Material Science Research India Volume 03, No. (1) 23-28 (2005)

SYNTHESIS OF POLYAMIDE [1,3-DICARBOXYMETHOXY BENZENE AND PROPLENEDIAMINE] COMPLEXES WITH LEAD, IRON AND COPPER

A.A. Samarkandy

Chemistry Department Faculty of Science,King Abdul Aziz University, Jeddah 21589 P.O.Box 80203 (Saudi Arabia)

(Received, Febrary 1, 2005)

ABSTRACT

Polyamide [1,3-dicarboxymethoxybenzene and proplenediamine] complexes with Pb^{2+}, Fe^{3+} and Cu^{2+} were prepared by melt condensation of bis-1,3-[DCMB] and [PD] and charaterized by elemental and thermal analysis as well as different spectroscopic techniques. T he data gathered showed that polyaminde, ligand coordinates with metal ions in a bidentate manner through NN donation. The metal ions are surrounded by coordinated water molecules and anions so as to establish the octahedral geometry.

Key words:- Spectroscopic, [1,3-dicarboxymethoxy benzene (DCMB) and proplenediamine (PD)] thermal analysis TGA, DTA.

INTRODUCTION

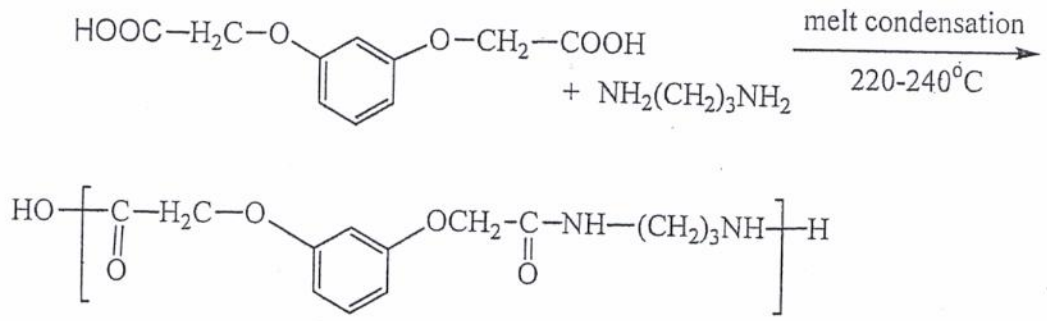
Mononuclear and heterobi-trinuclear polymer complexes of nickel (11), Copper (II) and oxovanadium (IV) chloride with 2-acrylamido-1-phenyl-2-amino-thiourea (APATH) monomer derived from amidation of acryloyl chloride with 2-amino-1-phenyl thiourea have been prepared[1].

Transition metal polymer complexes with mixed ligands have played a vital role in the development of coordination chemistry. The oxygen-bridged homo- and heterobinuclear complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical process and as industrial and homogeneous catalysis[2].

Recently several coordination polymers have been prepared which act as chelating groups in binding polyvalent metal ions[3]. Polyamine ligands such as ethylenediamine diethylenetriamine or triethelene tetramine were found to have excellent chelating properties[4]. To which a metal ion can be chelated in several ways. One of these is the use of a suitable number of functional groups (NH_2, OH, CO...etc) by which coordination with metal ions causes polymer complex[5]. Such polymer complexes exhibit a higher thermal stability than the parent polymer. In the present investigation, we report the complexation of polyamide derived from 1,3-dicarboxymethoxybenzene with some transition metal chlorides. The polymer complexes are characterized, their structures are elucidated and their thermal stabilities are studied.

MATERIALS AND METHODS

1,3-dicarboxymethoxybenzene was prepared according to the previously methode[6]. Polyamide was prepared by reaction of 1,3-dicarboxymethoxybenzene with proplenediamine by melt condensation according to the following scheme :



Polyamide

The reaction was carried out in a three necked flask dipped in an oil bath (thermostatically controlled) provided with a mechanical stirrer and Dean-Stark trap to collect water produced. A pipette was inserted through a stopper down to the flask to introduce a slow dry deoxygenated nitrogen gas in order to facilitate the removal of the water produced. When the reaction is completed, the polyamide was dissolved in DMF then precipitated by adding a large amount of distilled water with vigarous stirring. The precipitate was then gathered by filtration and dried in a vacuum oven at 40°C. All other chemicals were of highest purity (Aldrich or Merck chemicals) and were used chemicals.

Solid complexes were prepared by refluxing equimolar quantities of polyamide (in DMF) and the metal chloride for about four hours. The mixture was allowed to cool and the solid complexes so formed were separated by adding a large amount of distilled water filtered off, washed with water and dried in a vaccum oven at 40°C for 3 days.

Characterization of polymer complexes :

Elemental analysis (C, H and N) of polyamide and its complexes were carried out at the Microanalytical Centre, Cairo University, Giza, Egypt. Metal ion contents were determined by EDTA titration under appropriate conditions[7] while the percent of coordinated water molecules was determined by dehydration at ~ 130 °C. IR spectra were measured by the Perkin - Elmer 598 (4000-200 cm^{-1}) spectrophotometer as KBr discs. Electronic absorption spectra were recorded on the Perkin-Elmer λ_{3B} double beam spectrophotometer using the Nuiol-mull technique thermal analysis (TGA and DTA) were measured by the Shimadzu XD-30, Thermal Analyzer (Faculty of Science, Menoufia University). Samples were heated in platinum cell in dynamic nitrogen atmosphere with a heating rate 10 °C./min. ^{1}H-NMR spectra were recorded on a Varian analytical EM 390 spectrophotometer using 6D-DMSO as a solvent and TMS as internal reference:

RESULTS AND DISCUSSION

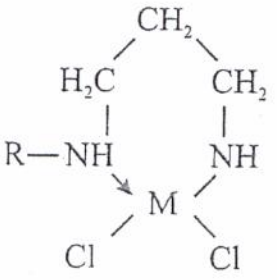
Elemental analysis (C, H and N) of the polyamide under study and its Pb^{2+}, Fe^{3+} and Cu^{2+} complexes show a satisfactory agreement between the proposed and found values (cf. Table 1). All the solid complexes are insoluble in common organic solvents and do not posses sharp melting points but decompose on heating above 300°C, thus measurements is expected due to their polymeric nature.

Table 1. Microanalytical analysis of polyamide and its complexes

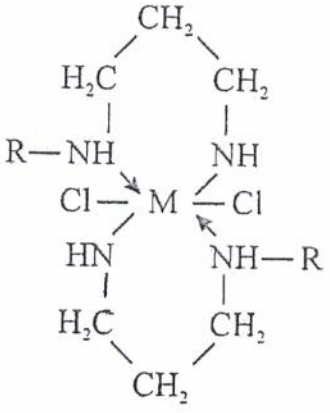
		Elemental analysis (Calc. / found)			
Complex	Colour	C%	H%	N%	M%
I	Brownish	53.71 / 53.9	6.0 / 6.4	10.4 / 0.2	–
IIa	Green	35.8 / 35.6	3.9 / 4.1	6.8 / 7.2	14.9 / 15.3
IIb	Green	37.1 / 36.8	3.8 / 4.2	6.9 / 7.1	14.4 / 14.2
IIc	Pink	35.8 / 36.2	3.4 / 4.1	7.2 / 7.1	14.2 / 14.6
IIIa	Green	41.9 / 42.1	4.6 /4.5	8.2 / 8.1	9.3 / 9.3
IIIb	Green	42.6 / 42.3	4.7 / 4.5	7.9 / 8.1	8.7 / 8.6
IIIc	Pink	43.1 / 43.2	4.0 /4.8	7.9 /8.3	8.6 /8.5
I-(polyamide)		IIa→IIc (M:L) (1:1)		IIa→IIIc (M:L) (1:2)	

The μeff. Values of the majority of solid complexes, measured at room temperature, show lower values than in case of many NN donor complexes the lower magnetic moments are due to antiferromagnetic interactions as a consequence of dimeric or polymeric structural arrangements[8]. The IR spectrum of polyamide ligand is studied and compared to those of its complexes, the important band frequencies are listed in Table 2. The IR spectrum of polyamide molecule shows broad and intense one at 3400 and 1160 cm^{-1} due to the stretching and bending (ν_{OH} and δ_{OH}) frequencies of the OH group respectively. The stretching vibrational band of NH group (ν_{NH}) appears at 3100 cm^{-1} while that of $\nu_{C=N}$ appears at 1650 cm^{-1}. The latter band may arise from the keto-enole tautomerism taking place in the free polyamide. The stretching vibrational frequency of the carbonyl carboxyl group (ν_{C-O}) appears at 1720 cm^{-1}. On the othe hand, the IR spectra of the metal complexes, show the absence of the stretching vibrational band of the C = N group, so it seems the coordination process precludes the keto-enol tautomerism as a result of delocalization of the lone pair of electrons on nitrogen atoms taking place in the complexation process. This is taken as an evidence for the contribution of this nitrogen atom to complex formation, which is supported by the shift of the band due to the NH group to lower frequency. On the other hand, the frequency of (ν_{C-O}) remains nearly unaltered, but increased in intensity in the IR spectra of solid complexes. A further support for the contribution of the NH groups of polyamide ligand to complex formation is the appearance of only one new band at 490-465 cm^{-1} due to ν_{M-S} stretching frequency.

The ^1H NMR spectrum of polyamide is recorded in ^6d- DMSO and compared to that of its Cu^{2+} complex. For the free ligand, the singlet signal at δ = 3.3 ppm (4 protons) is due the CH_2-CH_2-protons while the weak broad signal at 3.7 ppm is due to NH-C-proton. The other NH group (end groups) have also a singlet band at 8.2 ppm. The later two signals are strongly affected on complexation with Cu^{2+} ion indicating their participation in complex formation So, the mode of bounding in this case can be represented as :



(1:1) (M:L)



(1:2) (M:L)

R =

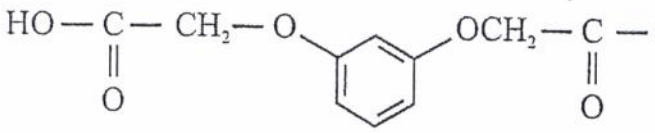


Table 2. ^{1}R spectra data for polyamide and its complexes

Complexes	IR cm^{-1}	Assignments
I	3400	OH stretching
	3100	NH stretching
	2900	C-H stretching–CH_2–
	1720	C=O Carbonyl
	1650	C=N Stretching
(IIa, IIIa)	3400	OH Stretching
	2900	NH Stretching
	1700	C–O Carbonyl
	470	M–N
(IIb, IIIb)	3380	OH Stretching
	2850	NH Stretching
	1700	C=O
	470	M–N
(IIc, IIIc)	3390	OH Stretching
	3000	NH Stretching
	1690	C=O
	485	M–N
1 (Polyamide)	IIa→IIc (M:L) (1:1)	IIIa→IIIc (M:L) (1:2)
a) Pb^{2+}	b) Fe^{3+}	c) Cu^{2+}

The electronic absorption spectra of the polyamide derived from 1,3-dimethoxycarboxybenzene and its complexes measuresd using the Nujol mull technique, show mainly the charge transfer band of the free molecule at ≅ 25974 cm^{-1} whil Pb^{2+} complex shows a band at 15780 cm^{-1} due to $^4A_2 \rightarrow {}^4T_1$ (p) transition in tetrahedra field[9] whereas Fe^{3+} complex shows band at 14265 and 13675 cm^{-1} respectively du to the square planar configuration in both These transitions are not observed in th spectrum of Cu^{2+} complex but only th charge transfer band at 24096 cm^{-1}.

Thermogravimetric analysis of the polyamide ligand and its complexes (a represented in Fig. 1) show that each of them degrade in three steps.

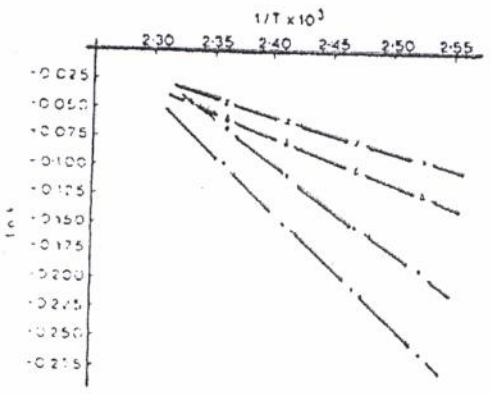
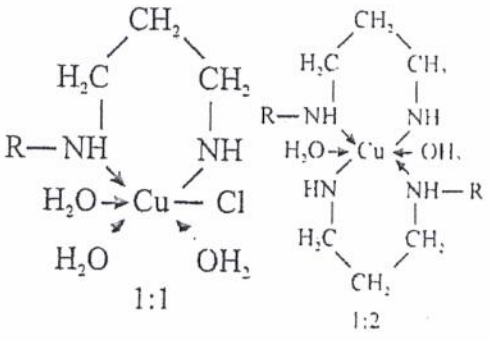


Fig. 1. Arrhenius plot of the degradation constant for PD polymer (x) and of complexes of D with Pb (o), Fe (Δ) and Cu(•).

In case of metal chelates, the first step in the decomposition sequence starts at 90°C due to the evaporation of physically adsorbed water moklecules, while the second step corresponding to the removal of chloride ion (in the form of HCl molecules) takes place at 180 °C. The final step is the degradation of the anhydrous complex which occurs at temperatures higher than 480 °C leading to be more stable than their corresponding free polymer ligand which is in accordance with the results obtained previously[10,11] which due to the formation of stable five membrered rings structures,



The synthesis of thermally stable polychelates and their thermal decomposition now promises an interesting area in the chemical of heat-resistant polymers. The values of energy of activation (E_a) range 20.3-11.6 kJ mol^{-1} for dehydration ot the polymer complexes were determined from TG and DTA curves.

REFERENCES

1. A.Z. El-Senbati, A. B. Abd El-Moiz and A. M. Hassanein Polymer Degradation and stability 48, 35-44. (1955).
2. El-Sonbati, A. Z., Synth. React. Inog. Met.-Org., 21, 203 (1991).
3. Diab, M.A. and A.Z. El-Sonbati, Polymer complexes part XIV-Thermal stability of poly (5-vinylsalicylidene-anthranilic acid) homopolymer and polymer complexes of 5-vinylsalicylidene anthiranilic acid with some transition metal salts Polv Degrad Stab, 29, 271 (1990).
4. Shambhu, N. M., M. C. Theodoratis and G.D. Digenis, Some transition metal

chloride complexes of pyridinaldazine and pyrrolaldazine Schiff Bases., *Polyhedron*, **1**, 21 (1977).

5. Bjones, M.E., D.A. Thorton and R.F. Weeb, New coordination polymers of 1,4-bis(2-prime-hydroxyphen-vlazomethene) phenylene., *Makromol. Chem.*, **49**, 69 (1961).
6. Vogel, V. I., T*ext book of paractical organic chemistry* 4th ed. pp. **754**, 1168 (1978).
7. Frank, J. W., The analytical use of ethylenediamine-tetracetic acid Van Nostrand, New York (1965).
8. Sinn, E. and C. M. Harris, Polyamine ligand chelating with Cu^{2+} ions in presence of chloromethylated PSt resins., *Coord. Sci.*, **B5**, 39 (1969).
9. Figgis, B. N. and J. Levis, Poly (metal tetrathiooxalates) a structural and charge-transport study, *Prog. Inor. Chem.*, **6**, 197 (1964).
10. Diab, M. A., A. Z. El-Sonbati, A.Z. El-Sanabari and F.I. Taha, Polymer complexes part VIII-Thermal stability of poly (2-acrylamidopyridine) and its polymer complexes with some transition metal chlorides. Polymer complexes with some transition metal chlorides, *Poly Degrad Stabl.*, **24**, 51 (1998).
11. El-Mossalamy, E.S.H. and Khalil, A.A., Polymerization of lanthanide acrylonitrile complexes, *Annali di Chimica*, **92**, 7-8 (July-August), pp 741-749 (2002).