

SYNTHESIS, CHARACTERIZATION AND STABILITY DETERMINATION OF 1ST ROW TRANSITION METALS IN IRVING WILLIAM ORDER.

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Summary: The present study is conducted to determine the stability of series of complexes with different metals fall into the sequences $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. This is known as the Irving Williams order and is general for many ligands. The stabilities of the complexes formed by various metals follow some regular trends, such as those involving size and charge effects. One of the earliest correlations was the Irving-Williams series of stability. For a given stability of complexes with dipositive metal ions follows the order: $Ba^{+2} < Mn^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. This order arises in part from a decrease in size across the series and in part from ligand field effects. According to Irving-Williams Series, the stability order of the considered metals (Zn, Ni, Co, Cu) is $Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. Stability of the complexes determined as by U.V spectroscopy. Atomic Absorption techniques applied for the estimation of metals present in the samples. And IR technique was applied for the determination of Functional groups present in it.

Introduction:

The Stability of different complexes with di positive metal ions follows the order ($Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$) [1,2] which is a selected complexes of Irving William order determine by the same ligand (Acetanalide+ β -naphthol) and stability confirmed by the different techniques like U.V and metal confirmed by the AAS and EDTA and Calculated values.

The Stability of the complexes of the non transition metal of the same group has been found in the following order provided that the ligand is not changed from one ion to the next.

$Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+} > Be(II) > Mg(II) > Ca(II) > Sr(II) > Ba(II) > Ra(II) > Al(III) > Sc(III) > Y(III) > La(III)$ [1]

There are also some exceptions to the above order. e.g EDTA complex of the Mg(II) is less stable than that of the Ca(II)

Crystal Field Effect And The Natural Order(or Irving William Order) Of Stability of high spin complexes of the ion between Mn(II) and Zn(II) with the given ligand frequently vary in the order:[3]

$Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) < Zn(II)$ [5]

This order is called natural order(sometime called Irving William Order) of stability is consistent with charge to radius ratio concept , since the radii of these ions are in the order[4,5]:

$Mn(II)(=0.91 \text{ \AA}) > Fe(II)(=0.83) > Co(II)(=0.82) > Ni(II)(=0.78) > Cu(II)(=0.69) < Zn(II)(=0.74)$

The high spin complexes[6] of these ions are primarily octahedral with the exception of those of Cu(II) which forms tetrahedrally distorted octahedral complexes.

The stability of series of complexes with different metals fall into the sequences $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. [7] This is known as the Irving Williams order and is general for many ligands. The stabilities of the complexes formed by various metals follow some regular trends, such as those involving size and charge effects.

One of the earliest correlations was the Irving-Williams series of stability [8,9] of complexes with dipositive metal ions follows the order: $Ba^{+2} < Mn^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. This order arises as a part from a decrease in size across the series and in part from ligand field effects.

Experimental:

All the solvents used were of analytical grade, all other chemicals were from PGD, Trade Mark and used as obtained.

Procedure:

In an ethanolic solution of Actanilide an ethanolic solution of β -naphthol was added in small installments in 1:1 molar ratio, with continuous stirring. The reaction mixture was then stirred and

refluxed for at least one hour. After refluxing it was allowed to cool down and crystals appeared which were purified by recrystallized using different methods, the best product was obtained by evaporation at low temperature using mixture of solvents. Synthesis of complexes Ni (II), Co(II), Zn(II), Mn(II), Cu(II), Fe(II) in 50% ethanol/water was added to a hot ethanolic solution of the respective ligand in 1:2 ratio, and refluxed for 3 to 4 hour. On cooling a few drops of ethanolic solution were added. The precipitates were filtered; washed with a small amount of ethanol and dried in a desicator under vacuum and Purified it by the help of ethanol When the temperature was in the range of 5-10C crystals appeared. Number of solvent mixtures were tried, for example ethanol/n-hexane, CH_2Cl_2 /n-hexane, ether/n-hexane. Crystals appeared in ethanol/n-hexane, CH_2Cl_2 /n-hexane mixtures on slow evaporation at 0-5°C.

Physical properties

General physical properties i.e state, colour, melting point, % yield and solubilities of complexes are given in Table 1:

Table 1:

Compound	State	Color	Melting Point	% Yield
ACBN-Mn(II)	Crystal	Dark Brown	55 °C	70 %
ACBN-Fe(II)	Crystal	Chocolate color	47 °C	71 %
ACBN-Co(II)	Crystal	Light cream	60 °C	68 %
ACBN-Ni(II)	Crystal	Greenish brown	48 °C	64 %
ACBN-Cu(II)	Crystal	Blackish Brown	54 °C	69 %
ACBN-Zn(II)	Crystal	Light brown	57 °C	65 %

Result and Discussion:

Several spectroscopic techniques were used for the characterization and stability determination of complex i.e UN, IR. AAS and chemical method for metal determination.

Estimation of Metal Ions by AAS And EDTA:

The amount/L of metals were estimated by using EDTA titration. They were also determined and estimated by using AAS. Metal complex were digested through Conc; HNO_3 to convert the metal present

in the complex completely into the corresponding nitrates. After making the solution metal were determined by

EDTA titration using appropriate indicator. This value were confirmed by AAS technique.

Metal estimated by AAS, EDTA and calculated value.

Table: 2

Compound	Metal estimated by AAS (g/L)	Metal estimated by EDTA(g/L)	Calculated metal(g/L)
ACBN-Mn(II)	0.06	0.05	0.05
ACBN-Fe(II)	0.015	0.07	0.07
ACBN-Co(II)	0.05	0.06	0.07
ACBN-Ni(II)	0.05	0.025	0.026
ACBN-Cu(II)	0.07	0.08	0.06
ACBN-Zn(II)	0.05	0.05	0.05

IR-Discussion:

All the complexes and ligands synthesized were characterized by IR spectroscopy. The functional groups presents were confirmed by the IR frequency values as in the Table: 3. The Aromatic (Strech+Bend) are all similar to each other no special changes occurs in this region. The peaks appears in N-H region are all most similar. And in the

case of ACBN+Ni complex the peak appears in NO₂ groups region at 834cm⁻¹ showing the presence of nitro group in the complex which acts as an electron withdrawing group.

The peaks appears in the C-N region confirms the presence of C-N bond in the complexes.

Table: 3

Compounds	IR frequencies in cm-1						
	Aromatics (Strech+Bends)	CH ₃ -C	C-N	N-H	C-H	-NO ₂	COOH
Co(A.A) ₂	3238,690	1368,1425	1260	906	1308	-	-
Ni(A.A) ₂	3244,690	1378,1311	1257	1593	1368	-	-
AMNA	3268	1430	1263	1329	1599	867	-

U.V Studies for Chelates:

The stability of all the Chelates was determined by U.V studies.

Stability and λ_{max} Determination for Complexis

λ_{max} was determined by using appropriate solvents and was confirmed by repeating λ_{max} for several days using fresh solvent solution in comparison with the first solution every time. Selected metal chelates were found more stable as

compared to in solid form. Mn (II) chelate was least stable both in solid as well as in solution form, it was decomposed after a week in solution form. Stability of Fe and Co chelates was observed almost same, they decompose in solution after two weeks. Ni and Cu showed similar pattern of stability in solution form, they were decomposed after almost four weeks. Zn chelate was found most stable both in solid as well in solution forms. It was studied for ten weeks and was found no change in λ_{max}

of both in solution as well as in solid (freshly prepared solution) forms. Selected stability graph of Co^{+2} -chelate is given in Fig 1. So Irving-Williams order was observed in the selected metals group, though with less stability difference.

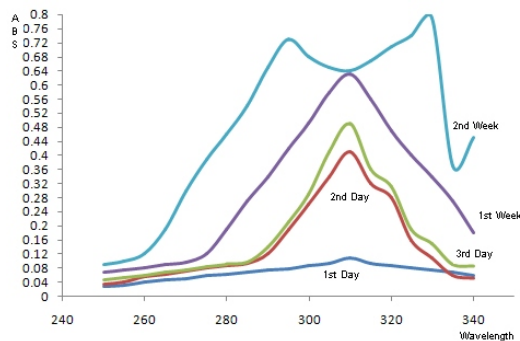


Fig 1 Stability Graph of Co^{+2} Chelate

Table

CHELATES.	λ_{max}
ACBN-Mn(II)	310
ACBN-Fe(II)	310
ACBN-Co(II)	310
ACBN-Ni(II)	330
ACBN-Cu(II)	320
ACBN-Zn(II)	320

Conclusion:

The Synthetic procedure of all preparations were straight forward .The products were isolated as crystals and were easily recrystallized for purification. ,IR and AAS studies confirmed the formation of required compounds. The result of both techniques were supported each other. Stabilities were determined by U.V studies.

Solubility showed that chelates were soluble in most of the Polar solvents and insoluble in non-polar solvents.

According to Irving-Williams Series, the stability order of the considered metals (Zn, Ni, Co, Cu, Mn and Fe) is $\text{Mn}^{+2} < \text{Fe}^{+2} < \text{Co}^{+2} < \text{Ni}^{+2} < \text{Cu}^{+2} < \text{Zn}^{+2}$. Stability determination of the complexes

of these metals were carried out by U.V Technique. They were all found more stable in solid forms as compared to in solution forms for weeks. They all followed almost the same order of stability as was suggested in Irving-William order, the least stable chelate found was of Mn^{+2} , Fe^{+2} and Co^{+2} showed almost same strength, Ni^{+2} and Cu^{+2} Chelates showed similar behavior, the most stable chelate found was of Zn^{+2} .

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