

Polyamide [1,3-Dicarboxymethoxybenzene and Ethylene Diamine] Complexation with Some Metal Ions

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ABSTRACT. Polyamide [1,3-dicarboxymethoxybenzene and ethylene diamine] complexes with Cd^{2+} , Fe^{3+} and UO_2^{2+} were prepared by melt condensation of bis-1,3-[DCMB] and [ED] and characterized by elemental and thermal analysis as well as different spectroscopic techniques. The data gathered showed that polyamide, ligand coordinates with metal ions in a bidentate manner through N,N donation. The metal ions are surrounded by coordinated water molecules and anions so as to establish the octahedral geometry.

KEYWORDS: Spectroscopic, [1,3-dicarboxymethoxybenzene (DCMB) and ethylene diamine (ED)], Thermal analysis TGA, DTA.

Introduction

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

Some novel wholly aromatic polyamide-hydrazides containing various proportions of para and meta phenylene units were prepared and used as semi permeable membranes for water desalination by reverse osmosis separation performance^[12]. Also metallized plastic films through transition metal complexation were synthesized charecteized^[3-8].

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 inter-

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 vacuum 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^[14] 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. ¹H-NMR spectra was recorded on a Varian analytical EM 390 spectrophotometer using d⁶-DMSO as a solvent and trimethylsilene (TMS) as internal reference.

Results and Discussion

Elemental analysis (C, H and N) of the polyamide under study and its Cd²⁺, Fe³⁺ and UO₂²⁺ complexes show a satisfactory agreement between the proposed and measured values as illustrated in (Table 1). All the solid complexes are insoluble in common organic solvents and do not possess sharp melting points but decompose on heating above 300°C. Thus measurements are expected due to their polymeric nature.

TABLE 1. Microanalytical analysis of polyamide and its complexes.

Complex	Elemental analysis (calc. / measured)				
	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), IIIa → IIIc (M:L) (1:2)

a) Cd²⁺, b) Fe²⁺, c) UO₂²⁺

The μ_{eff} values of the majority of solid complexes, measured at room temperature, show lower values than in case of many N,N donor complexes, the lower magnetic moments are due to antiferromagnetic interactions as a consequence of dimeric or polymeric structural arrangement^[15]. The IR spectrum of polyamide ligand was 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 $\nu_{\text{C=N}}$ appears at 1650 cm^{-1} . The latter band may arise from the keto-enol tautomerism taking place in the free polyamide. The stretching vibrational frequency of the carbonyl carboxyl group ($\nu_{\text{C-O}}$) appears at 1720 cm^{-1} . On the other hand, the IR spectra of the metal complexes, show the absence of the stretching vibrational band of the C = N group, so it seems that 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 ($\nu_{\text{C-O}}$) remains nearly unaltered. 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 $\nu_{\text{M-S}}$ stretching frequency.

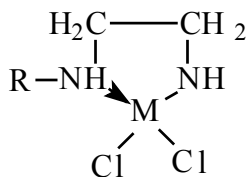
TABLE 2. IR spectra data for polyamide and its complexes.

Complexes	IR cm^{-1}	Assignments
I $\nu_{\text{C-o}} = 1710 \text{ cm}^{-1}$	3400 3100 2900 1720 1650	OH stretching NH stretching C-H stretching $-\text{CH}_2-$ C = O Carbonyl C = N Stretching
(IIa, IIIa)	3400 2900 1700 470	OH Stretching NH Stretching C-O Carbony; M-N
(IIb, IIIb)	3380 2850 1700 470	OH Stretching NH Stretching C = O M-N
(IIc, IIIc)	3390 3000 1690 485	OH Stretching NH Stretching C = O M-N

I (Polyamide), IIa \rightarrow IIc (M: L) (1:1), IIIa \rightarrow IIIc (M:L) (1:2)

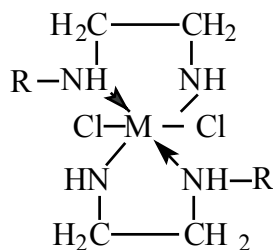
a) Cd^{2+} , b) Fe^{3+} , c) UO_2^{2+}

The ^1H NMR spectrum of polyamide is recorded in $\text{d}^6\text{-DMSO}$ and compared to that of its UO_2^{2+} complex. For the free ligand, the singlet signal at $\delta = 3.3$ ppm (4 protons) is due the $\text{CH}_2\text{-CH}_2\text{-}$ protons while the weak broad signal at 3.7 ppm is due to NH-proton. The other NH group (end groups) gave also a singlet band at 8.2 ppm. The later two signals are strongly affected on complexation with UO_2^{2+} ion indicating their participation in complex formation. So, the mode of bonding in this case can be represented as:



(1:1) (M:L)

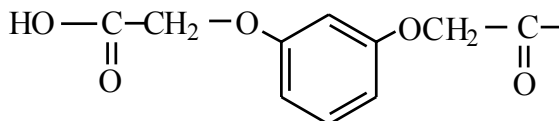
M = metal



(1:2) (M:L)

L = ligand

R =



The electronic absorption spectra of the polyamide derived from 1,3-dimethoxycarboxybenzene and its complexes, measured using the Nujol mull technique, show mainly the charge transfer band of the free molecule at $\cong 25974 \text{ cm}^{-1}$ while Cd^{2+} complex shows a band at 15780 cm^{-1} due to $^4\text{A}_2 \rightarrow ^4\text{T}_1$ (p) transition in tetrahedral field^[16] whereas Fe^{3+} complex shows band at 14265 and 13675 cm^{-1} respectively due to the square planar configuration in both. These transitions are not observed in the spectrum of UO_2^{2+} complex but only the charge transfer band at 24096 cm^{-1} .

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

In case of metal chelates, the first step in the decomposition sequence starts at 190°C due to the evaporation of physically adsorbed water molecules, while the second step corresponding to the removal of chloride ion (in the form of HCl molecules) takes place at 250°C . The final step is the degradation of the anhydrous complex which occurs at temperatures higher than 580°C leading to be

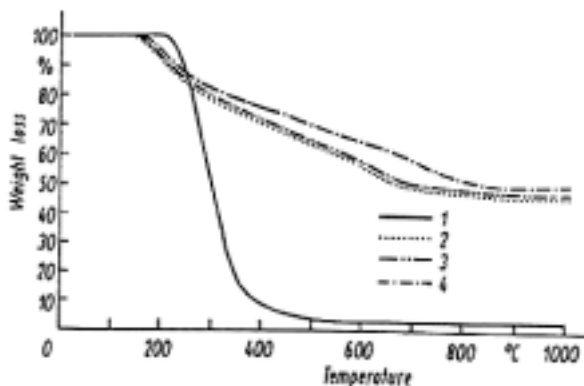
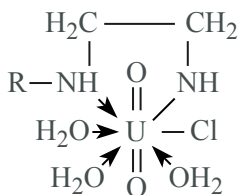
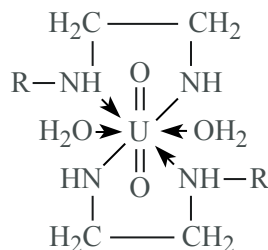


FIG. 1. TG curves of bis-1,3-[DCMB] and [ED] metal chloride polymer complexes. 1-bis-1,3-[DCMB] and [ED], 2-Cd²⁺ poly., 3-Fe³⁺ poly. and 4-UO₂²⁺ Polymer complexes.

more stable than their corresponding free polymer ligand which is in accordance with the results obtained previously^[17-18] which is due to the formation of stable five member rings structures,



1 : 1



1:2

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متراكبات البولي أميد المحضرة من [١، ٣ ثنائي كربوكسي ميثوكسي البنزين و الإثيلين ثنائي الأمين] مع بعض الأيونات الفلزية

فوزية محمد النويصر

قسم الكيمياء ، كلية العلوم ، جامعة الملك عبد العزيز

جدة - المملكة العربية السعودية

المستخلص . يتناول هذه البحث تحضير متراكبات البولي أميد من [١، ٣ ثنائي كربوكسي ميثوكسي البنزين والإثيلين ثنائي الأمين] مع أيونات الكادميوم والحديد واليورانيوم بالصهر والتكثيف لمشتقات هذه التراكبات . وقد تم فحص وتحديد التركيب الجزئي للبوليمر والمتراكبات المشتقة من استخدام القياسات الطيفية المختلفة والتحليل العنصري والحراري للعناصر المكونة لها .