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Articles

Equilibria of Complex Formation between Bivalent and Trivalent Metal Ions and Macrocyclic Tridentate Amine

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The acidity constants of 1,4,7-triazacyclononane hydrochloride $\{(H_3\text{-}[9]\text{-ane-}N_3)^{3+}\cdot 3Cl^-\}$ at different temperatures 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 KNO_3 at 20 °C and 32 °C. The mole fractions of different species were calculated and discussed. The thermodynamic parameters for the complexes under investigation were also evaluated.

Introduction

The structure and formation constants for the monocomplexes of 1,4,7-triazacyclononane hydrochloride $\{(H_3\text{-}[9]\text{-ane-}N_3)^{3+}\cdot 3Cl^-$; (tacn)} were determined by spectrophotometric (Yang and Zompa, 1976), X-ray, and cyclic voltammetric methods (Van Der Merwe et al., 1985). The few studies of complexes containing cyclic triamines indicate that these complexes exhibit thermodynamic and kinetic stability normally associated with macrocyclic complexes (Lindoy and Busch, 1971; Christensen et al., 1974). These recent studies revealed that these types of ligands are σ-donors and good π-donors.

A survey of literature reveals that studies of transition metal complexes with tacn using the pH-metric technique are scarce. The present work presents data on the complexing strength of this cyclic tridentate amine. The formation constants of the complexes of tacn 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 KNO_3 at 20 °C and 32 °C have been determined using the Calvin−Bjerrum pH-titration technique (Irving and Rossetti, 1954).

Experimental Section

Materials. The ligand (tacn) was prepared as described previously (Yang and Zompa, 1976). The structure and purity of the compound were checked by IR spectroscopy and microanalysis. Metal salts ($MnCl_2\cdot H_2O$, $FeCl_2\cdot 4H_2O$, $FeCl_3\cdot H_2O$, $CoCl_2\cdot 6H_2O$, $CoCl_3\cdot 6H_2O$, $CuCl_2\cdot xH_2O$) of analytical grade (BDH) were supplied.

Solutions. A solution of 1×10^{-2} M of the ligand was prepared and standardized by standard KOH solution. Aqueous solutions of Mn(II), Fe(III), Co(II), Co(III), and Cu(II) as chlorides and Fe(II) as sulfate were prepared and standardized by EDTA titration (Vogel, 1951). Carbonate-free KOH solution was prepared in CO_2-free twice distilled water and standardized against potassium hydrogen phthalate. The standard solution of KOH was then used to standardize HNO_3 solution potentiometrically.

Physical Measurements. Conductance measurements were carried out at 20 °C with a CM 25 conductivity meter, using an immersion cell. The pH measurements were performed at 20 °C and (32 ± 0.1) °C using a DRLONDE digital pH-meter with a combined glass electrode with a sensitivity of 0.01 pH unit. The temperature was controlled by using a double-jacketed cell through which water from a constant-temperature bath was circulated.

Poteniometric Titrations. The Calvin−Bjerrum (Irving and Rossetti, 1954) titration technique was used to determine the protonation constants of the ligand and the formation constants of its metal chelates at 20 °C and 32 °C in aqueous solutions of 0.1 M ionic strength. The following mixtures were prepared and the total volume in each case was made up to 50 cm^3: mixture A: 5 cm^3 0.1 M HNO_3 + 5 cm^3 0.1 M KNO_3; mixture B, mixture A + 20 cm^3 1×10^{-2} M tacn; mixture C, mixture B + 20 cm^3 1×10^{-2} M metal ion. These mixtures were individually titrated three times at 20 °C and 32 °C, potentiometrically against 3×10^{-2} M KOH solution in an atmosphere of N_2 gas. Three minutes were required after each addition of the titrant.

Results and Discussion

Conductometric titrations between metal ions and 1,4,7-triazacyclononane hydrochloride (tacn) were carried out at 20 °C. The results showed the formation of ML and ML_2 complexes between the ligand (tacn) and Fe(II), Fe(III), Co(II), Co(III), and Cu(II), although in the case of Mn(II) only a ML species is observed. The conductance values of the chelates increased with increase in the ligand concentration. This may be attributed to the liberation of H^+ ions (Issa et al., 1969) as a result of the chelation between the metal ion and three nitrogen atoms.

The potentiometric titration curve B (Figure 1) of the free ligand gives two separate buffer regions. The first one is between $a = 1$ and $a = 2$ (a is the 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 $\bar{n}_H$ (average number of protons associated with the ligand) using the following

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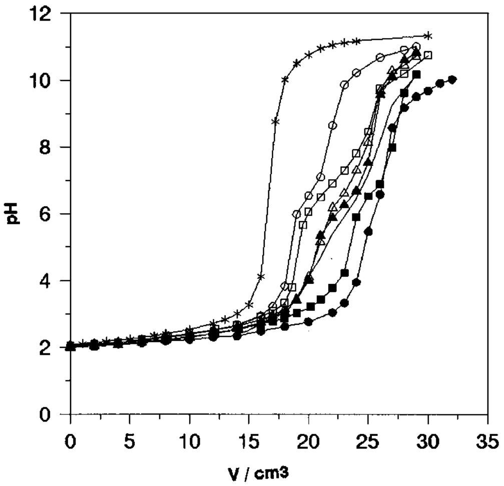

Figure 1. Potentiometric titration curves of Mn(II) −□−, Fe(II) −△−, Fe(III) −■−, Co(II) −, Co(III) −▲−, and Cu(II) −●− and tacn with 0.03 M KOH at 20 °C. Mixture A (−*−): 5 cm^3 0.1 M HNO_3 + 5 cm^3 M KNO_3. Mixture B (−○−): mixture A + 20 cm^3 1 × 10^{-2} M tacn. Mixture C: mixture B + 20 cm^3 1 × 10^{-2} M metal ion.

Table 1. Acid Dissociation Constants of (H_3-[9]-ane-N_3)$^{3+}$ at 293 K and 305 K, I = 0.1 M (KNO_3)

reaction	pK_a at 293 K		pK_a at 305 K
$H_3L^{3+} \rightarrow H_2L^{2+} + H^+$	pK_a = (strong)		pK_{a1} = (strong)
$H_2L^{2+} \rightarrow HL^+ + H^+$	pK_{a2} = 6.8	6.82[a]	pK_{a2} = 6.3
$HL^+ \rightarrow L + H^+$	pK_{a3} = 10.5	10.42[a]	pK_{a3} = 10.2

[a] Values taken from Yang and Zompa (1976).

relation (Irving and Rossetti, 1954)

$$\bar{n}_{\mathrm{H}} = y + \frac{(\nu_1 - \nu_2)(N^\circ + E^\circ)}{(\nu_0 + \nu_1)T^\circ_{C_{\mathrm{L}}}} \qquad (1)$$

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 in curves A and B, respectively, $N°$ is the normality of KOH, $E°$ is the initial concentration of free acid, $T^\circ_{C_L}$ is the total concentration of free ligand, and v_0 is the starting volume.

Interpolation at half $\bar{n}_H$ values gave log K_a 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. This is because the first ionization step of the ligand can be considered as that of a strong acid. The suggested equilibria of the ligand and the pK^H values obtained at 20 °C and 32 °C are shown in Table 1. The results are in agreement with the pK^H values reported earlier (Yang and Zompa, 1976).

The strong acid behavior of tacn may be explained by the close NH_2^+ groups, which result from the cyclic nature of the amine. The first acid dissociation constant is much greater than that of noncyclic polyamines (Childers et al., 1971). The second acid dissociation constant is also at least an order of magnitude more acidic than that of some open chain tridentate amines such as {1,3,5-triaminocyclohexane (Childers et al., 1971) (cis.cis tach), 1,2,3-propanetriamine (Pure and Schwarzenbach, 1950a), and diethylenetriamine (Pure and Schwarzenbach, 1950b)}.

The titration curves C (Figure 1) of the (1:2) metal−ligand solutions are well separated from those of ligand solution B in the pH range 6.1 to 8.3. It is worth mentioning that the pH values do not change during the titration time, ruling out any hydrolysis occurring under these experimental conditions and thus the formation of hydroxo species (extensive hydrolysis is unlikely). The metal−ligand titration curves show two inflections at (pH ≤ 6) and (pH ≤ 10) 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 (pH ≤ 7) confirming the 1:1 species.

The stepwise formation of complexes formed can be represented by the following equations:

$$M^{n+} + H_3L^{3+} \rightarrow (ML)^{n+} + 3H^+ \qquad (2)$$

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

From the titration curves, $\bar{n}$ (average number of ligand molecules attached per metal ion) and pL (free ligand exponent) values were calculated using the following relation (Irving and Rossetti, 1954)

$$\bar{n} = \frac{(v_3 - v_2)(N^\circ + E^\circ)}{(v_0 + v_2)\bar{n}_{\mathrm{H}} T^\circ_{C_{\mathrm{M}}}},$$

$$\mathrm{pL} = \log\left(\frac{\sum_{n=0}^{n=2}\beta_n^{\mathrm{H}}\left[\frac{1}{10^{\mathrm{B}}}\right]^n}{T^\circ_{C_{\mathrm{L}}} - \bar{n}T^\circ_{C_{\mathrm{M}}}}\cdot\frac{(v_0 + v_3)}{v_0}\right) \qquad (4)$$

where v_3 is the volume of alkali in the case of the M−tacn chelate curve required to reach the same pH with A and B curves. $T^\circ_{C_M}$ is the total concentration of the metal ion. In Figure 2 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. This can be explained in view of the coordination mode of Cu(II) with tacn, since the addition of a fifth or sixth nitrogen to the coordination sphere of Cu(II) in aqueous solution is not thermodynamically favorable (Zompa, 1978). The equilibrium

$$CuL_2^{2+} \rightleftharpoons CuL^{2+} + L \qquad (5)$$

lies far to the right and dissociation occurs. At 32 °C only 1:1 complex species are formed for all the metal ions under investigation.

The mole fraction α_M, α_{ML}, α_{ML_2} can be calculated from the potentiometric data using the experimental stability constant for ML and ML_2 complexes and initial concentrations of the metal ions and the ligand (Beck, 1970). It was found that the species ML and ML_2 fitted the experimental data with a minimum sum of squares of residuals and a standard deviation of (σ = 0.08−0.10). The species distribution curves can be obtained by plotting α (α = mole fraction of the species) vs log [L]. A representative curve for α as a function of log [L] is depicted in Figure 3. Closely related plots were obtained for other metal−ligand complexes. In the case of the presence of a low concentration of the ligand (1 × 10^{-17} mol dm^{-3}), almost all of the metal ions will be present as free ions (α_M = 98.95). On increasing the concentration of ligand, the concentration of the metal ion tends to decrease while that of ML (α_{ML} = 18.50) species tends to develop. At [L] = 46.31 × 10^{-14} M, 7.94 × 10^{-13} M, 5 × 10^{-12} M, 2 × 10^{-12} M, 1 × 10^{-12} M,

Table 2. Formation Constants and Thermodynamic Parameters of M(II), M(III), and $(H_3\text{-}[9]\text{-ane-}N_3)^{3+}$ at 293 K and 305 K, $I = 0.1$ M (KNO_3)[a]

complex	log K_1 at 293 K	log K_2 at 293 K	log K_1 at 305 K	$-\Delta G$/kJ·mol^{-1}	$-\Delta H$/kJ·mol^{-1}	ΔS/J·K^{-1}·mol^{-1}
$(Cu[9]aneN_3)^{2+}$	15.55		14.60	87.24	128.33	421
$(Co[9]aneN_3)^{2+}$	14.63	7.03	14.01	81.76	85.55	281
$(Co[9]aneN_3)^{3+}$	13.65	6.41	12.97	75.33	99.81	328
$(Fe[9]aneN_3)^{2+}$	14.51	6.42	13.75	80.36	106.94	351
$(Fe[9]aneN_3)^{3+}$	13.24	6.15	13.05	75.92	28.52	94
$(Mn[9]aneN_3)^{2+}$	8.33		7.02	40.88	99.81	328

[a] δ log $k \pm 0.02$, $\delta (\Delta H) \pm 0.2$ kJ·mol^{-1}, $\delta (\Delta S) \pm 0.3$ J·K^{-1}·mol^{-1}.

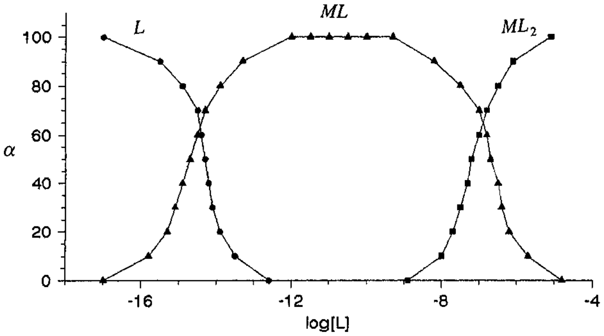

Figure 2. Distribution diagram for tacn−Co(II) complexes at 20 °C.

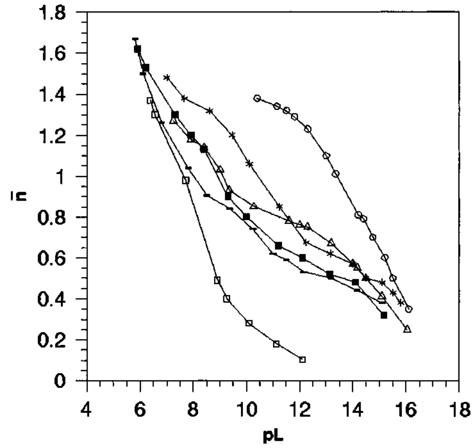

Figure 3. Formation curves ($\bar{n}$ vs pL) of Mn(II) −□−, Fe(II) −△−, Fe(III) −−−, Co(II) −*−, Co(III) −■−, and Cu(II) −○− with tacn at 20 °C.

and 1 × 10^{-6} M for Cu(II)−, Co(II)−, Fe(III)−, Co(III)−, Fe(II)−, and Mn(II)−tacn complexes respectively, the concentration of ML species reaches a maximum. On further increase in the ligand concentration, the ML_2 concentration increases at the expense of ML. At certain concentrations of the ligand, the concentration of the two species ML and ML_2 have the same value. For example, the concentration is 7.94 × 10^{-7} M and 1 × 10^{-7} M for Co(II)− and Co(III)−tacn complexes respectively. On increasing the concentration of the ligand, [ML] decreases and at the same time [ML_2] increases. At high [L], the ML_2 species predominates and the ML species vanishes.

The stability constants of 1:2 tacn complexes were calculated, and the data are listed in Table 2. For bivalent metal complexes, the stability decrease in the following order: Cu(II) > Co(II) > Fe(II) > Mn(II).

The same sequence was observed in the complexes of trivalent ions. This order is in agreement with the order of stability reported by Irving and Williams (1953), as well as that suggested by Grinberg and Yatsimeriski (1952).

The acid dissociation constants and the metal−ligand stability constants were calculated at constant ionic strength ($I = 0.1$ M KNO_3) and at two different temperatures (293 K and 305 K). The results recorded in Table 2 were used for calculation of the thermodynamic parameters, free energy change (ΔG), enthalpy (ΔH), and entropy (ΔS) from the metal−ligand stability constants using the following relations:

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

$$\Delta S = 2.303R\log K + \frac{\Delta H}{T} \quad (6)$$

$$\Delta G = -2.3RT\log K, \quad R = 8.3143\ \text{J·K}^{-1}\text{·mol}^{-1} \quad (7)$$

The ΔS values are positive for the chelates, showing that the entropy is favoring the 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.

Literature Cited

Beck, M. T. *Chemistry of Complex Equilibria*; Van Nostrand Reinhold: London, 1970; pp 73−145.
Childers, Ray F.; Wentworth, R. A. D.; Zompa, L. J. *Inorg. Chem.* **1971**, *10*, 302−306.
Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351−384.
Grinberg, A. A.; Yatsimeriski, K. B. *Bull Acad. Sci. USSR, Div. Chem. Sci.* **1952**, *48*, 239−244.
Irving, H. M.; Rossetti, H. S. *J. Chem. Soc.* **1954**, 2904−2910.
Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192−3210.
Issa, R. M.; Masoud, M. S.; Zayan, S. E. *Egypt J. Chem.* **1969**, *12*, 309−321.
Lindoy, L. F.; Bursch, D. H. *Prep. Inorg. React.* **1971**, *6*, 1−61.
Pure, J. E.; Schwarzenbach, G. *Helv. Chim. Acta* **1950a**, *33*, 985−995.
Pure, J. E.; Schwarzenbach, G. *Helv. Chim. Acta* **1950b**, *33*, 995−1005.
Van Der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 1208−1213.
Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 2nd ed.; Longmans: London, New York, 1951.
Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499−1502.
Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531−2536.

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