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STABILITY CONSTANTS OF POLYNUCLEAR COMPLEX IONS OF SOME FIRST-ROW TRANSITION ELEMENTS

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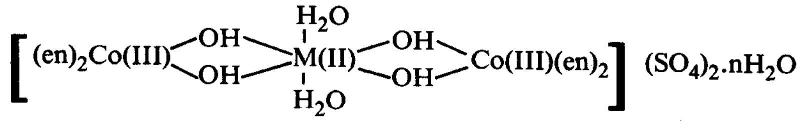
Abstract

Cis-$[Co(III)(en)_2(OH)_2]^+$ *and* cis-$[Cr(III)(en)_2(OH)_2]^+$ *can be regarded as ligands capable of being co-ordinated to metal ions through oxygen atoms forming a series of polynuclear complexes with the general formula:* $\{$cis-$[M(III)(en)_2(OH)_2]^+\}_nM'$ *(where* $M(III) = Co(III)$ *or* $Cr(III)$ *and* $M' =$ *metal ions). The stability constants of the polynuclear complexes:* $\{$cis-$[Co(III)(en)_2(OH)_2]^+\}M'$ *and* $\{$cis-$[Cr(III)(en)_2(OH)_2]^+\}$ M' *in which* M' *was Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cr(II)(Cr(III) complex ligand only) and Fe(II)(Cr(III) complex ligand only) were determined using a pH titration method. Both sets of stability constants follow the Irving-Williams sequence of stability constants. Comparison of the two sets of stability constants shows that the polynuclear complexes belonging to* cis-$[Co(III)(en)_2(OH)_2]^+$ *are more stable than those belonging to* cis-$[Cr(III)(en)_2(OH)_2]^+$*, which is in agreement with the fact that the acid dissociation constants of* cis-$[Co(III)(en)_2(OH)_2]^+$ *are smaller than those of* cis-$[Cr(III)(en)_2(OH)_2]^{3+}$.

Introduction

The idea of treating *cis*-$[Co(en)_2(OH)_2]^+$ as a dibasic ligand (H_2L) capable of co-ordinating to any metal ion through oxygen atoms was first introduced by Mori, Hatta and Shibahara[1]. They prepared a series of polynuclear complexes in solid state, with the general formula as shown, by mixing metal(II) sulphate with $[Co(en)_2(OH)_2]X$ at a proper pH.



$$\left[(\mathrm{en})_2\mathrm{Co(III)}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\rightleftarrows}}\overset{\mathrm{H_2O}}{\underset{\mathrm{H_2O}}{\mathrm{M(II)}}}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\rightleftarrows}}\mathrm{Co(III)}(\mathrm{en})_2\right](\mathrm{SO_4})_2.n\mathrm{H_2O}$$

(M(II) = Mg, Co, Ni (n = 7), Zn and Cd (n = 5))

Particularly the above polynuclear complex with Co(II) in the centre had identical appearance (pink powder) and IR spectrum as Werner's "pink sulphate" prepared by simple air oxidation of cobalt(II) sulphate and ethylenediamine. It seems that polynuclear complex ions: $\{cis\text{-}[\mathrm{Co(III)(en)_2(OH)_2}]^+\}_n\mathrm{M}'$ are formed in the solution in the same way as other ML_n complex ions being formed from L co-ordinating to M ions. Since *cis*-$[\mathrm{Cr(III)(en)_2(OH)_2}]^+$ has similar formula,.structure and property to *cis*-$[\mathrm{Co(en)_2(OH)_2}]^+$, polynuclear complex ions: $\{cis\text{-}[\mathrm{Cr(en)_2(OH)_2}]^+\}_n\mathrm{M}'$ should be formed in the solution when mixing metal(II) sulphate with *cis*-$[\mathrm{Cr(III)(en)_2(OH)_2}]^+$ at a proper pH. The stability constants of these polynuclear complex ions can be determined by pH titration method previously designed for determining stability constants of complexes of dibasic ligands(H_2L) in general[2]. The method is divided into two parts: Part I involves determination of first and second acid dissociation constants(K_{a1} and K_{a2}) of *cis*-$[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$ and *cis*-$[\mathrm{Cr(en)_2(H_2O)_2}]^{3+}$, Part II involves determination of stability constants of polynuclear complex ions.

Part I A set of relationships necessary for determining acid dissociation constants are derived as follows

Introducing a term called 'degree of formation of ligand-proton complex' ($\bar{n}_A$)

$$\bar{n}_A = \frac{\text{Total concentration of proton bound to ligand}}{\text{Total concentration of ligand}}$$

$$= \frac{T_H - H^+}{T_L} \qquad (1)$$

where T_H = total concentration of dissociable hydrogen

T_L = total concentration of L

Total concentration of proton bound to ligand is

$$[LH] + 2[LH_2] = K_{a2}^{-1}[H^+][L] + 2K_{a1}^{-1}K_{a2}^{-1}[H^+]^2[L] \qquad (2)$$

$$\text{Total concentration of ligand} = [L] + [LH] + [LH_2]$$

$$= [L] + K_{a2}^{-1}[H^+][L] + K_{a2}^{-1}K_{a1}^{-1}[L][H^+]^2 \qquad (3)$$

$$\therefore \bar{n}_A = \frac{K_{a2}^{-1}[H^+] + 2K_{a2}^{-1}K_{a1}^{-1}[H^+]^2}{1 + K_{a2}^{-1}[H^+] + K_{a2}^{-1}K_{a1}^{-1}[H^+]^2} \qquad ((2)/(3))$$

or $$\bar{n}_A + (\bar{n}_A - 1)K_{a2}^{-1}[H^+] + (\bar{n}_A - 2)K_{a2}^{-1}K_{a1}^{-1}[H^+)^2 = 0 \qquad (4)$$

Equation (4) shows the relationship between $\bar{n}_A$ and $[H^+]$, that is $\bar{n}_A$ varies with $[H^+]$. During the course of pH titration, $[H^+]$ varies which is recorded using pH meter so that the variation of $[H^+]$ is known. The variation of $\bar{n}_A$ can also be determined from the pH titration data.

The derivation of an expression for determining $\bar{n}_A$ is as follows:

The total concentration of dissociable hydrogen (T_H) at any point during titration $= 2T_L - [Na^+] + [OH^-]$

$2T_L$ is the total initial concentration of dissociable hydrogen

Na^+ is the concentration of Na^+ from the titrant (i.e. NaOH) and accounts for the reduction of total initial acidity due to neutralisation by alkali.

$[OH^-]$ is usually negligible in comparison with the other terms and appears on account of hydrolysis.

$$\text{But } [Na^+] = \frac{VN}{V^\circ}$$

where V = Volume of titrant added / ml
N = concentration of titrant
V° = total volume of solution being titrated

$$\therefore T_H = 2T_L - \frac{VN}{V^\circ} + [OH^-]$$

Substitute for T_H in (1) $$\therefore \bar{n}_A = (2T_L - \frac{VN}{V^\circ} + [OH^-] - [H^+])/T_L \qquad (5)$$

Since $\bar{n}_A$ and $[H^+]$ can be determined for all the points of the titration, the values of K_{a1} and K_{a2} can be determined from equation (4) as follows:

In the high pH range of titration, $[H^+]$ is small and if $K_{a1}^{-1}$and K_{a2}^{-1} are not too large, then the term $(\bar{n}_A - 2)K_{a2}^{-1}K_{a1}^{-1}[H^+]^2$ is negligible compared to $\bar{n}_A + (\bar{n}_A - 1)$ $K_{a2}^{-1}[H^+]$ and equation (4) reduces to

$$\bar{n}_A + (\bar{n}_A - 1)K_{a2}^{-1}[H^+] = 0$$

$$K_{a2}^{-1} = \frac{\bar{n}_A}{(1 - \bar{n}_A)[H^+]}$$

$$\log K_{a2}^{-1} = \log\bar{n}_A - \log(1 - \bar{n}_A) + pH \qquad (6)$$

Using equation (6), an average value of $\log K_{a2}$ is obtained from the experimental data in the high pH regions. As the value of K_{a2} is known, an average value of $\log K_{a1}$ can be obtained from equation (4).

Part II A set of relationships necessary for determining stability constants are derived as follows

We define the degree of formation of metal-ligand complex ($\bar{n}$) as the average number of ligand bound to metal per molecule of metal.

$$\bar{n} = \frac{\text{total concentration of ligand bound to metal}}{\text{total concentration of metal}}$$

$$\text{Total concentration of ligand bound to metal} = \sum_1^n n\beta_n[L]^n[M]$$

$$\text{Total concentration of metal} = \sum_0^n \beta_n[L]^n[M], \quad \beta_0 = 1$$

$$\text{where } \beta_n = K_1K_2K_3 \ldots\ldots\ldots\ldots K_n$$

[L] = free ligand concentration
[M] = free metal concentration

$$\bar{n} = \frac{\sum_1^n n\beta_n[L]^n}{\sum_0^n \beta_n[L]^n}$$

$$\therefore \sum_0^n (\bar{n}-n)\beta_n[L]^n = 0 \qquad (7)$$

A "formation curve" is defined as a plot of $\bar{n}$ against $-\log[L]$ which can be calculated either from equation (7) (if $\beta_1, \beta_2, \beta_3, \ldots\ldots \beta_n$ are known) or from the combination of the titration curve of ligand alone and that of the mixture of ligand and metal. The latter is clarified in the following.

Let 'a' be a point on the titration curve of the ligand with the same pH as a point 'b' on the titration curve of the mixture of ligand and metal (Figure 1).

$$[H^+]_a = [H^+]_b, [OH^-]_a = [OH^-]_b, \bar{n}_{Aa} = \bar{n}_{Ab} \qquad (8)$$

The total concentration of dissociable hydrogen at point 'a' (T_{Ha})

$$= 2T_L - [Na^+]_a + [OH^-]_a \qquad (9)$$

The total concentration of dissociable hydrogen at point 'b' (T_{Hb})

$$= 2T_L - [Na^+]_b + [OH^-]_b \qquad (10)$$

Rearranging equation[1] we obtain $[H^+]_a = T_{Ha} - \bar{n}_{Aa}T_L$ (11)

In the presence of metal, $\bar{n}_A$ is defined as:

$$\bar{n}_A = \frac{\text{Total concentration of proton bound to ligand}}{\text{Total concentration of ligand not bound to metal}}$$

$$= (T_H - [H^+])/(T_L - \bar{n}T_M)$$

$$\bar{n}_{Ab} = (T_{Hb} - [H^+]_b)/(T_L - \bar{n}_bT_M)$$

$$[H^+]_b = T_{Hb} - \bar{n}_{Ab}T_L + \bar{n}_{Aa}\bar{n}_bT_M \qquad (12)$$

According to equation (8), equation (11) = equation (12)

$$T_{Ha} - \bar{n}_{Aa}T_L = T_{Hb} - \bar{n}_{Ab}T_L + \bar{n}_{Aa}\bar{n}_bT_M \quad (\bar{n}_{Aa} = \bar{n}_{Ab} \text{ from (8)})$$

Substituting for T_{Ha} and T_{Hb} from equations (9) and (10), $2T_L - [Na^+]_a + [OH^-]_a =$

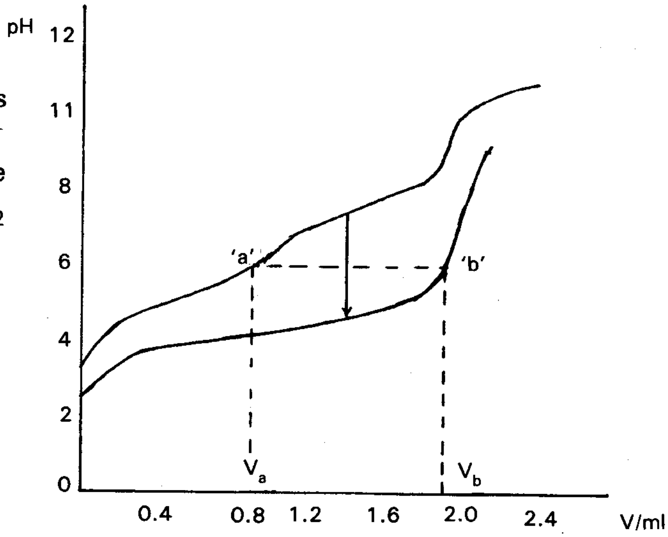
$$2T_L - [Na^+]_b + [OH^-]_b + \bar{n}_{Aa}\bar{n}_bT_M, ([OH^-]_a = [OH^-]_b \text{ from (8)})$$

$$\bar{n}_b = \frac{[Na^+]_b - [Na^+]_a}{\bar{n}_{Aa}T_M}$$

But $Na^+ = \frac{VN}{V^\circ}$ as mentioned before, $\therefore\ \bar{n}_b = \frac{N(V_b - V_a)}{V^\circ\bar{n}_{Aa}T_M}$ (13)

Figure 1

The top titration curve belongs to 0.01 M *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ The bottom titration curve belongs to 0.01 M *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ + 0.005 M Cu^{2+}



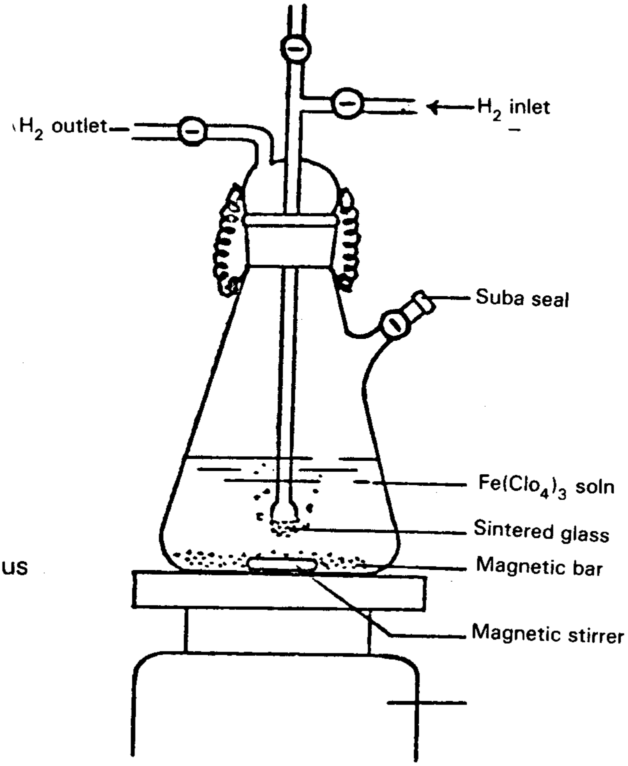


Figure 2

Apparatus for preparing ferrous perchlorate solution

Total concentration of ligand not bound to metal $= T_L - \bar{n}T_M = [L] + [LH] + [LH_2]$

$$\therefore\ T_L - \bar{n}T_M = [L] + K_{a2}^{-1}[H^+][L] + K_{a1}^{-1}K_{a2}^{-1}[L][H^+]^2$$

$$[L] = \frac{T_L - \bar{n}T_M}{1 + K_{a2}^{-1}[H^+] + K_{a1}^{-1}K_{a2}^{-1}[H^+]^2}$$

$$-\log[L] = \log\left\{\frac{1 + K_{a2}^{-1}[H^+] + K_{a1}^{-1}K_{a2}^{-1}[H^+]^2}{T_L - \bar{n}T_M}\right\} \tag{14}$$

Applying equations (13) and (14), the values of $\bar{n}$ and $-\log[L]$ can be determined for all the points on titration curves and hence a formation curve is obtained.

If only ML and ML_2 are formed in the solution, equation (7)

becomes $\bar{n} = \dfrac{\beta_1[L] + 2\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2}$

Rearrangement yields $\dfrac{\bar{n}}{(1-\bar{n})[L]} = \dfrac{(2-\bar{n})[L]}{1-\bar{n}}\beta_2 + \beta_1$

Therefore the values of β_1 and β_2 are obtained from the straight line plot of

$$\frac{\bar{n}}{(1-\bar{n})[L]} \text{ vs. } \frac{(2-\bar{n})[L]}{1-\bar{n}}$$

If three complexes (i.e. ML, ML_2, ML_3) are formed in the solution, equation[7] becomes $\bar{n} + (\bar{n} - 1)\beta_1[L] + (\bar{n} - 2)\beta_2[L]^2 + (\bar{n} - 3)\beta_3[L]^3 = 0$. Only three points on the formation curve (i.e. three pairs of values of $\bar{n}$ and [L]) are required to solve the equation to obtain the values of $\ _1$, β_2 and β_3.

Materials and Methods

Cis-$[Cr(III)(en)_2(H_2O)_2]^{3+}$ was prepared from anhydrous chromic sulphate through a series of complexes as follows

Tris-*(ethylenediamine) chromium(III) sulphate*[3] Powdered anhydrous chromium(III) sulphate (45 g) and 99% ethylenediamine (50 ml) were refluxed on a steam-bath overnight. The orange yellow mass formed was washed with alcohol and dried in air.

Tris-*(ethylenediamine) chromium(III) chloride*[3] The above complex sulphate (42.2 g) was dissolved in a mixture of water (39.6 ml) and concentrated hydrochloric acid (6.6 ml) at 60°C - 65°C. The solution was filtered and a mixture of concentrated hydrochloric acid (35.6 ml) and alcohol (55.4 ml) was added to the filtrate while cooling in ice-water. Recrystallisation of the crude product in a mixture of water and alcohol (1:1) at 65°C yielded yellow precipitates of the chloride on cooling.

Tris-*(ethylenediamine)* The above complex chloride (6.5 g) was dissolved in minimum amount of water (65°C). Addition of sodium perchlorate to the solution yielded yellow precipitates of the perchlorate.

Cis-*dichloro*-bis-*(ethylenediamine) chromium(III) perchlorate*[4] The above complex perchlorate (6.5 g) and concentrated hydrochloric acid (65 ml) were fused and warmed in a water-bath (75°C) for 5 hours. The violet-red solution was then evaporated to dryness on a water-bath. Grinding and washing the crude product in 50% methyl alcohol yielded violet powder of the *cis*-dichloro perchlorate.

Cis-*aquohydroxo*-bis-*(ethylenediamine) chromium(III) dithionate*[5] A solution of the *cis*-dichloro perchlorate (4.3 g) in water (36 ml) was heated on a hot-plate until the colour changed from violet to orange-red. Addition of pyridine (7.2 ml) and excess of sodium dithionate, while cooling in ice, separated the *cis*-aquohydroxo dithionate in the form of fine red powder.

A stock solution of cis-$[Cr(III)(en)_2(H_2O)_2]^{3+}$ *in* ClO_4^- *medium* *Cis*-$[Cr(en)_2(H_2O)(OH)]S_2O_6$(0.9 mmoles) was dissolved in a solution of perchloric acid (1.2 mmoles) and (water (30 ml). The solution was cooled in an ice-water bath, then slowly eluted through a column (1.5 cm diameter) containing (BDH) amberlite resins IRA 401 (in the perchlorate form) (24 ml). The concentration of *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$ in the effluent water was determined by spectrophotometric method (0.017 M; $A_{490\ nm} = 0.993$, $\varepsilon_{490\ nm}^{*} = 57$, $l = 1$ cm).

Cis-$[Co(III)(en)_2(H_2O)_2]^{3+}$ was prepared from cobaltous chloride hexahydrate through a series of complexes as follows

Trans-*dichloro*-bis-*(ethylenediamine) cobalt(III) chloride*[6] A 10% solution of ethylenediamine (600 g) was added to a solution of cobaltous chloride hexahydrate (160 g) in water (500 ml) with constant stirring. The solution was aerated vigorously for 10½ hours. Concentrated hydrochloric acid (350 ml) was then slowly added into the solution while heated on a steam-bath. The solution was left evaporating on the steam-bath until a crust formed over the surface (750 ml). Green crystals separated on cooling.

Carbonato-bis-*(ethylenediamine) cobalt(III) chloride* A solution of sodium carbonate (38 g) in water (100 ml) was added into a solution of the *trans*-dichloro chloride (41 g) in water (650 ml). The total solution was then heated on a steam-bath with stirring for 1 hour and then filtered when hot. The filtrate was concentrated to 200 ml and red precipitates of the product separated on cooling.

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* ε_{490} was obtained from visible spectrum of a solution of *cis*-$[Co(en)_2(H_2O)_2]Br_3$ of a known concentration. *cis*-$[Co(en)_2(H_2O)_2]Br_3$[5] could be obtained in a pure crystalline state, of which molecular weight was determined by titration against a standard solution of NaOH.

*Carbonato-*bis*-(ethylenediamine) cobalt(III) perchlorate* The carbonato chloride (5.8 g) was dissolved in warm water (40 ml), then sodium perchlorate (10 g) was added with stirring and the red product precipitated immediately.

A stock solution of cis*-$[Co(III)(en)_2(H_2O)_2]^{3+}$ in ClO_4^- medium* Carbonato-*bis*-(ethylenediamine) cobalt(III) perchloride (0.4233 g or 0.00125 moles) was dissolved in water (20 ml) and Analar perchloric acid; SG 1.70, concentration 71-73% W/W (0.31 ml) was added. Nitrogen gas was bubbled through the solution for 2½ hours to remove carbondioxide. The solution was then transferred quantitatively to a 50 ml volumetric flask and made up to the mark (0.025 M).

All M^{2+} ions, except for Fe^{2+} and Cr^{2+}, were obtained from commercially available M(II) perchlorate solids. Stock solutions of Fe^{2+}, Cr^{2+} were prepared as follows

A stock solution of Fe^{2+} in ClO_4^- medium Ferric perchlorate solution (0.227 M, $[H^+]$ = 0.186 M, 100 ml) was hydrogenated in the apparatus shown in figure 2, containing Adam's catalyst (PtO_2, 0.3 g). After passing hydrogen gas through the solution, with stirring, for several hours; PtO_2 was reduced to platinum black and the solution turned pale green. The concentration of ferrous ion was determined by titration against standard 0.1 N $KMnO_4$ solution under nitrogen atmosphere (0.227 M).

A stock solution of Cr^{2+} in ClO_4^- medium A violet solution of chromic perchlorate hexahydrate (23 g) in water (120 ml) containing a few drops of Analar 72% perchloric acid, was reduced in the reduction compartment of the apparatus shown in Figure 3. Nitrogen was passed through the apparatus throughout the reduction with the stopcocks B and D closed and A and C open. The electrodes were connected to the electrical circuit shown in Figure 3. After nineteen hours, the solution turned sky blue, then the mercury level was raised to shut off the oxidation compartment. With A, C closed but B, D and F open (H also open to D and J); the pressure of nitrogen forced the chromium(II) solution up the tube and into the storage vessel. After all the solution had been transferred, F was closed, H and J were open only to the main line. The storage vessel was disconnected from the preparative system and then connected to the system shown in Figure 4. The concentration of chromous perchlorate solution was determined by spectrophotometric method (0.206 M, A_{710nm} = 1.013, ε_{710nm} = 4.92 and l = 1 cm).

Titration procedures Titrations of solutions (25 ml) of the appropriate complex ligand (0.01 M), in the presence (0.0033 M or 0.005 M) and in the absence of metal ions with 2M NaOH were carried out in a double-walled glass vessel maintained at 25°C by the circulation of water from a thermostat-bath (figure 5, nitrogen atmosphere was applied only in the case of Fe^{2+} and Cr^{2+}, titrant was delivered from agla syringe fitted with a micrometer). The ionic strength was adjusted to 3M ClO_4^- with "Analar" sodium

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**cis*-$[Co(en)_2(H_2O)_2](ClO_4)_3$ is explosive.

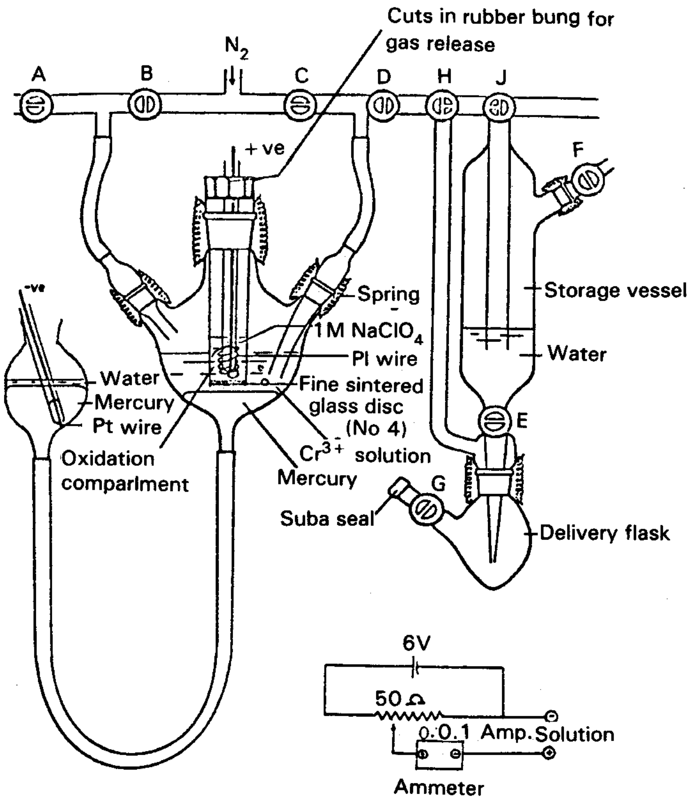

Figure 3 Apparatus for preparing chromous perchlorate solution

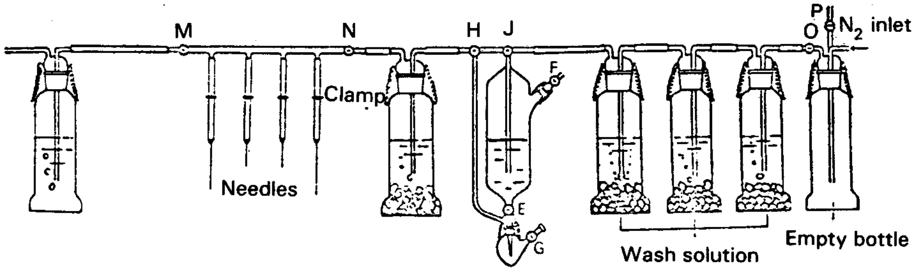

Figure 4 Apparatus for storing and dispensing chromous perchlorate solution

perchlorate monohydrate. The pH of the solution was measured by means of a Radiometer PHM64, Research Digital pH-meter, with a combined glass-electrode filled with saturated NaCl instead of the usual saturated KCl. Since the quantity required in the calculation of acid dissociation constants is $[H^+]$ but not $\{H^+\}$ (i.e. the activity of acid) as pH values generally imply, it would be more convenient if the reading on the pH meter were $-\log[H^+]$. To accomplish this, the pH meter was calibrated against a standard solution of $3M(Na)ClO_4$ of which $[H^+] = 0.00109$ M. by turning the buffer knob until the reading on the screen was 2.963 (i.e. -log 0.00109).* End-points of titrations of excess free acid in solutions were located by analytical (derivative) methods[7]

Results and Discussion

Comparisons of titration curves of the appropriate complex ligand, in the presence and in the absence of metal ions for all cases show the lowering of pH as the result of complexation of ligands to M^{2+} ($mLH_n + M = ML_m + mnH$) (Figure 1). The formation curves of $\{cis\text{-}[Co(en)_2(OH)_2]^+\}_nM$ complexes are compared in Figure 6, and the formation curves of $\{cis\text{-}[Cr(en)_2(OH)_2]^+\}_nM$ complexes are compared in Figure 7. The titrations with Cr(II) and Fe(II) were carried out in the case of $cis\text{-}[Cr(en)_2(H_2O)_2]^{3+}$ but not in the case of $cis\text{-}[Co(en)_2(H_2O)_2]^{3+}$ because any electron-transfer reaction between $cis\text{-}[Cr(en)_2(H_2O)_2]^{3+}$ and Fe(II) (or Cr(II)) is expected to be slow enough for the equilibrium of $cis\text{-}[Cr(en)_2(H_2O)_2]^{3+}$, Fe(II) (or Cr(II)) and the polynuclear complexes to virtually establish; but the electron-transfer reactions in the case of $cis\text{-}[Co(en)_2(H_2O)_2]^{3+}$ would be too fast to obtain any reliable equilibrium data. The formation curves for Cu(II) levels off at $\bar{n} \sim 2$ which means that Cu(II) forms 1:1 and 2:1 complexes. The range of the formation curves is limited by the solubility of complexes and metal hydroxides; therefore the curves for Mn(II), Cr(II), Fe(II), Co(II), Ni(II) and Zn(II) are incomplete. However the formation curves for Ni(II) and Zn(II) have the tendency to go up to $\bar{n} = 3$ which means that Ni(II) and Zn(II) form 1:1, 2:1 and probably 3:1 complexes. For Mn(II), Fe(II) Cr(II) and Co(II); at least 1:1 complex must be formed and there is a possibility of forming higher-ratio complexes. The acid dissociation constants ($\log K_{a1}$ and $\log K_{a2}$) for $cis\text{-}[Co(en)_2(H_2O)_2]^{3+}$ and $cis\text{-}[Cr{:}en)_2(H_2O)_2]^{3+}$ were calculated from equations (4) and (6), and given in Table 1. The stability constants ($\log K_1$ and $\log K_2$) of the polynuclear complexes in the case of Cu(II) were obtained from the straight line plot of $\frac{n}{(1-\bar{n})[L]}$ vs. $\frac{(2-\bar{n})[L]}{1-\bar{n}}$ and given in Table 1. For

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*This method of preparation is valid providing that the activity coefficient of H^+ is constant over the range of titration.

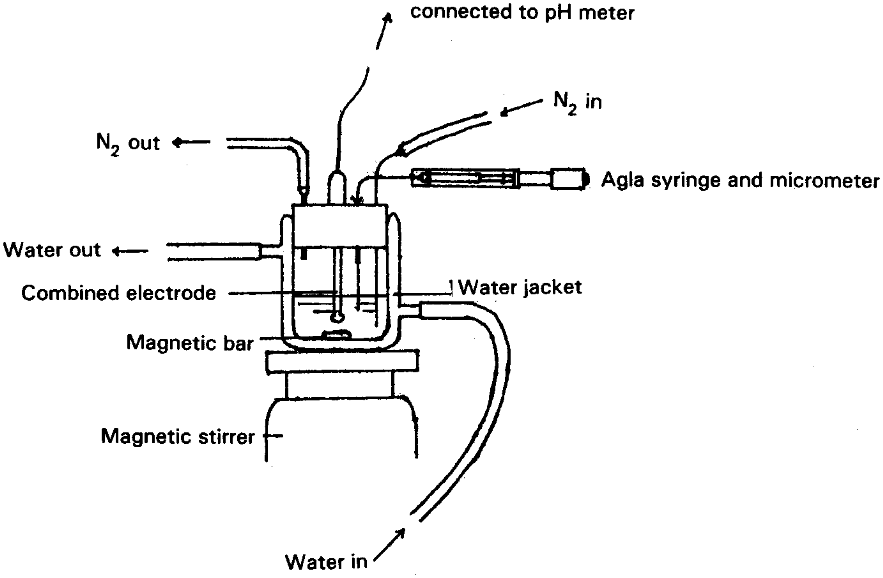

Figure 5 Apparatus for preparation and titration of solutions containing Cr^{2+} and Fe^{2+}

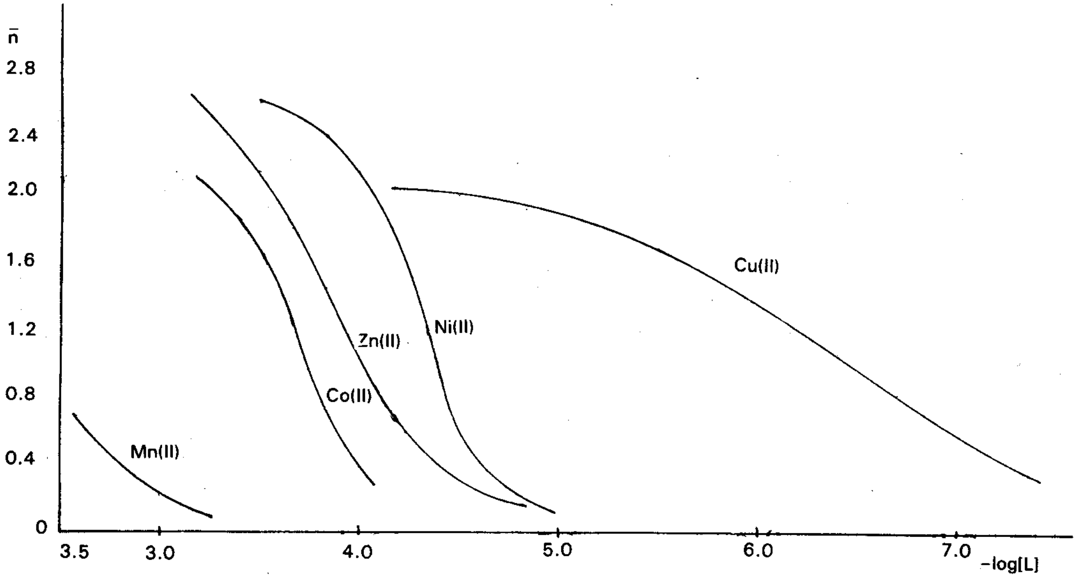

Figure 6. Comparison of the titration curves of $\{cis\text{-}[Co(en)_2(OH)_2]^+\}_nM$ polynuclear complex ions in 3M ClO_4^- medium at 25°C

other cases, we chose the values of $\bar{n}$ and [L] from the best three points around $\bar{n}$ = 0.5 - 1.0 on the corresponding formation curves and apply these values to the equation: $\bar{n} + (\bar{n}-1)\beta_1[L] + (\bar{n}-2)\beta_2[L]^2 + (\bar{n}-3)\beta_3[L]^3 = 0$ to obtain a set of three inhomogeneous equations. Solution of these equations yielded only reliable values of β_1 since ML is formed predominantly when $\bar{n}$ = 0.5 - 1.0. For these cases, only the values of $\log K_1$ are tabulated (Table 1). However Cannon and Benjarvongkulchai calculated the values of β_2 for all the polynuclear complexes: {cis-$[Co(en)_2(OH)_2]^+$} M′ from the straight line plot of $\frac{\bar{n}}{(1-\bar{n})L}$ vs. $\frac{(2-\bar{n})L}{1-\bar{n}}$[9].

Table 1

Ligand	*cis*- $Co(en)_2(H_2O)_2^{3+}$				*cis*- $Cr(en)_2(H_2O)_2^{3+}$			
metal ion	**$-\log K_{a1}$**	**$-\log K_{a2}$**	**$\log K_1$**	**$\log K_2$**	**$-\log K_{a1}$**	**$-\log K_{a2}$**	**$\log K_1$**	**$\log K_2$**
H^+	5.86	8.35			4.96	7.55		
Cr(II)			—	—			3.9	—
Mn(II)			3.1	—			2.5	—
Fe(II)			—	—			2.8	—
Co(II)			4.1	—			2.9	—
Ni(II)			4.6	—			3.1	—
Cu(II)			7.1	6.0			5.6	4.4
Zn(II)			4.4	—			3.2	—

$\log K_1$'s for the cases of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ and *cis*-$[Cr(en)_2(H_2O)_2]^3$ are plotted against atomic number of metals in Figure 8. In both cases, the values of $\log K_1$ for the divalent metals follow the Irving-Williams sequence of stability constants: Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) which is also the order of electron affinity of M(II). The plot also shows that for the same metal ion, the polynuclear complex ion formed with *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ has higher value of $\log K_1$ than that formed with *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$. This can be explained in terms of the difference in the acid strength of the two ligands. The table shows that $-\log K_{a1}$ and $-\log K_{a2}$ of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ are larger than those of *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$ which means that *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ is less acidic than *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$; hence *cis*-$[Co(en)_2(OH)_2]^+$ has greater affinity for proton or metal ion, which are both a positive entity, than *cis*-$[Cr(en)_2(OH)_2]^+$. Once a ligand is bound more strongly to the same metal, its complex is more stable and hence a higher value of logK.

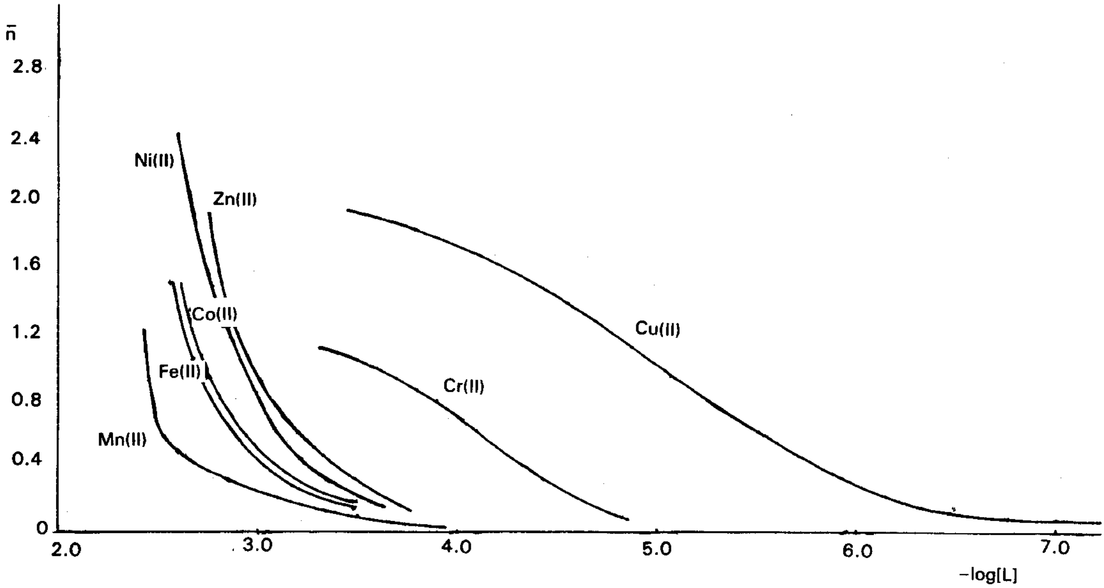

Figure 7 Comparison of the formation curves of $\{cis\text{-}[Cr(en)_2(OH)_2]^+\}_nM$ polynuclear complex ions in 3M ClO_4^- medium at 25°C

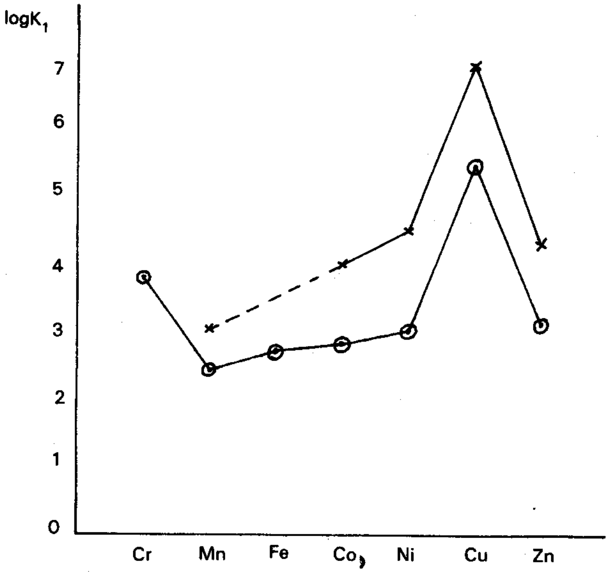

Figure 8 Comparison of the values of logK$_1$ where (× × ×) are those for $\{cis\text{-}[Co(en)_2(OH)_2]^+\}M$ and (OOO) are those for $\{cis\text{-}[Cr(en)_2(OH)_2]^+\}M$

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บทคัดย่อ

ไอออนเชิงซ้อน *cis*-$[\mathrm{Co(III)(en)_2(OH)_2}]^+$ และ *cis*-$[\mathrm{Cr(III)(en)_2(OH)_2}]^+$ อาจจะถือได้ว่าเป็นลิแกนด์ซึ่งสามารถใช้อะตอมออกซิเจนของมันในการสร้างพันธะโคออดิเนชั่นกับไอออนของโลหะต่าง ๆ เกิดเป็นไอออนเชิงซ้อนโพลีนิวเคลียร์ต่าง ๆ ซึ่งมีสูตรทั่วไปเป็น $\{cis\text{-}[\mathrm{M(III)(en)_2(OH)_2}]^+\}_n\mathrm{M}'$ (ในที่นี้ M(III) = Co(III) หรือ Cr(III) และ M′ = ไอออนของโลหะต่าง ๆ) เราได้ทำการทดลองหาค่าคงที่ความเสถียรของไอออนเชิงซ้อนโพลีนิวเคลียร์เหล่านี้ซึ่งมี M′ เป็น Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cr(II) และ Fe(II) (ยกเว้น $\{cis\text{-}[\mathrm{Co(en)_2(OH)_2}]^+\}_n$Fe(II) และ $\{cis\text{-}[\mathrm{Co(en)_2(OH)_2}]^+\}_n$Cr(II)) โดยวิธี pH titration ซึ่งพบว่าสำหรับลิแกนด์แต่ละตัวค่าคงที่ความเสถียรมีค่าเรียงตามลำดับชนิดโลหะไอออนดังนี้ Mn(II) Fe(II) Co(II) Ni(II) Cu(II) Zn(II) ซึ่งเป็นลำดับที่พบสำหรับลิแกนด์ทั่วไป เรียกว่า Irving–Williams sequence of stability constants จากการเปรียบเทียบค่าคงที่ความเสถียรของไอออนเชิงซ้อนโพลีนิวเคลียร์ที่เกิดจาก *cis*-$[\mathrm{Co(III)(en)_2(OH)_2}]^+$ และที่เกิดจาก *cis*-$[\mathrm{Cr(III)(en)_2(OH)_2}]^+$ พบว่าไอออนเชิงซ้อนโพลีนิวเคลียร์ที่เกิดจาก *cis*-$[\mathrm{Co(III)(en)_2(OH)_2}]^+$ มีความเสถียรมากกว่าไอออนเชิงซ้อนโพลีนิวเคลียร์ที่เกิดจาก *cis*-$[\mathrm{Cr(III)(en)_2(OH)_2}]^+$ ซึ่งผลที่ได้เป็นไปตามที่คาดไว้จากความจริงที่ว่าค่าคงที่ของการแตกตัวเป็นไอออนของกรด *cis*-$[\mathrm{Co(III)(en)_2(H_2O)_2}]^{3+}$ มีค่าน้อยกว่าค่าคงที่ของการแตกตัวเป็นไอออนของกรด *cis*-$[\mathrm{Cr(III)(en)_2(H_2O)_2}]^{3+}$.