SUMMARY

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Modern technological demands for materials possessing suitable mechanical, thermal and electrical properties at high temperatures have led to considerable work in the field of (a) organic, (b) inorganic and (c) inorganic-organic polymers. Coordination or chelate polymers form a group of inorganic-organic polymers in general and may be obtained from (i) the chain formation by the alternate linking of metal and ligand, (ii) the insertion of metal into preformed polymeric ligand and (iii) the polymerisation of coordination complexes.

Coordination polymers may possess good thermal stability which may be influenced by the nature of the coordinated metal; if these polymers have "through-conjugation", they can possess favourable semi-conducting properties.

With the above considerations, we planned

(a) (i) to prepare various multifunctional ligands,
    (ii) to prepare their polymeric complexes, and
    (iii) to study their spectral, magnetic and thermal properties; and

(b) (i) to prepare suitable monomeric coordination complexes, and
    (ii) to polymerise them through suitable functional groups.

The coordination polymers or coordination complexes obtained with different ligands are considered ligandwise.

Azo-ligands :

Azo-ligands studied for the preparation of coordination polymers were bis-azo di(salicylaldehyde) BASA, bis-azo di(salicylaldoxime)BASAO and bis-azo di (acetylacetone) BAAC. Their spectra were studied and considered for keto-enol and azo-hydrazone tautomerism.

The cobalt complex of BASA prepared in pyridine is shown to be a linear polymer containing water and pyridine. The magnetic moment of the complex suggests octahedral nature of the monomeric complex. Measurement of electrical resistivity over a range of temperature indicate semiconducting behaviour of the polymer. High thermal stability of the octahedral unit can be concluded from the thermometric (T.G.A. and D.T.A) studies. The absorption spectra of the polymer in the ultraviolet, visible and infra-red region were studied and are discussed in relation to the structure of the polymer.

The cobalt complex of BASA prepared in dimethylformamide (without using pyridine) is considered to have low degree of polymerisation, with reference to the linear chain; however, additional ligand molecules are considered coordinated to different Co-atoms with the formation of three dimensional net work. Its absorption spectrum in the visible region and magnetic-moment were determined.

The copper complex with BASA prepared in pyridine, is shown to be a linear polymer containing water and pyridine. Its spectral, magnetic and thermometric sutdies were carried out and are discussed in relation to its structure.

The copper complex with BASA prepared in dimethylformamide (without using pyridine) is also shown to be a linear polymer.

The nickel complex of BASA prepared in pyridine is shown to be non-polymeric. Its magnetic moment indicate binuclear octahedral nature of the complex. Its spectra and thermometric studies were also carried out.

If IR frequency of coordinated CO is related to the stability of the complex, the stability is in order.

$$\mathrm{Co} \sim \mathrm{Ni} < \mathrm{Cu}$$

We suggest that the thermal fission of the azo ligand involving the evolution of nitrogen is catalysed by the metal ion chelated to salicylaldehyde. Such a reaction is facilitated by Ni or Cu but appears to be inhibited by Co.

The nickel complex with BASAO is shown to be a linear polymer. Nickel in the complex is considered to be binuclear 5-coordinate. On the basis of magnetic moment determination. Its spectral and thermometric studies were also carried out.

The copper complex of BAAC is shown to be trinuclear. The crystals are hard to grind. Its spectral, thermometric and magnetic studies were made and the results are used to discuss its structure. For the purpose of comparison, copper complex of AAC (azo-diacetylacetone) was prepared and is shown to possess normal behaviour.

Phemol-anil ligands :

Schiff bases of salicylaldehyde with benzidine and p-phenylenediamine were prepared but they did not yield the transition metal (Cu, Ni, Co) complexes. Hence bis (salicylaldehydo) metal complexes were treated with diamines to get the Schiff base complexes.

The copper complex with salicylaldehyde and benzidine (SAB-Cu) is considered to have a low degree of polymerisation which would increase on heating. Its spectral, magnetic and thermometric studies were made.

The cobalt complex with salicylaldehyde and benzidine (SAB-Co) is suggested to be a linear polymer, containing excess benzidine. Its spectral, magnetic and thermometric studies were carried out.

The nickel complex with salicylaldehyde and benzidine (SAB-Ni) is considered to be a dimer containing ammonia. Its spectral, thermometric and magnetic studies were carried out.

The copper complex with salicylaldehyde and p-phenylenediamine is considered to be a linear polymer, possibly forming intermolecular links through additional p-phenylenediamine molecules. Its spectral, thermometric and magnetic studies were carried out.

The cobalt complex with salicylaldehyde and p-phenylenediamine (SAP-Co) is also considered to form a linear chain with intermolecular linking through p-phenylenediamine. Its spectral, theromoetric and magnetic studies were carried out.

The nickel complex with salicylaldehyde and p-phenylenediamine is suggested to be a dimer, containing ammonia. Its spectral, thermometric and magnetic studies were made.

On the basis of these observations it can be suggested that nickel complexes differ from cobalt and copper complexes (i) nickel complexes may be dimeric whereas copper and cobalt complexes can be dimeric or polymeric (ii) only one of the two aldehyde groups of bis(salicylaldehydo) nickel get transformed into anil with benzidine or p-phenylenediamine wheras both groups get converted into anils in case of Cu and Co-complexes. Further, the thermal unstability is greater for the complexes of Schiff bases with p-phenylenediamine than with those of Schiff bases with benzidine.

Oxime-anil ligands :

Schiff bases of 2,3-dioxybutyranilide-2-oxime with benzidine or p-phenylenediamine could not be prepared; hence its complexes were prepared by treating metal salt with the oxime ketone and diamine.

The copper complex OB-CuCl prepared from copper chloride, oxime-ketone and benzidine is formulated as a dimer and related to its thermal magnetic and thermometric nature.

The nickel complex OB-NiCl prepared from nickel chloride, oxime-ketone and benzidine is also formulated as a dimer and related to its spectral, magnetic and thermometric behaviour.

The copper complex OP-CuCl prepared from copper chloride, oxime-ketone and p-phenylenediamine is shown to be monomeric and undergoing dimerisation on heating. Its spectral, thermometric and magnetic studies were made.

The nickel complex (OP-NiCl) prepared from nickel chloride, oxime-ketone and p-phenylendaiamine is also shown to be monomeric and undergoing dimerisation on heating. Its spectral, thermometric and magnetic studies were made.

The copper complex (OB-Cu) prepared from copper acetate, oxime-ketone and benzidine was studied for its spectral, thermometric and magnetic behaviour and is formulated as a dimer.

The cobalt complex (OB-Co) prepared from cobalt acetate, oxime-ketone and benzidine was studied for its thermometric, magnetic and spectral behaviour and is formulated as a dimer or a polymer.

The copper complex (OP-Cu) prepared from copper acetate, oxime-ketone and p-phenylenediamine was studied for its thermometric, magnetic and spectral properties and is formulated as a dimer.

The cobalt complex (OP-Co) prepared from cobalt acetate was studied for its spectral, thermometric and magnetic behaviour and is formulated as a dimer, with additional p-phenylenediamine forming intermolecular links.

The iron complex (OB-Fe and OP-Fe) were also prepared and their magnetic moments were determined.

The anil formation appears to be influenced by the nature of the metal ion with which the oxime-ketone ligand may be considered chelated. Thus only one of the two coordinated CO groups of the oxime-ketone converted into Schiff base in presence of copper whereas both CO groups of the oxime-ketone ligand molecules get transformed into anils in presence of cobalt.

Further thermal decomposition reactions of Schiff base complexes with benzidine appear to be different from those of Schiff base complexes with p-phenylenediamine.

N-Ligands from oxime-ketone :

Transition metal complexes of N-ligands were prepared from the metal salt, oxime-ketone and p-toluidine, thiosemicarbazide, semicarbazide or hydrazine.

The complex OT-Ni(c) prepared using p-toluidine in cold differe from the complex OT-Ni(R) prepared using p-toluidine and heating only one of the two coordinated CO group of the two ligand molecules get converted into Schiff base in the first case, whereas both CO groups are converted into Schiff base in the second case. The complexes OT-Co(c) and OT-Co(R) prepared under similar conditions to OT-Ni(C) and OT-Ni(R) however possess the same structure and resemble OT-Ni(C). Their spectral, magnetic and thermal studies were carried out.

The complex (OTS-Ni) prepared using oxime-ketone and thiosemicarbazone resembles the complex (TSO-Ni) obtained using preformed oxime-thiosemicarbazone. In both cases the ligand act as dibasic acid.

In the complex (TSO-Co) obtained using oxime-thiosemicarbazone, the ligand acts as a monobasic acid.

The complexes (OZ-Cu) were prepared using hydrazine.

It has been shown that hydrazone is formed in the case of Ni and Fe complexes, azine is formed in the case of Cu complex, whereas both azine and hydrazone are formed in the case of Co complex.

Azine and hydrazide ligands :

Cu and Co complexes of B-resorcyladazine were prepared, and their magnetic moments were determined. They may be represented as a monomer or a dimer.

Cu, Ni and Co complexes of oxalyldihydrazide were prepared and their magnetic moments were determined. They are considered to form dimers.

Polymerisation of double malonates :

Double malonates $K_2M(Mal)_2$ aqx (where M = Cu, Ni or Co) were prepared and attempt was made to polymerise them with formaldehyde.