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# COMPLEX FORMATION BETWEEN $[Co(OH)_2tren]^+$ AND DIVALENT METAL IONS

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The stability constants of complex formation between $[Co(OH)_2tren]^+$ as a ligand and some divalent metal ions were determined by Bjerrum's method. The values of log $K_1$ and log $K_2$ in this order are: Co, 2.85, 3.0; Ni, 3.0, 3.5; Cu, 6.3, 5.0; Zn, 3.6, 3.0; Cd, 2.6, 2.2. Some relevant 1:2 and 1:3 complexes have been isolated as the perchlorates.

A series of trinuclear complex salts, $[M^{II}\{(OH)_2Co\ en_2\}_2(H_2O)_2](SO_4)_2 \cdot nH_2O$ (n = 7 for $M^{II}$= Mg, Co, Ni and n = 5 for $M^{II}$= Zn, Cd) were obtained by Mori, Hatta, and Shibahara$^{1)}$ by mixing a solution of $M^{II}SO_4 \cdot nH_2O$ and one containing $[Co(OH)_2en_2]^+$ and $SO_4^{2-}$. It was felt of interest to the present authors to measure the stabilities of such complexes in aqueous solution. The intricacy caused by the isomerization could be avoided when cis-$[Co(OH)_2tren]^+$ (tren = N, N', N"-triaminotriethylamine) is chosen as the cationic "ligand." Thus the present letter describes the result of the determination of stability constants of complexes between cis-$[Co(OH)_2tren]^+$ and some divalent metal ions by Bjerrum's method.

Tren and cis-$[Co(OH)_2tren]X$ were prepared after Kimura et al.$^{2)}$ with a slight modification. Thus cis-$[Co(OH)_2tren]X$ was prepared from $[CoCl_2tren]Cl$ and silver oxide, bypassing the preparation of $[CoCO_3tren]X$. Most frequently the solution to be titrated contained $1.195 \times 10^{-4}$mol of $M(ClO_4)_2$, $3.347 \times 10^{-4}$mol of $[Co(OH)(H_2O)tren](ClO_4)_2$, and $1.053 \times 10^{-4}$mol of $HClO_4$ in 0.050 $dm^3$, the ionic strength being adjusted to 0.1 with $NaClO_4$. The M:L ratio in this mixture was ca. 1:3; solutions of other compositions were also examined in a few cases. The mixture was titrated with an 0.1200 N NaOH solution under $N_2$ atmosphere by use of an Orion 801A pH meter. The concentration of the free ligand [L] and the average coordination number $\bar{n}$ were calculated from the titer and the hydrogen ion concentration on the assumption that only 1:1 and 1:2 complexes were formed. The acid dissociation constants $K_{a1}$ and $K_{a2}$ necessary for this calculation were determined also by titration to be $10^{5.31}$ and $10^{7.71}$, respectively, at 25°C and I = 0.1 ($NaClO_4$). The stability constants, $K_1 = [ML]/\{[M][L]\}$, and $K_2 = [ML_2]/\{[ML][L]\}$ were then obtained by linear fitting according to the equation, $Y = K_1K_2X - K_1$, where $X = (2-\bar{n})[L]/(\bar{n}-1)$ and $Y = \bar{n}/\{(\bar{n}-1)[L]\}$/ Figs. 1a and 1b illustrate two such X-Y plots, the former showing the best and the latter the poorest linearity. The values of log $K_1$ and log $K_2$ obtained are given in Table 1. They are seen to be in the order of Irving-Williams series. From the usual behavior of $Cu^{2+}$, it does not seem necessary to consider the formation of $ML_3$ complex for this ion. This can be substantiated by the formation curve, $\bar{n}$ vs. pL shown in Fig. 2. For the other ions it was difficult to conclude from the result of the titration

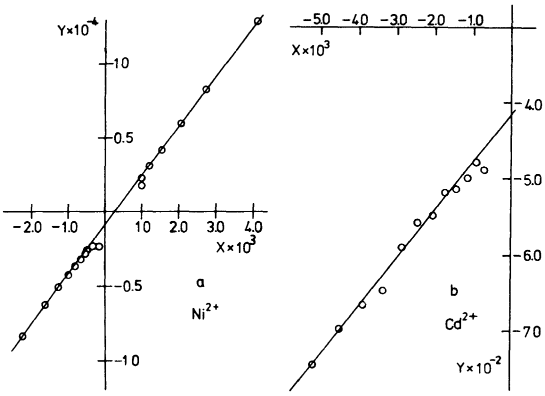

Fig. 1 X-Y plots for determination of stability constants

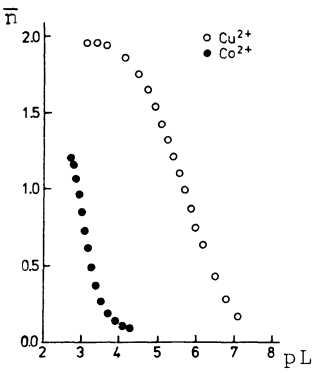

Fig. 2 Formation curves

Table 1. Stabilities of complexes between $[Co(OH)_2tren]^+$ and divalent metal ions

| M | $M_t:L_t$ in solution | $\log K_1$ | $\log K_2$ |
|---|---|---|---|
| Co | 1:1.8 | 2.80 | 2.99 |
| | 1:3 | 2.85 | 2.97 |
| | 1:4.5 | 2.89 | 2.99 |
| Ni | 1:3 | 3.00 | 3.53 |
| | 1:4.2 | 3.10 | 3.41 |
| Cu | 1:1.8 | 6.29 | 4.98 |
| | 1:3 | 6.32 | 5.05 |
| | 1:3.6 | 6.30 | 5.06 |
| Zn | 1:3 | 3.6 | 3.0 |
| Cd | 1:3 | 2.6 | 2.2 |

whether $ML_3$ is formed or not. Attempts to obtain the values of $K_3$ by successive approximations have not so far been successful, since $\bar{n}$ is usually small. Thus the decision as to whether the greater values of $K_2$ as compared with $K_1$ in some cases have a real meaning or else are the result of neglect of the formation of 1:3 complex must await more precise analyses including consideration of hydrolysis of $M^{2+}$ ions, formation of hydroxyl complexes MLOH and hydrogen complexes M(LH). However, the fair constancy of the $K_2$ values despite the variation in the $M_t:L_t$ in solution seems to imply low concentrations of the 1:3 complexes.

Isolation of the relevant heteronuclear complex ions $[M^{II}\{(OH)_2Co\ tren\}_n]^{2+n}$ as crystalline salts was realized by use of $ClO_4^-$ as the counter ion. In this respect the solubility tendency is quite different from the case of $[M^{II}\{(OH)_2Co\ en_2\}_2]^{4+}$, which can be readily crystallized as the sulfate but not as the perchlorate. Thus, a solution of $[Co(H_2O)_2tren](ClO_4)_3$ was prepared by adding 5 N $HClO_4$ dropwise to a mixture of 2 g of $[Co(OH)(H_2O)tren](ClO_4)_2$ and 15 ml of water. A solution of $2.3\times10^{-3}$ mol of $M(ClO_4)_2\cdot nH_2O$ in a little water was added, and to this mixture was added 4 N NaOH drop by drop until the precipitate persisted after stirring. The pH at this stage was 6.8 for M = Co, 8.1 for Ni, and 6.6 for Zn (which are not claimed to be the exact optimum). In the case of M = Cu, 3.5 g of $NaClO_4$ was added after the pH reached 6.5; without the addition of this reagent no precipitate appeared. After 1 hour's mixing the precipitate was filtered, washed first with an ice-cold $NaClO_4$ solution, then with ethanol, and air-dried. Yield 1.4 - 1.7 g. The complex salts obtained had the composition, $[M^{II}\{(OH)_2Co\ tren\}_3](ClO_4)_5\cdot 3H_2O$ for M = Co, Zn, Ni, the former two being isomorphous, and $[M^{II}\{(OH)_2Co\ tren\}_2](ClO_4)_4\cdot 2H_2O$ for M = Cu. Analogously, a compound $[Cd\{(OH)_2Co\ tren\}_2Cl_2](ClO_4)_2\cdot 5H_2O$ was obtained by starting with 0.5 g of $[Co(OH)(H_2O)tren](ClO_4)_2$ and 0.13 g of $CdCl_2\cdot 2.5H_2O$. Crystallization of 1:3 complexes for M = Co, Zn, Ni in spite of the low concentration of such species as suggested by stability determinations may be a result of lattice stabilization,[3)] and might be compared with the crystallization of $[Mg(NH_3)_6](ClO_4)_2$ from aqueous solution in spite of the low stability of the 1:6 complex.

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