The formation constants of 1:2 (metal-ligand) chelates of 2-mercaptomethylbenzimidazole (MMB) and 2-mercaptoethylbenzimidazole (MEB) with Co(II), Ni(II) and Zn(II) have been determined by the method of Irving and Rossotti in 50% (v/v) aq. ethanol at an ionic strength of 0.1 M (NaClO₄) and temp = 30°C. The order of stabilities is Zn(II) > Co(II) > Ni(II) (for MMB) and Zn(II) > Ni(II) > Co(II) (for MEB). The reversal in the stabilities of Co(II) and Ni(II) in going from MMB to MEB is discussed.

In continuation of our earlier studies on the coordinating tendencies of substituted benzimidazoles, we report herein the formation constants of complexes of the type ML₂ (where M = Co(II), Ni(II) and Zn(II) and L = 2-mercaptomethylbenzimidazole (MMB) or 2-mercaptoethylbenzimidazole (MEB)], determined pH-metrically by the method of Irving and Rossotti in 50% (v/v) aq. ethanol at 30° and I = 0.1 M (NaClO₄).

The ligands MMB and MEB were prepared by the literature method. The pH meter readings (B) in the aquo organic medium were corrected by the method of Van Uitert and Haas. The experimental details were similar to those reported earlier.

The metal-ligand titration curves were found to be below the ligand titration curve and the pH region of complexation was found to be well below the pH of hydrolysis of these metal ions. Hence the decrease in pH in the metal-ligand titration curve could be attributed to the release of protons upon complexation. The maximum n values obtained for the metal-ligand systems were between 1.4 and 1.7 suggesting the formation of both 1:1 and 1:2 complexes. From the nature of the metal-ligand formation curves it was clear that log K₁ and log K₂ do not differ much from one another and hence they have been calculated by the method of least squares. These values along with the proton-ligand formation constants are presented in Table 1. The order of formation constants (log β₂) is: Zn(II) > Co(II) > Ni(II) (for MMB complexes) and Zn(II) > Ni(II) > Co(II) (for MEB complexes).

The order of stabilities for both the systems suggests that the complex formation occurs by the replacement of the proton of the mercaptide group. Thus these two ligands, MMB and MEB, behave as monoprotic bidentate type, the sites of coordination being via pyridyl nitrogen of the benzimidazole moiety and the
mercaptide sulphur. This results in the formation of a five-membered chelate ring with MMB and a six-membered chelate ring with MEB. Further the reversal in the relative order of stabilities of Co(II) and Ni(II) complexes in going from MMB to MEB may be due to some steric hindrance offered by MMB for the formation of planar bis-chelates. The order of stabilities Ni(II) > Co(II) is known for ligands which form planar bis-chelates, while the order Co(II) > Ni(II) is observed in a number of cases where the coordinating groups hinder the formation of planar bis-chelates.

The distribution curves for the Ni(II)-MMB and Ni(II)-MEB systems (Fig. 1) are typical and all other M(II)-ligand systems showed similar behaviour. The distribution diagrams show the same qualitative changes in the degree of formation as a function of free ligand concentration, i.e. the quantities of M(II) and ML₂ change monotonically as a function of the free ligand concentration and that of the intermediate species, ML, attains a certain maximum value.

References