6.1 to 8.3. Thus, the complexation occurs by replacement of H^+ ions. It is worth mentioning that the pH values do not suffer change during the titration time, ruling out any hydrolysis occurring under experimental conditions. Thus, the formation of hydroxo species is not detected. The metal-ligand titration curves show two inflections at m = 0–3 region and m = 3–6 region for Fe(III), Fe(II), Co(III) and Co(II) complexes. This is in agreement with 1 : 1 and 1 : 2 complex species. On the other hand Mn(II) and Cu(II) show one inflection at m = 0–3 confirming the 1 : 1 species. The formation of complexes formed can be represented by the following equation:

$$M^{n+} + H_3L^{3+} \rightarrow ML^{n+} + 3H^+$$

$$ML^{n+} + H_3L^{3+} \rightarrow ML_2^{n+} + 3H^+$$

From these titration curves, n^- (average number of ligand molecules attached per metal ion) and pL (free ligand exponent) values were calculated using the relations:

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)\bar{n}_H Tc_M{}^0}$$

$$pL = \log\left(\frac{E_{n=0}^{n=1}\beta_n^H[H^+]}{Tc_l{}^0 - \bar{n}Tc_M{}^0} \cdot \frac{(V^\circ + V_3)}{V^\circ}\right)$$

(where V_3 is the volume of alkali in the case of C curve required to reach the same pH with A and B curves. $Tc_M{}^0$ is the total concentration of the metal ion.

The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of metal complexation equilibria. The values of $\bar{n}$ extend between 0.2 and 1.8 for Fe(III), Fe(II), Co(III) and Co(II) complexes confirming the formation of 1 : 1 and 1 : 2 complex species in solution. On the other hand in the case of Mn(II) and Cu(II) complexes $\bar{n}$ values are between 0.2 and 1.38 showing that only 1 : 1 complex species are liable to be formed at 20°C.

At 32°C only 1 : 1 complex species are formed for all metal ions under investigation.

The stabilty of $(H_3[9]aneN_3)^{3+}$ complexes are calculated and the data given in Table 2. The order of the log K_i values for the metal ion was found to be $Cu^{2+} > Co^{2+} > Fe^{2+} > Co^{3+} > Fe^{3+} > Mn^{2+}$, in agreement with Irving and Williams order[10].

TABLE 2

DISSOCIATION CONSTANTS AND THERMODYNAMIC PARAMETERS AT 20 AND 32°C FOR METAL COMPLEXES AT $\mu = 0.1$ M ($NaNO_3$)

Complex	at 293 K		at 305 K	–ΔG	–ΔH	ΔS
	log K_1	log K_2	log K_1	KJ/mol	KJ/mol	J/mol
$(Cu[9]aneN_3)^{2+}$	15.50	—	14.60	85.62	128.33	421
$(Co[9]aneN_3)^{2+}$	14.60	7.00	14.00	81.76	85.55	281
$(Co[9]aneN_3)^{3+}$	13.60	6.40	12.90	75.33	99.81	328
$(Fe[9]aneN_3)^{2+}$	14.50	6.10	13.75	80.36	106.94	351
$(Fe[9]aneN_3)^{3+}$	13.20	6.10	13.00	75.92	28.52	94
$(Mn[9]aneN_3)^{2+}$	8.30	—	7.00	40.88	99.81	328

The acid dissociation constants and the metal-ligand stability constants were calculated at constant ionic strength ($\mu = 0.1$ M $NaNO_3$) and at two different temperatures (293 and 305 K). The results recorded in Table 2 are used for calculation of the thermodynamic parameters, free energy change (ΔG), enthalpy (ΔG) and entropy (ΔS) for metal-ligand stability constant using the following expressions:

$$\Delta G = -2.303RT \log K$$

$$\Delta H = 2.303R\,\frac{T_1T_2}{T_2 - T_1}\log\frac{K_2}{K_1}$$

$$\Delta S = 2.303R\log K + \frac{\Delta H}{T}$$

The ΔS values are positive for the chelates showing that the entropy is favourable for complex formation. These reactions are exothermic as evidenced by the negative value of ΔH. The ΔG values are negative for all these chelates showing that these reactions are spontaneous.

REFERENCES

1. Rita Yang and Leverett J. Zompa, *Inorg. Chem.*, **15**, 1499 (1976).
2. Magdalena J. Van Der Marwe, Jan C.A. Boeyens and Robert D. Hancock, *Inorg. Chem.*, **24**, 1208 (1985).
3. L.F. Lindoy and D.H. Busch, *Prep. Inorg. React.*, 6 (1971).
4. J.J. Christensen, D.J. Eattough and R.M. Izat, *Chem. Rev.*, **74**, 351 (1974).
5. A.I. Vogel, A Text Book of Qualitative Inorganic Analysis, Second Edition Longmans, London, NewYork (1951).
6. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
7. R.H. Childers, R.A.D. Wentworth and L.J. Zompa, *Inorg. Chem.*, **10**, 302 (1971).
8. J.E. Pure and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 995 (1950).
9. G. Schwarzenbach and J.E. Pure, *Helv. Chim. Acta*, **33**, 985 (1950).
10. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1958).

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