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## Studies on some binary complexes of Th (IV) and UO<sub>2</sub> with vitamin-U At constant temperature

**Birodh Ram****Abstract**

The Co-ordination compounds bear an important role in analytical, bio and electro chemistry. In this paper, the formation constants of binary complexes of Actinide metal ions Th (IV) and UO<sub>2</sub> (II) with vitamin-U (Methylmethionine Sulfonium Chloride) have been carried out at constant temperature  $25 \pm 0.1$  °C and ionic strength  $\mu=0.2M$  using Irving–Rossotti method. Various factors influencing the formation and stabilities of binary complex.

**Keywords:** Binary complexes, vitamin-U, at constant temperature

**Introductions**

The ligand vitamin-U (Methyl Methionine Sulfonium Chloride MMSC) is an  $\alpha$ - amino acid. This compound contains both NH<sub>2</sub> group and an acid group COOH capable of forming chelate ring. It also contains sulphur atom and chloride ion. Vitamin-U is very important for hair growth, mucoso, antiulcer (Konrad, Ichikalwa *et al.*) etc. Thermal analysis of vitamin-U and some of its Ni<sup>+2</sup> complexes have been studies. Polarographic determination of stoichiometry and stability constants of complexes of vitamin-U with metal ions (Romero *et al.*) has been carried out.

The vitamin-U was obtained from Fluka (AR Grade) other reagents used were sodium perchlorate, perchloric acid, sodium hydroxide, thorium nitrate, uranyl nitrate (BDH AR Grade). The metal contents of the prepared solutions under analysis were determined by complexometric titration (Vogal, West).

**Material and method**

Ionic strength was maintained at 0.2M dm<sup>-3</sup> with the use of sodium perchlorate Systronics pH meter 361 with readability +0.01 was used for potentionmetric studies. The pH meter was calibrated with buffer solutions and calibrations was checked intermittently. All potentiometric titrations were carried out at  $25 + 0.1$  °C using carbonate free NaOH solution following the procedure (Irving and Rossotti, Mavani *et al.*) Irving - Rossotti titration technique (Vogel, West) was used for the determination of formation constants.

The proton ligand and material ligand formation constants of vitamin-U were calculated by measuring the magnitude of the proton displacement during the titration of ligand in absence and in presence of metal ions respectively. The proton ligand and binary metal ligand formation constants are presented in Table 1.

**Table 1:** Proton ligand and binary metal ligand formation constant of vitamin-U at temperature  $25 \pm 0.1$  °C.

Ligand PK <sup>H</sup> Values	Metal ligand Formation constants	
	Th (IV)	UO <sub>2</sub> (II)
pK <sub>1</sub> <sup>H</sup> = 8.36±0.03	log K <sub>1</sub> = 8.60 ± 0.03	log K <sub>1</sub> = 8.57 ± 0.02
pK <sub>1</sub> <sup>H</sup> = 2.08±0.03	log K <sub>2</sub> = 8.26 ± 0.19	log K <sub>2</sub> = 7.60 ± 0.26
	log K <sub>B</sub> = 16.88 ± 0.20	log K <sub>B</sub> = 16.22 ± 0.26

The importance of the equilibrium data of actinide ions with different legands are useful in solvent extraction, ion exchange, precipitation reactions, separation procedures etc.

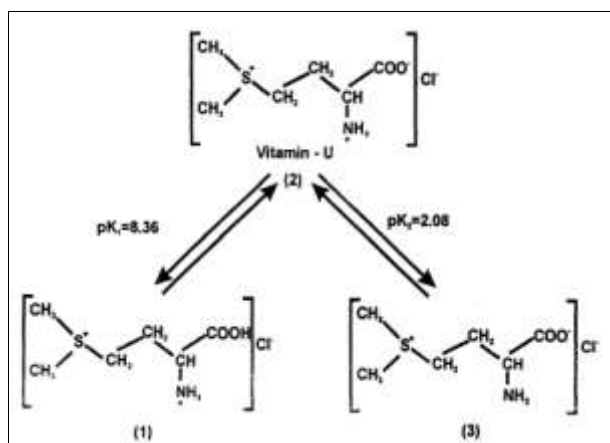
**Results and Discussion**

The protonation of vitamin-U and mechanism of M-vitamin-U, ML complex formation is as

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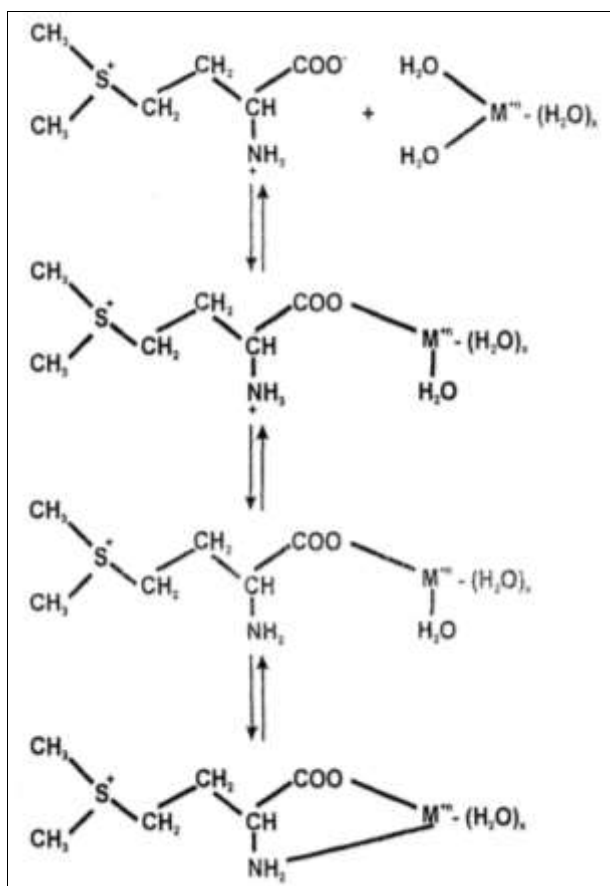
follows:

Protonation of vitamin-U

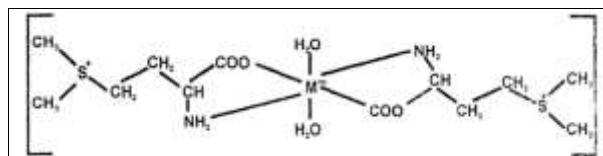
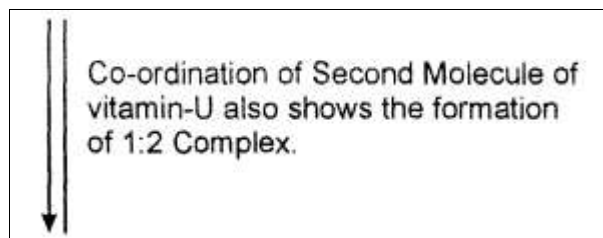


The ligand coordinates through the nitrogen of NH<sub>2</sub> group and oxygen of COOH group of the α-amino acid moiety of the vitamin-U. Unlike lanthanides, actinide ions use their 5f electrons readily for bonding. As the atomic number in actinide increases, the reduction in ionic radius i.e. actinide contraction is observed 5f electrons of actinides interact much more with ligands than 4f electrons of lanthanides.

**Mechanism of M-vitamin-U, complex formation:**



[1:1 Complex]



As a result the spin orbital coupling and ligand field effects of 5f elements are of comparable value. Thorium has +4 most common stable oxidation state and the usual coordination numbers are 8, 9 (sometimes 10). Th<sup>+4</sup> is bigger in size and more resistant to hydrolysis than other (+4) ions. In the present investigation, the precipitation of Th<sup>+4</sup> with the increase in pH of the solution was observed at ~4.20. The ionic size and charge govern the complexing tendencies of various ions. Complexes exhibit extraordinary stereochemistry. Generally stability order is M4<sup>+4</sup> > MO<sub>2</sub><sup>+2</sup> > M<sup>+3</sup> < MO<sub>2</sub><sup>+</sup> for anions, the complexing abilities order with actinide ion is: F > NO<sub>3</sub> > Cl > ClO<sub>4</sub> and CO<sub>3</sub><sup>-2</sup> > C<sub>2</sub>O<sub>4</sub><sup>-2</sup> > SO<sub>4</sub><sup>+2</sup>. Eight coordination with different geometries is very common for +4 oxidation states. In the present investigation, Th<sup>+4</sup> is forming more stable chelate with vitamin-U than UO<sub>2</sub><sup>++</sup>. It is important to note that after first chelation there is no appreciable decrease in the second chelation (log K<sub>1</sub> = 8.60, log K<sub>2</sub> = 8.26) for Th<sup>+4</sup> ion.

The uranyl ion has been greatly studied for stereochemistry, the uranyl ion has O-U-O axial unit which is surrounded by 4-6 ligands in solution. Usually the ligands lie close to a plane perpendicular to O-U-O axis. The chelating ligands may also be accompanied by coordinated solvent molecules or other ligands (in case of vitamin-U chloride ion is also present). There is a difference in the log K<sub>1</sub> = 8.57 & log K<sub>2</sub> = 7.60 values in case of uranyl chelate as expected statistically.

### Conclusion

In the above discussion, It is found that the binary ML (H<sub>2</sub>O) complexes of Th (IV) and UO<sub>2</sub> (II) with L = vitamin-U ligand has been studied to determine their stability. It is interesting because these data are useful to understand the role of metal ions in various biochemical reactions.

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