

## Case studies 1 : 1,2-ethanediamine as the ligand

Polyamines are found in biological systems and are able to coordinate to different metal ions.

A lot of the behaviour of such polyamines has been elucidated by the rather extensive study of the complex formation of various metal ions with 1,2-ethanediamine (here abbreviated as *en*).

In the table is given data for the stability of complexes between metal ions and *en* at 25 °C and a salt medium of about 1 M.

M <sup>2+</sup>	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>3</sub>
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	See question 5	4.59	2.09

In order to determine stability constants, the acidity constants of the corresponding acids to *en* have to be known.

1. Define the two acidity constants

This was established by measurements of pH in solutions of known amounts of acid and *en* in 1 M potassium nitrate. From the following two measurements it is possible to determine the acidity constants with sufficient accuracy:

Measurement	C(HNO <sub>3</sub> )/ M	C(en) / M	pH
1	0.1003	0.06326	7.33
2	0.1003	0.2524	10.38

2. From these two measurements find the value for the two acidity constants.  
(Hints: find the average protonation number – analogous to the average ligand number, *the degree of formation of the system*; now determine approximated values of the three degrees of formation,  $\alpha$ , of the different, more or less protonated forms of *en* (to two significant figures).
3. Compare the values found to the first approximation with the two pK-values which are the best fit to the above measurements (7.49, and 10.20, respectively) and discuss the deviations.

As is seen from the table, the stability (expressed as log K's) of Men<sup>2+</sup> varies through the M's. The same variation is seen for the corresponding Men<sub>2</sub><sup>2+</sup>

4. Comment on the variation of logK<sub>1</sub> and logK<sub>2</sub>.

In all cases  $K_1$  is greater than  $K_2$ .

5. How could that be explained?
6. Give different estimates of  $\log K_1$  for  $\text{Cd}^{2+}$ , which is missing in the table, while using the other data in the table

The stability in the Cd-case was determined in a series of experiments, and the  $K_1$  was determined by this measurement: A solution with the following concentrations (in M):  $C(\text{Cd}^{2+})=0.0990$ ;  $C(\text{en})=0.0787$ ;  $C(\text{HNO}_3)=0.101$  and  $C(\text{KNO}_3)=1.00$  showed to have a pH of 6.43. The same solution was equipped with an amalgamated cadmium-electrode, and in the second half cell with an identical electrode was placed a solution with the composition;  $C(\text{Cd}^{2+})=0.00990$ ;  $C(\text{HNO}_3)=0.101$  and  $C(\text{KNO}_3)=1.00$ . The potential difference was measured to 25.6 mV at 25 °C.

7. Find  $\log K_1$  from this experiment.  
(hint: first find  $\alpha_0$  and  $\alpha_1$  and then the amount of *en* which is not bound to  $\text{Cd}^{2+}$ . Now the concentration of free *en* is determined, and then the value of  $\log K_1$ . Use 3 significant figures throughout the calculation)

It appears from the table that the largest constants are found for nickel and copper.

8. Sketch the stereochemistry of the  $\text{Ni}(\text{en})_3^{2+}$  ion

The constants for the two first steps in the copper case are rather large, while that for the third step is quite small.

9. Give a plausible explanation of this fact.
10. Discuss the value in the chromium case of  $\log K_3$ , which is not given in the table.