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INORGANIC CHEMISTRY

PART –III

1. “An inner metallic ligand is essentially a chelating ligand ,but the reverse is not true” ---Justify.

Answer: Inner metallic ligand with both neutral and acidic donors satisfied coordination number and charge but chelating ligand with neutral donors satisfies coordination number only. For example $[\text{Co}(\text{en})_3]^{3+}$ where ethylene diamine is a chelating ligand but not inner metallic ligand while in $[\text{Co}(\text{gly})_3]$, where glycine acting as an inner metallic ligand.

2. What is the difference in colour which arises due to cis and trans form of $[\text{Co}(\text{en})_2\text{Cl}_2]$ complex?

Answer : The cis isomer will have more intense colour compared to that of trans isomer.

3. KReO_4 is colourless where as KMnO_4 is intense purple --- explain.

Answer: Both the central elements are in oxidation state +7 and are tetrahedrally surrounded by four oxide ions. The colour is due to C→T transition of the type : ligand to metal ion. The 5d orbitals of Re are at a higher energy than the 3d orbitals of Mn. The antibonding M.O.'s of KReO_4 are more antibonding than those of KMnO_4 . This means that ligand to metal C.T, transition will appear at much higher energy for KReO_4 than for KMnO_4 . As the transition in KReO_4 appears at the near UV we see the compound as colourless. For KMnO_4 the transition is very much within the visible region and we observe a purple colour.

In keeping with these transition it is an experimental fact that KMnO_4 is a better oxidising agent than KReO_4 . In fact a low energy C.T. band (as in KMnO_4) indicates that requisite energy for a redox reaction is more easily available and hence a redox reaction should proceed more favourably with KMnO_4 than with KReO_4 .

4. Hexa aquairon(III) is nearly colourless .On the addition of potassium thiocyanate a blood red colour develops --- explain.

Answer: Iron (III) is a d^5 system. Water is a weak field ligand. Hence hexaaquairon (III) is high spin. The $d \rightarrow d$ transition is high – spin d^5 complex are doubly forbidden and hence we see very weak colour. However iron(III) is an oxidant while thiocyanate ion is a reductant. So in the presence of thiocyanate ion charge transfer transition occurs (being of the ligand to metal type). $C \rightarrow T$ transition is allowed and in this particular case is very favoured so that low energy transition in the visible range takes place. Being an allowed transition the intensity is very high .

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