In rxn (iii),

since four molecules of H_2O are replaced by one molecule of trien, there is an increase of three molecule one proceeding from reactants to the products and hence there is a greater increase magnitude of ΔH° in the same direction.

Thus ΔS° would have a larger (+ve) value. This implies that ΔG° would be a larger negative quantity and it is larger than that of rxn (ii).

Therefore the magnitude of (−ve) ΔG° value increases in the order $[Cd(CH_3NH_2)_4]^{2+} < [Cd(en)_2]^{2+} < [Cd(trien)]^{2+}$.

Thus $[Cd(trien)]^{2+}$ is more stable than $[Cd(en)_2]^{2+}$ which is more stable than $[Cd(CH_3NH_2)_4]^{2+}$.

Q: $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ explain

$[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ it is explained with the help of chelate effect. Two factors may be considered to be responsible for such effect.

The first one is to considered the difference of dissociation betn $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$.

[If one NH_3 molecule dissociates it has little probability of returning to its former side. But If one of the $-NH_2$ group of en dissociates, the ligand is written by the other end still attached to the metal.

The dissociated 'N' atom can move only a few picometers away and can swing back and attached to the metal ion. Thus, the chelate has a smaller probability of dissociation than the non-chelate complex.]

The second one is to considered the following equm:

$$[Co(NH_3)_6]^{2+} + 3en \rightleftharpoons [Co(en)_3]^{2+} + 6NH_3$$

Since in the bonding in 'en' is very similar ΔH for this rxn should be approximating zero. The change in entropy of this rxn will be proportional to the difference in the no. of particles present in the system. The rxn proceed to the right with an increase in no. of particles. Hence entropy factor favours the production of the chelate complex. Therefore $[Co(en)_3]^{3+}$ complex is more stable than $[Co(NH_3)_6]^{3+}$ complex.

Inner metallic Complexes

Q. State examples of inner metallic complex.

There are some chelating ligands which contain a neutral donor group and acidic donor group in their structure and they satisfy both the primary and secondary valency of the metal ion and form neutral chelate.

These chelate compounds are non-electrolytes with very low solubility in water but high solubility in organic solvent.

Such non-electrolytic chelates are known as inner metallic complexes or simply inner metallic complexes of the first order.

Examples of such ligands are acac, gly, DMG, etc and the complexes are $[Pt(gly)_2]^0$; $[Ni(DMG)_2]^0$, $[Be(acac)_2]^0$, $[Co(gly)_3]^0$, $[Co(acac)_3]^0$ etc.

When the chelating ligand containing both neutral and acidic donor group can not satisfy the primary valency of the metal ion, the resulting complex itself becomes an ion and requires other ion for charge neutralisation. The complex form is known as the inner complexes of 2nd order.

e.g; $[\overset{IV}{Si}(acac)_3]Cl$, $[B(acac)_2][FeCl_4]$, $K[Pt(acac)Cl_2]$