*Asian Journal of Chemsitry* Vol. 8, No. 3 (1996), 517–520

# Mixed Ligand Complexation of Praseodymium(III) with Some Merocapto Ligands—A Potentiometric Study

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Systems of Pr(III) ion 2MPG-MSA and Pr(III) ion-2MPG-NALC were studied by pH titration method by maintaining metal : primary ligand : secondary ligand ratio as 1 : 5 : 5 ($M \neq X = Y$) and their stability constants are reported.

## INTRODUCTION

Interaction of Pr(III) with N-2-mercapto propionyl glycine (2MPG), mercapto succinic acid (MSA) and N-acetyl-L-cystein (NALC) at 25°C in aqueous medium was studied. pH titration data based on Calvin-Bjerrum[1] titration technique were employed for the calculation of proton-ligand and metal-ligand stability constants.

The development in the study of mixed ligand complexes has been very fast in the recent years[2–4] and their study is of interest to analytical chemists[5] and bioinorganic researchers.[6]

An exhaustive literature survey was, therefore, undertaken and it was revealed that generally mixed ligand complexation has been studied potentiometrically by maintaining metal : primary ligand : secondary ligand ratio as 1 : 1 : 1 ($M = X = Y$). It was also revealed that not much work was done on the present ligands and almost negligible work on their complexation with Pr(III) ion. Hence the present work was undertaken to investigate the mixed ligand complexation of Pr(III) with these ligands by maintaining the ratio of metal : primary ligand : secondary ligand as 1 : 5 : 5 ($M \neq X = Y$). The stability constants of the ternary complexes, $\log K_{MXY}$, were computed adopting the method given by Lorra[7]

## EXPERIMENTAL

The Pr(III) salt was dissolved in doubly distilled water and standardised by the method of Flascha.[8] All the other solutions were also prepared in doubly distilled water. The pH measurements were carried out on ELICO digital model LI-122 pH meter (accuracy ± 0.01 pH unit) with a combined electrode type CL-51 having pH range 0–14. The method of Calvin-Bjerrum as modified by Irving and Rossotti[9] was used to obatin $\log K_i^H$ and Thompson and Lorras method was employed to obtain $\log K_{MXY}$.

### Calculation of stability constants

(a) *Proton-Ligand Stability Constants*: Proton-ligand stability constants have been calculated as a proton-ligand formation number, $\bar{n}_A$. The proton-ligand stability constants $\log K_i^H$ are calculated by

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(i) Half integral method,
(ii) Method of pointwise calculation, and
(iii) Least squares method.

(b) *Calculation of Stability Constants of Mixed Ligand Complexes*: For the calculation of stability constants of mixed ligand complexes the two types of equilibria possible are given as

$$\left.\begin{array}{ll} M + X = MX, & MX + Y = MXY \\ M + Y = MY, & MY + X = MXY \end{array}\right\} \begin{array}{l}\text{Stepwise}\\ \text{equilibria}\end{array}$$

$$M + X + Y = MXY \quad \text{Simultaneous equilibria}$$

where X and Y represent the two different ligands.

## Simulatneous equilibria

When the mixed ligand titration curve MXY does not coincide with either MX or MY curve, the equilibrium involved in simultaneous and the determination of stability constant has been carried out by Thomson and Lorras method.[7]

When $T_M^0 = T_X^0 = T_Y^0$,

$$K_{MXY} = \frac{T_M^0 - (A)B/2}{(1/8)(A)^3B} \qquad (1)$$

where

$$A = \frac{2T_X^0 + 2T_Y^0 + P - T_{OH} - H^+}{\dfrac{4[H^+]^2}{K_1K_2 + K'_1\,K'_2} + \dfrac{2[H^+]}{K_2 + K'_2}} \qquad (2)$$

But when $T_M^0 \neq T_X^0 = T_Y^0$ (present work)

$$K_{MXY} = \frac{(1/2)(T_X^0 + T_Y^0) - ([A]X)}{\{T_M^0 - [(1/2)(T_X^0 - T_Y^0) - ([A]X]\}(1/4)[A]^2X} \qquad (3)$$

where

$$A = \frac{\dfrac{\{2T_X^0 + 2T_Y^0 + P - T_{OH} - [H^+]\}}{4[H]^2 + 2[H]}}{(K_1K_2) + (K'_1\,K'_2\,)(K_2 + K'_2\,)} \qquad (4)$$

## RESULTS AND DISCUSSION

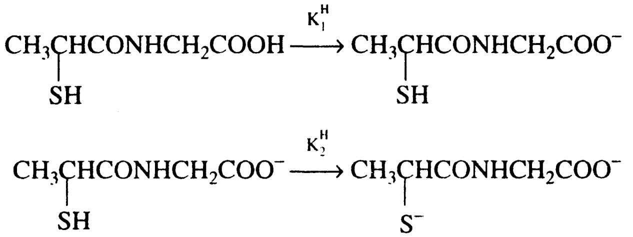
Determination of proton-ligand stability constants was carried out by the half integral method. Formation curve for $\bar{n}_A$ against pH was constructed and the values of log $K_1^H$ and log $K_2^H$ were found out as the pH at $\bar{n}_A = 0.5$ and 1.5 for all the three ligands and the results obtained are given in the following Table 1:

TABLE-1
PROTONATION CONSTANTS OF LIGANDS

| Ligand | log $K_1^H$ | log $K_2^H$ |
|---|---|---|
| 2MPG | 8.36 | 3.50 |
| MSA | 10.86 | 4.89 |
| NALC | 9.72 | 3.17 |

The log $K_i^H$ values were also calculated adopting pointwise calculation and least squares mothod. It has been observed that log $K_i^H$ values obtained by all the three methods were almost same.

2 MPG is a ligand of novel type bearing —SH, —CONH and —COOH groups; however, pH titration curves of this ligand show two well separated steps of neutralisation and hence two protonation constants are calculated. The ionisation of N-2-mercaptopropionylglycine may be represented by the following equation:



$$CH_3\underset{SH}{C}HCONHCH_2COOH \xrightarrow{K_1^H} CH_3\underset{SH}{C}HCONHCH_2COO^-$$

$$CH_3\underset{SH}{C}HCONHCH_2COO^- \xrightarrow{K_2^H} CH_3\underset{S^-}{C}HCONHCH_2COO^-$$

MSA has been shown to be useful analytical reagent because of its reducing[10] and complexing[11] properties. MSA contains three dissociable protons, namely two from the two different —COOH groups and one from —SH group. The value of log $K_3^H$ is described due to deprotonation of carboxalic group near to the—SH group and values of log $K_2^H$ and log $K_1^H$ arise from dissociation of secondary —COOH group and —SH group respectively.

NALC is a mucolytic agent[12, 13] and is reported to be used in the isolation of mycobacteria from sputum. It has three dissociable protons. The dissociation of proton from carboxyl group occurs at such a low pH value that the pH range studied here is less than 2; this group is always fully ionised, hence only two protonation constants were evaluated for two other groups, namely —$NH_2^+$ and —SH.

As our aim was to study the interaction of the present ligands Pr(III) ions the protonation constants of these ligands were investigated at the identical experimental conditions set for Pr(III) mixed ligand studies. Because of the vast differences in experimental conditions in the present study and those given in literature, a comparison of the present log $K_i^H$ values and the literature values has no relevance. The results are set out in Table-2.

TABLE-2

P = 0.008395 M N = 0.3906 $T_L^0$ = 0.002 N
$T_M^0$ = 0.0004 N $\mu$ = 0.1 M ($NaClO_4$) $V^0$ = 50 mL

| $H^+ \times 10^5$ | $T_{OH} \times 10^3$ | $A \times 10^5$ | $X \times 10^{-2}$ | log ($K_{MXY}$) |
|---|---|---|---|---|
| | | Praseodymium(III)-2MPG-MSA | | |
| 1.1481 | 11.7592 | 1.4920 | 1.4929 | 10.2545 |
| 1.0715 | 11.7886 | 1.7018 | 1.3015 | 10.1403 |
| 1.0000 | 11.8180 | 1.9409 | 1.1349 | 10.0260 |
| 0.9332 | 11.8474 | 2.2136 | 0.9898 | 9.9119 |
| 0.8710 | 118768 | 2.5244 | 0.8633 | 9.7977 |
| | | Mean log ($K_{MXY}$) = 10.026 | | |

| $H^+ \times 10^4$ | $T_{OH} \times 10^3$ | $A \times 10^3$ | $X \times 10^{-4}$ | $\log (K_{MXY})$ |
|---|---|---|---|---|
| | | Praseodymium(III)-2MPG-NALC | | |
| 2.0893 | 5.3760 | 10.8502 | 4.9092 | 14.5312 |
| 1.9498 | 5.4266 | 12.4143 | 4.2757 | 14.4142 |
| 1.8197 | 5.4773 | 14.2023 | 3.7240 | 14.2973 |
| 1.6982 | 5.5279 | 16.2464 | 3.2435 | 14.1805 |
| 1.5849 | 5.5785 | 18.5830 | 2.8250 | 14.0638 |
| | | Mean $\log (K_{MXY}) = 14.2974$ | | |

The formation of mixed ligand complexes can be concluded initially by noting the pH of precipitation for MX, MY and MXY titration curves. It is expected that the mixed ligand titration would give a higher value of pH of precipitation than the binary metal complex titration which was found to be true in this work. The mixed ligand complex formation can be further confirmed by comparing the mixed ligand curve with the theoretical composite curve. The composite curve was drawn by computing the difference between the titration curves as (MX–X) + (MY + Y) or (MX + MY) – (X – Y). The composite curve has been found to be non-superimposable on the experimental MXY curve.

The nature of complex equilibria was investigated according to the method suggested by Carey and Martell. The deviation of mixed ligand complex curve was from pH 2.80 to 3.95. The horizontal difference between the mixed ligand complex curve and the composite curve remained nearly constant in the pH range 2.80 to 4. Since the mixed ligand curve did not coincide with either of the binary complex titration curves, the mixed ligand complex formation was, therefore, assumed to be taking place by simultaneous and not by stepwise equilibrium and both the ligands were considered to have been attached simultaneously to the metal ion.

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(*Received*: 24 November 1995; *Accepted*: 20 February 1996) AJC-1083