SUMMARY

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PYROLYSIS OF POLYCHELATES

Pyrolysis has been used extensively as a technique for analysis and synthesis. Pyrolytic fragmentation and identification of the fragments serve as an effective means of determining the nature and structure of polymers. In recent years, pyrolytic methods jointly with various instrumental methods such as, gas chromatography, mass spectrometry, etc. have gained increased attention and usage. Pyrolytic scission reactions accompanied by cross-linking and recombination reactions lead to the synthesis of various products - pyrolyzates.

Pyrolytic methods have also been adopted for the understanding of thermal stability and for preparing high temperature-resistant polymers. Some chleates and chelate polymers have been pyrolyzed to understand their thermal stability, thermal degradation, thermo-mechanical behaviour, electrical and magnetic behaviour, etc. Intensive research initiated in the past two decades in an attempt to synthesize polymer systems of desired properties capable of withstanding prolonged exposure to elevated temperatures has been three-pronged, supplemented by pyrolytic methods.

Few studies are known on the formation of products by the pyrolysis of polychelates. Since polychelates having "through-conjugation" have interesting electrical and magnetic properties, their products of pyrolysis can have unusual electrical and magnetic properties. On pyrolysis, the unpaired electron-spins of the transition metal ion clusters can reorient parallel or anti-parallel, and the organic part of the polychelate may get transformed into radical or biradical which may get stabilised.

Keeping the above considerations in view, the work was planned as follows:

(i) Preparation of bis-bidentate or polydentate ligands of different characteristics and having different functional groups;

(ii) Preparation of polychelates of the above ligands with transition element ions in general;

(iii) Study of IR spectra and electrical and magnetic properties of the above polychelates;

(iv) Study their thermal behaviour using DTA and TGA techniques; (heating rate 20°C per minute in static air)

(v) Pyrolysis of the polychelates under controlled conditions of specific temperature range and continuous evacuation.

(vi) Study of the residual products of pyrolysis for their spectral, magnetic and electrical properties.

Results of these studies and their discussion are summarized below.

(I) Polychelates of Chloranilic acid (MCA) and their Pyrolysis

(a) Polychelates - CoCA, NiCA, CuCA, MnCA, FeCA and PbCA:

All these polychelates were found to have metal-to-ligand ratio of one-to-one and are formulated as linear polymeric chains.

The magnetic moments of the polychelates of cobalt(II), nickel(II), manganese(II) and iron(II) indicate 6-covalent nature of the metal ion with octahedral crystal field surrounding the metal ion, while in the case of copper(II) polychelate, copper ion is considered to be 5-covalent with square pyramidal crystal field. Lead(II) polychelate is diamagnetic as anticipated. There is no spin-pairing in any of these polychelates indicating weak crystal field of the ligand surrounding the metal ion.

All these polychelates are semiconducting.

The thermal studies (DTA and TGA) show that both coordinated and lattice water may be considered lost in case of NiCA and MnCA. In these compounds, water-coordination to metal ion may not be strong and heating may lead to tetragonal distortion. DTA studies of CuCA and FeCA show endothermic peak at/near 150°C and there is no weight loss at this temperature in the corresponding TGA studies. Meso phase formation may be a possibility and the peak may be attributed to solid-solid (solid-smectic) transition.

(b) Pyrolyzed polychelates (pyrolyzed at 310-30°C)
CoCA(PL), NiCA(PL), CuCA(PL), MnCA(PL), FeCA(PL) and PbCA(PL).

There is a difference in the amount of lattice/coordinated water when structures of MCA(PL) and MCA are compared in general.

The magnetic moments of CoCA(PL), NiCA(PL), CuCA(PL) and MnCA(PL) are comparable to those of CoCA, NiCA, CuCA and MnCA respectively. In case of FeCA(PL), the magnetic moment has a somewhat higher value. The diamagnetic PbCA has become paramagnetic on pyrolysis.

(C) Pyrolyzed polychelates (pyrolyzed at 530-60°C)
CoCA(PH), NiCA(PH), CuCA(PH), MnCA(PH), FeCA(PH)
and PbCA(PH):

These products have a ratio of metal-to-ligand (C_6) as one-to-one in CoCA(PH), MnCA(PH) and PbCA(PH), while three-to-one in NiCA(PH), CuCA(PH) and FeCA(PH).

It is suggested from the IR spectral data that bands attributed to C-Cl and C-H are not observed.

In case of polychelates of Ni(II), Cu(II) and Fe(II), 2,5-dihydroxy p-benzoquinone is found as a sublimate on the wall of the tube after pyrolysis. On pyrolysis under continuous evacuation, the polychelates of chloranilic acid are considered to undergo dechlorination forming free radicals followed by depolymerisation eliminating modified ligand monomer or cross-polymerisation extending cross-conjugation.

The magnetic moment of PbCA(PH) is 2.6 B.M. per metal atom. It is related to radical formation and trapping in solid state. The high magnetic moment of FeCA(PH) may be attributed not only to the ferromagnetic interactions between iron atoms but also to the free-radical nature of the ligand and its magnetic interactions with iron atoms.

(II) Polychelates of 3,3'- diacetyl 4,4'-dihydroxy diphenyl sulphone (MDAS) and their pyrolysis:

(a) Polychelates - CoDAS, NiDAS, CuDAS:

The ratio of metal-to-ligand in the polychelates is found to be one-to-one and indicates linear polymeric chain nature of the polychelates. From magnetic moment studies, CoDAS, NiDAS and CuDAS are attributed to have octahedral, tetrahedral and square planer nature of the crystal field around the metal ion respectively. All these polyehelates are semiconducting.

Thermal studies show that in all three cases there is loss of ammonia on heating. Loss of sulphur dioxide is possible on heating upto 330°C in case of CoDAS but not in case of CuDAS and NiDAS indicating greater thermal stabilisation of the ligand in CuDAS and NiDAS than in CoDAS. For DTA peaks at 160°C and 185°C for NiDAS there is no corresponding weight loss in TGA in this temperature range. It indicates solid-solid phase transitions.

(b) Pyrolyzed polychelates -CoDAS(P), NiDAS(P), CuDAS(P):

The products have a ratio of metal-to-ligand (C_{16}) as one-to-one.

From magnetic moment studies, CoDAS(P), NiDAS(P) and CuDAS(P) are considered to have octahedral, tetrahedral and square planar crystal field around the cobalt, nickel and copper ions respectively.

The IR spectral data of CoDAS(P) indicate that the phenyl rings are highly substituted. It is suggested that pyrolysis involves loss of ammonia and abstraction of hydrogen by radical mechanism followed by recombination/ cross-polymerisation and cyclization.

III. Chelates of 2,4-dinitroso resorcinol (MDNR) and their Pyrolysis:

(a) Chelates - CoDNR, NiDNR, CuDNR, FeDNR and PbDNR:

The ratio of metal-to-ligand in CoDNR, NiDNR and CuDNR is one-to-one and indicates linear polymeric chain nature of these polychelates. The ratio of metal-to-ligand is one-to-two in case of FeDNR and PbDNR.

It is suggested from magnetic moment studies that cobalt ion in CoDNR is 5-covalent with square pyramidal crystal field and nickel ion in NiDNR is 6-covalent with octahedral crystal field. CuDNR and PbDNR are diamagnetic. The ligand is considered to provide strong crystal field around cobalt and copper. ions.

From total weight loss observed in TGA studies the relative stability of the chelates is decreasing in the order -

$$\text{NiDNR} > \text{FeDNR} > \text{CoDNR} > \text{CuDNR}$$

PbDNR is explosive like lead-azide, lead styphnate, lead complex of nitro resorcinol, etc.

All polychelates are semiconducting. IR spectrum of the ligand shows the presence of both oxime and phenolic hydroxyl groups. The ligand is considered to be a tautomeric mixture of nitrosophenol and quinone oxime.

(b) Pyrolyzed polychelates - CoDNR(P), NiDNR(P), CuDNR(P)

Metal-to-ligand ratio is found to be one-to-one in case of CoDNR(P) and NiDNR(P) and two-to-one in case of CuDNR(P). The magnetic moment studies indicate tetrahedral stereochemical nature of cobalt and nickel in CoDNR(P) and NiDNR(P). Pyrolysis has resulted in weakening and reorientation of the crystal field.

In case of CuDNR, the ligand has seperated out in part on pyrolysis indicating depolymerisation. In the case of CoDNR(P) free phenolic group is observed in IR spectrum, indicating degradation leading to the formation of shorter polymeric chains.

(IV) Polychelates of 4-azo resorcinols (tetrazotized benzidine coupled with resorcinol - BAR and tetrazotized 4,4'-diamino stilbene 2,2'-disulphonic acid coupled with resorcinol-SAR) (MBAR and MSAR) and their pyrolysis:

(a) Polychelates - CoBAR, NiBAR, CuBAR, FeBAR, MnBAR, PbBAR, CoSAR, NiSAR, CuSAR:

Metal-to-ligand ratio is found to be one-to-one in case of CoBAR, two-to-one in case of CuBAR, NiBAR, FeBAR, MnBAR, NiSAR and CuSAR, two-to-three in case of PbBAR and three-to-one in case of CoSAR.

It is suggested from magnetic moment studies that (i) cobalt ion is 4-covalent with tetrahedral crystal field around the metal ion in CoBAR.

(ii) nickel and iron ions are 6-covalent with octahedral crystal field around the metal ions in NiBAR and FeBAR and (iii) PbBAR is diamagnetic.

The relative stability observed from the weight losses in TGA studies is decreasing in order

$$\text{FeBAR} > \text{NiBAR} > \text{CoBAR}$$

$$\text{CuSAR} > \text{CoSAR}$$

(b) Pyrolyzed polychelates-CoBAR(P), NiBAR(P), CuBAR(P) FeBAR(P), MnBAR(P),CoSAR(P), NiSAR(P),CuSAR(P):-

Metal-to-ligand ratio is one-to-one in CoBAR(P) , two-to-one in NiBAR(P), CuBAR(P), FeBAR(P), MnBAR(P), NiSAR(P) and CuSAR(P) and three-to-one in CoSAR(P).

CoBAR(P), FeBAR(P),CoSAR(P) and NiSAR(P) are ferromagnetic. Nickel ions have octahedral stereochemistry in NiBAR(P) and copper ions have lower value of magnetic moment indicating antiferromagnetic interactions. in CuBAR(P).

IR spectral data of CoBAR(P) and FeBAR(P) indicate that the band attributed to p-substituted aromatic ring, and azo group are not observed. Band attributed to azo group is very weak in the spectrum of CoSAR(P) and not observed in the spectrum of NiSAR(P).

The dyes undergo fission reaction evolving nitrogen. The thermal fission of azo groups is not inhibited selectively by any metal ion chelated to azo group.

(V) Polychelates of 1-azo 2-hydroxy 3-naphthoic acids (tetrazotized benzidine coupled to 2-hydroxy 3-naphthoic acid -BAN) and tetrazotized 4,4'-diamino stilbene 2,2'-disulphonic acid coupled with 2-hydroxy 3-naphthoic acid -SAN; (MBAN and MSAN) and their pyrolysis:

(a) Polychelates - CoBAN, CuBAN, CoSAN, NiSAN, CuSAN:

Metal-to-ligand ratio is one-to-one in CoBAN and CuBAN, two-to-one in CoSAN, four-to-one in NiSAN and three-to-one in CuSAN. Cobalt ion in CoBAN and CoSAN is 6-covalent with octahedral crystal field.

The relative stability of polychelates found from weight losses observed in TGA studies decreases in the order

CoBAN > CuBAN

CoSAN > CuSAN > NiSAN

All the polychelates are semiconducting.

(b) Pyrolyzed polychelates -CoBAN(P), CuBAN(P),CoSAN(P) NiSAN(P),CuSAN(P):

Metal-to-ligand ratio is one-to-one in CoBAN(P) and CuBAN(P), two-to-one in CoSAN(P), four-to-one in NiSAN(P) and three-to-one in CuSAN(P). On pyrolysis one azo and one carboxylic acid groups per ligand monomer are lost leaving basic metal compounds.

(VI) Concluding remarks:

Pyrolysis has been used as a technique for the synthesis of pyro-chelate-polymers and for understanding the changes in chelate polymers.

Pyrolysis of MCA resulted in dehydration and dechlorination followed by cross-polymerisation and depolymerisation. Pyrolysis of MDAS led to deammoniation and hydrogen-abstraction followed by cross-linking and cyclization. Pyrolysis of MDNR under controlled conditions resulted in (1) lowering of molecular mass, (2) depolymerization, (3) weakening of the crystal field around metal ion and/or (4) reorientation of crystal field. Pyrolysis of MBAR and MSAR resulted in partial denitrogenation which was not selectively inhibited by any of the metal ion linked to azo group. Pyrolysis of MBAN and MSAN led to partial denitrogenation and decarboxylation.

PbCA(PH) is paramagnetic. CoBAR(P), FeBAR(P), CoSAR(P) NiSAR(P), CoBAN(P), CoSAN(P) and NiSAN(P) are ferromagnetic. CuDNR(P) is diamagnetic while CuBAR(P) is antiferromagnetic. Stable radicals believed to be formed from the ligands are considered to contribute towards the magnetic behaviour.

Although semiconductivity of the pyrolyzed products could not be studied, it is believed that they should have high electrical conductivity and low energy barrier.

Thermal studies indicated solid-solid phase transitions in some polychelates such as CuCA, FeCA, NiSAN, etc.