

Synthesis and Characterization of Metal-Containing Coordination Polymers of Poly(methylene diphenylene terephthalamide)

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SYNOPSIS

Amino group-terminated poly(methylene diphenylene terephthalamide) (PMDTA) was prepared using a phosphorylation technique that was then converted into Schiff's base coordination polymers by their reaction with Co(II), Ni(II), and Cu(II) complexes of salicylaldehyde [$M(\text{SAL})_2$] and 2-hydroxy-1-naphthaldehyde [$M(\text{NAPHTHAL})_2$]. The resulting coordination polymers were characterized by IR, elemental analysis, magnetic susceptibility measurements, and thermogravimetric analysis (TGA). TGA shows that coordination polymers are more thermally stable than is the ligand under similar conditions. On the basis of observed results, an oxygen- and nitrogen-coordinated structure for polyaramid-metal complexes has been proposed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyamides, commonly known as polyaramids, are generally prepared by the polycondensation of aromatic diamines and diacids. The polyaramides are considered as high-performance materials due to their superior thermal and mechanical properties. Recently, physicochemical studies of metal chelate polymers have received wide attention due to their importance associated with the problem of developing materials with high thermal stabilities.

Schiff's base complexes involving low molecular weight diamines and aldehydes have been extensively studied.¹⁻⁵ For the first time, we are studying the synthesis of polyaramide Schiff's base coordination polymers with a view to improve the properties of existing polyaramides, especially their thermal resistivity. In the present paper, we are reporting the synthesis of polyaramide Schiff's base coordination polymers using amino group-terminated PMDTA and [$M(\text{SAL})_2$] and [$M(\text{NAPHTHAL})_2$], where M is Co(II), Ni(II), or Cu(II).

EXPERIMENTAL

Materials

Salicylaldehyde (S. Merck, India), 2-hydroxy-1-naphthaldehyde (Fluka, A. G.), 4,4'-diaminodiphenyl methane (E. Merck), terephthalic acid (E. Merck), triphenyl phosphite (Wilson Chemicals, India), and metal salts [acetates of Co(II), Ni(II) and Cu(II), all E. Merck] were used without further purification. These reagents were of analytical or equivalent grade. Solvents like DMF, DMSO, and pyridine (Qualigen, Glaxo, India) were distilled before use.

Preparation of Amino-terminated PMDTA

Amino group-terminated PMDTA was prepared by a known technique.⁶ In a typical experiment, terephthalic acid (0.01 *M*) was dissolved in a mixture of solvents containing 150 mL DMF and 30 mL pyridine. Triphenyl phosphite (0.02 *M*) was added to it. This reaction mixture was brought to a constant temperature of $80 \pm 0.2^\circ\text{C}$ in an oil bath and was stirred continuously. Diamine (0.012 *M*) was then added to it slowly. The heating at 80°C was continued for another 1.5–2 h. The contents of the reaction mixture were poured into a large amount of methanol to precipitate the amino group-terminated PMDTA. The product was filtered, washed several times with methanol, and then dried at 80°C for 10–12 h. Weight-average molecular weight (M_w) was calculated viscometrically and was found to be 2000.

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Low molecular weight PMDTA dissolves in DMF upon heating and stirring.

Preparation of Cobalt(II), Nickel(II), and Copper(II) Complexes of Salicylaldehyde and 2-Hydroxy-1-naphthaldehyde

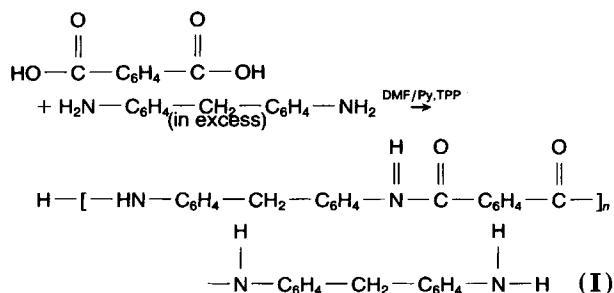
The complexes were prepared by mixing an aqueous solution of metal acetates with ethanolic solutions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde in a 1 : 2 molar ratio as per reported method.⁷ The resulting complexes were characterized by IR spectroscopy and elemental analysis.

Synthesis of Coordination Polymers

Solutions of PMDTA (2.0 g, 0.001 *M*) in 50 mL hot DMF and of respective metal complexes of aldehydes (0.001 *M*) in 50 mL hot DMF were refluxed for 6–8 h to obtain the resulting coordination polymers in solid forms. The precipitates were filtered, washed several times with hot DMF and alcohol, and then dried. These coordination polymers were air-stable, powdery, insoluble in water, and common organic solvents.

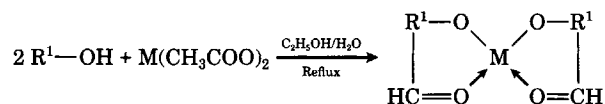
Schemetically, the overall route for the synthesis of coordination polymers may be represented as

(a) Synthesis of PMDTA Ligand

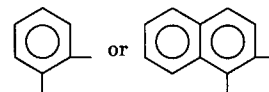


or $\text{H}_2\text{N}-\text{R}-\text{NH}_2$, where R = the polyamide repeating unit.

(b) Preparation of Metal Derivatives of Salicylaldehyde [$\text{M}(\text{SAL})_2$] and 2-Hydroxy-1-naphthaldehyde [$\text{M}(\text{naphthal})_2$]



where M = Co(II), Ni(II), or Cu(II) and $\text{R}^1 =$



(c) Synthesis of Coordination Polymers (Fig. 1)

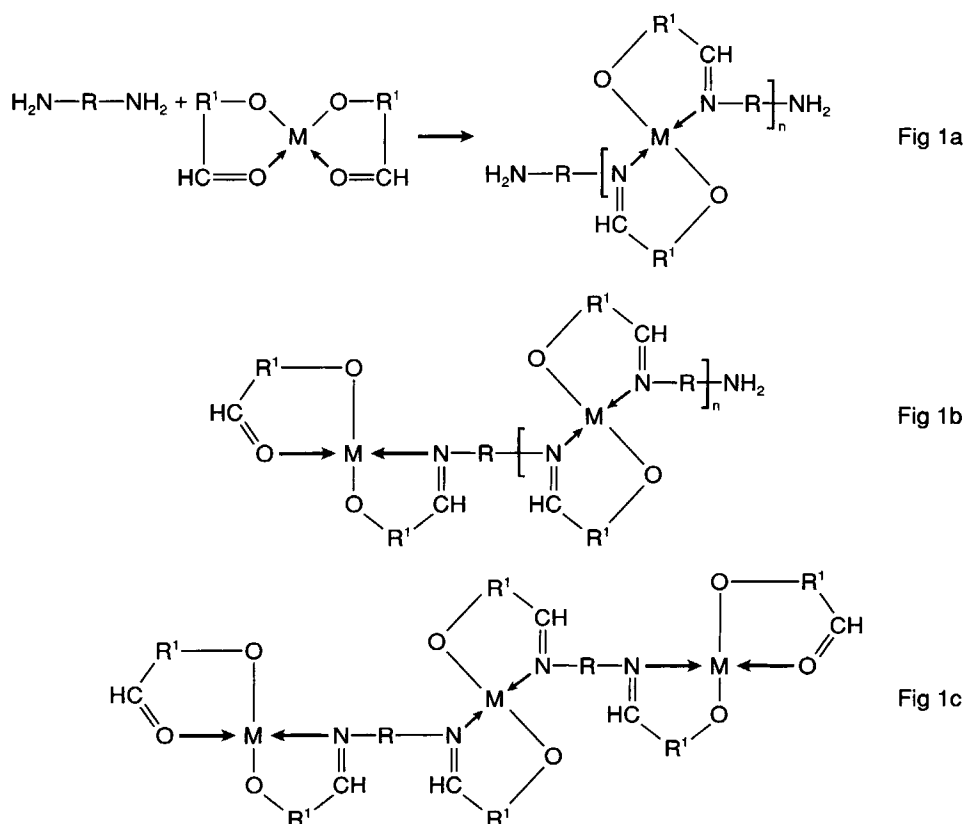


Figure 1 Schematic representation for the synthesis of coordination polymers.

Characterization

(a) Elemental Analysis

Percentage of C, H, and N of PMDTA and coordination polymers were determined with a Perkin-Elmer elemental analyzer 2400 model. Metal contents of the coordination polymers were determined by complexometric titration with EDTA after decomposing them with fuming nitric acid. Molecular weights of the coordination polymers could not be determined due to their insoluble nature.

(b) Spectral Studies

IR spectra of the ligand as well as the coordination polymers were recorded on a Perkin-Elmer infrared spectrophotometer Model 1430 using CsI pellets in the range 4000–200 cm^{-1} .

(c) Magnetic Susceptibility Measurements

The magnetic susceptibility measurements were done at room temperature with a Guoy's balance using $\text{HgCo}(\text{NCS})_4$ as a calibrant.

(d) Thermogravimetric Analysis

TGA was performed on Perkin-Elmer thermal analyzer TGA 7 with a professional computer 7700 in an inert atmosphere at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Composition

The analytical data is presented in Table I with the theoretical compositions based on assumed structures. If the average number of repeat units, n , for the polyamide is considered as 6, then the molecular weight according to formula I will be 2166, and when n is taken as 5, the molecular weight will be 1838. The average of these two values, i.e., 2002, is very close to our experimentally determined M_w . This indicates that the number of repeat units may vary between 5 and 6. However, for calculation of theoretical compositions, we have taken $n = 6$.

We observed a discrepancy between theoretical and calculated values for C, H, N, and M beyond experimental error. It may be explained by the fact that aromatic polyamides with moderately high molecular weight exhibit a strong tendency for moisture pickup,⁸ which gives rise to the discrepancy between the theoretical and experimental analyses.^{9–11} Extensive studies¹² of the sorption and desorption isotherms of water for numerous polyamides have led to the following proposal concerning the absorption of water by polyamides: Three molecules of water are absorbed on two neighboring amide groups in an accessible region. The first molecule forms a double H-bond between the CO groups (firmly bound water) and the other two molecules form a H-bond between the CO and the NH groups (loosely

Table I Analytical Data of PMDTA and Its Metal Coordination Polymers

No.	Compound	Elemental Analysis ^a			
		%C	%H	%N	%M
1	PMDTA	71.6	5.5	8.4	—
	$\text{C}_{139}\text{H}_{110}\text{N}_{14}\text{O}_{12} \cdot 9\text{H}_2\text{O}$	71.3	5.0	9.0	—
2	PMDTA-Co(II) SAL	70.0	5.1	7.2	3.2
	$[\text{C}_{320}\text{H}_{242}\text{N}_{28}\text{O}_{32}\text{Co}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	70.0	4.8	7.9	3.3
3	PMDTA-Ni(II) SAL	70.0	5.0	7.2	3.1
	$[\text{C}_{320}\text{H}_{242}\text{N}_{28}\text{O}_{32}\text{Ni}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	69.7	4.6	7.2	3.0
4	PMDTA-Cu(II) SAL	69.8	5.0	7.1	3.4
	$[\text{C}_{320}\text{H}_{242}\text{N}_{28}\text{O}_{32}\text{Cu}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	70.0	4.3	7.7	3.5
5	PMDTA-Co(II) NAPHTHAL	71.3	5.0	6.8	3.1
	$[\text{C}_{344}\text{H}_{254}\text{N}_{28}\text{O}_{32}\text{Ni}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	70.2	4.6	7.9	3.5
6	PMDTA-Ni(II) NAPHTHAL	71.3	5.0	6.8	3.0
	$[\text{C}_{344}\text{H}_{254}\text{N}_{28}\text{O}_{32}\text{Ni}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	71.2	4.8	7.5	3.2
7	PMDTA-Cu(II) NAPHTHAL	71.2	5.0	6.8	3.3
	$[\text{C}_{344}\text{H}_{254}\text{N}_{28}\text{O}_{32}\text{Cu}(\text{II})_3] \cdot 18\text{H}_2\text{O}$	70.4	4.6	7.2	4.0

^a For each compound, the upper values represent theoretical analysis and the lower values show the results obtained experimentally.

bound water). Similarly, in the present study, the number of water molecules sorbed to the amide groups may be considered as 1.5 per CONH group if we do not consider capillary condensation. Therefore, we have calculated theoretical values for C, H, N, and M for PMDTA and the coordination polymers with 9 water molecules per oligomeric unit of the ligand. It was observed that the theoretical values calculated (upper values in Table I) for the structure with metal aldehyde units at both ends [Fig. 1(C)] are close enough to the experimentally found values. This observation suggests that there are very few metal repeat units in the coordination polymers. The variable composition of coordination polymers at the end units, as shown in Figure 1(a)–(c), may also be responsible for the observed discrepancy between theoretical and experimental values.

IR Spectral Studies

The important IR bands of PMDTA and its coordination polymers are given in Table II. In the IR spectrum of PMDTA, a broad band appears in the region 3400–3200 cm^{-1} due to νNH vibrations of the amide group of PMDTA and the terminal amino

groups. The appearance of this band at slightly higher frequency and its broadness may be due to the H-bonding.¹³ The presence of one methylene group per unit of PMDTA was confirmed by the appearance of two strong bands at 2940 and 2860 cm^{-1} due to νCH symmetric and asymmetric¹⁴ stretching and a band at 1410 cm^{-1} due to the CH_2 bending mode.¹⁴ The PMDTA shows characteristic bands at 3000–2900 cm^{-1} due to aromatic C—H stretching.¹⁴ The amide I band, which has a main contribution from the C=O stretching of the amide group, appears at 1650 cm^{-1} .^{13(b)} The amide II band appears at 1510 cm^{-1} ,^{13(c)} the amide III band appears at 1330 cm^{-1} , and the amide IV and VI bands appear at 640 and 590 cm^{-1} in the spectrum of PMDTA. The out-of-plane NH deformation mode or the amide V band appears at 730 cm^{-1} . *p*-Substituted benzene ring vibrations appear at 850 cm^{-1} .

The spectra of metal coordination polymers of PMDTA have been compared with those of the PMDTA in order to elucidate the nature of coordination and participation of specific groups or moieties in the formation of coordination polymers. The band due to νNH is broadened further and appeared at the 3600–3200 cm^{-1} region in the spectra of co-

Table II Important IR Spectral Assignments of PMDTA and Its Metal Complexes (Wave Number in cm^{-1})

Assignments	Compounds					
	PMDTA Complexes					
	PMDTA	Co(II)-SAL	Cu(II)-SAL	Ni(II)-SAL	Co(II)-NAPHTHAL	Cu(II)-NAPHTHAL
νNH	3400–3200 (br)	3400–3180 (br)	3600–3160 (br)	3500–3160 (br)	3500–3240 (br)	3560–3200 (br)
$\nu_{\text{Ar}}-\text{CH}$	3000–2900 (m)	3040 (m)	3020 (m)	3060 (s)	3100 (w)	3100 (m)
$\nu\text{CH}(\text{asym})$	2940 (sh)	2960 (s)	2940 (s)	2940 (s)	2940 (s)	2940 (s)
$\nu\text{CH}(\text{sym})$	2860 (s)	2860 (s)	2880 (s)	2860 (s)	2880 (s)	2860 (s)
Amide I or C=O	1650 (s)	1660 (s)	1640 (s)	1650 (s)	1650 (s)	1655 (s)
Aromatic skeleton	1600 (s)	1595 (s)	1600 (s)	1605 (s)	1600 (s)	1600 (s)
Amide II	1520 (s)	1575 (s)	1530 (s)	1520 (s)	1530 (s)	1530 (s)
$\nu\text{C}=\text{N}$	—	1550 (sh)	1545 (sh)	1560 (sh)	1540 (sh)	1550 (sh)
δCH_2	1410 (s)	1415 (s)	1410 (s)	1410 (s)	1405 (s)	1410 (s)
Amide III or C—N (arom)	1330 (s)	1320 (s)	1330 (s)	1325 (s)	1330 (s)	1325 (s)
<i>p</i> -Substituted benzene vibrations	850 (s)	860 (s)	850 (s)	860 (s)	850 (s)	850 (s)
Amide V	730 (s)	725 (s)	725 (s)	730 (s)	730 (s)	730 (s)
Amide IV	640 (m)	645 (w)	650 (m)	640 (s)	650 (w)	640 (m)
Amide VI	590 (m)	590 (s)	590 (s)	585 (s)	585 (s)	585 (s)
$\nu_{\text{M}}-\text{O}$	—	680 (s)	670 (s)	660 (m)	650 (m)	660 (m)
$\nu_{\text{M}}-\text{N}$	—	500 (w)	495 (s)	490 (m)	485 (m)	490 (m)

s = strong; m = medium; w = weak; br = broad; asym = asymmetric; sym = symmetric.

ordination polymers. This indicates the involvement of the amino group in complexation. An additional band in the region $1550\text{--}1530\text{ cm}^{-1}$ along with the amide II band at 1510 cm^{-1} appears in the coordination polymers, which can be attributed to the creation of the C=N group as a result of the Schiff's base formation. Generally, this absorption band appears in the range $1690\text{--}1580\text{ cm}^{-1}$. The appearance of this band in the lower range suggests the involvement of azomethine nitrogen in the coordination. These bands assigned to the C=N stretching frequency are characteristic of Schiff's base coordinated to the metal ion, i.e., $\text{C}=\text{N} \rightarrow \text{M}$. This observation further supports the coordination through the terminal amino groups of PMDTA. The other bands of PMDTA show no appreciable change upon coordination. The absorption due to the acetate group was not observed in the IR spectra of coordination polymers.

The appearance of new bands in the region $680\text{--}630\text{ cm}^{-1}$ attributed to $\nu\text{M}-\text{O}$ and in the region $500\text{--}490\text{ cm}^{-1}$ attributed to $\nu\text{M}-\text{N}$ further confirms the coordination through nitrogen and oxygen.

Magnetic Susceptibility Measurements

The values of magnetic moments for different PMDTA-metal coordination polymers are given in Table III. The magnetic moments values in the range of 4.36–4.69 BM for PMDTA-Co(II) coordination polymers are consistent with the tetrahedral geometry.¹⁵ PMDTA-Ni(II) coordination polymers showed diamagnetic behavior that indicates their square planar geometry.¹⁶ In Ni(II) polymer, diamagnetism may be due to eight electrons being paired in four lower lying *d*-orbitals. PMDTA-Cu(II) coordination polymers show magnetic moment values in the range 1.65–1.85 BM, indicating square planar geometry for Cu(II) polymers.^{17,18}

Thermogravimetric Analysis

The TG curves for PMDTA and its coordination polymers have been depicted in Figure 2. TG data

of coordination polymers indicate the absence of coordinated water molecules due to the negligible weight loss up to 400°C . On comparing the TG data of PMDTA with that of coordination polymers, it was found that the coordination polymers show a single-step decomposition pattern unlike the two-step decomposition pattern of PMDTA. This indicates that the introduction of metal ion in polyaramide through the Schiff's base structure has minimized the initial decomposition of PMDTA. This is clear from the values of initial decomposition for PMDTA (220°C) and its coordination polymers (in the range $478\text{--}505^\circ\text{C}$).

The order of thermal stability on the basis of initial decomposition temperature was found to be

PMDTA-Cu(II)-NAPHTHAL

> PMDTA-Co(II)-SAL

\simeq PMDTA-Co(II)-NAPHTHAL > PMDTA

On comparing the energy of activation, as calculated by the Fuoss method,¹⁹ it was observed that the coordination polymers are more thermally stable than is PMDTA itself.

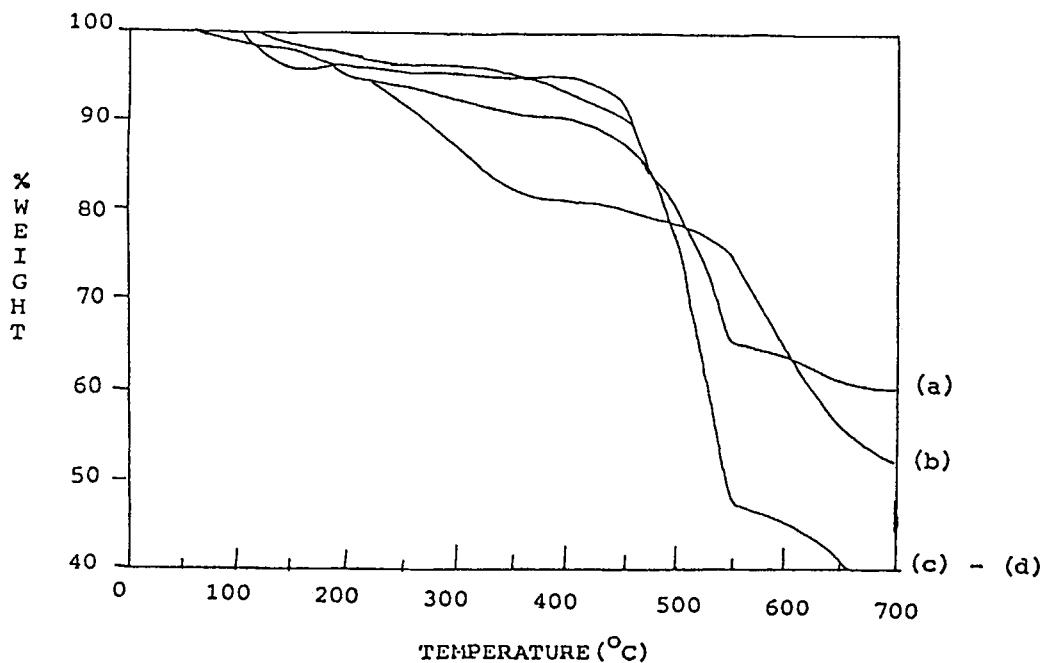
It was observed that the salicylaldehyde and 2-hydroxy-1-naphthaldehyde-based coordination polymers have almost similar thermal stabilities and degradation patterns. In naphthaldehyde coordination polymers, the additional aromatic ring may increase electron delocalization and also steric crowding. The substitution on the benzene ring usually has a deleterious influence on thermal stability.²⁰ But we observed the same thermal stability for Co(II)-SAL and Co(II)-NAPHTHAL coordination polymers of PMDTA, which suggests that electron delocalization and steric crowding are canceling each other's effect.

The enhanced thermal stability of the coordination polymers when compared with the ligand PMDTA may be due to the following facts:

1. The enhancement in molecular weight on joining two or more polyaramide units

Table III Magnetic Moment Values of PMDTA-Metal Coordination Polymers

No.	Compounds	μ_{eff} BM	Geometry Proposed
1.	PMDTA-Co(II)-SAL	4.69	Tetrahedral
2.	PMDTA-Co(II)-NAPHTHAL	4.54	Tetrahedral
3.	PMDTA-Ni(II)-SAL	Diamagnetic	Square planar
4.	PMDTA-Ni(II)-NAPHTHAL	Diamagnetic	Square planar
5.	PMDTA-Cu(II)-SAL	1.79	Square planar
6.	PMDTA-Cu(II)-NAPHTHAL	1.82	Square planar



Where :- (a) - PMDTA-Cu(II)-Naphthal (b) - PMDTA
(c) - (d) - PMDTA-Co(II)-Sal - PMDTA-Co(II)-Naphthal

Figure 2 Thermogravimetric analysis of PMDTA and its coordination polymers.

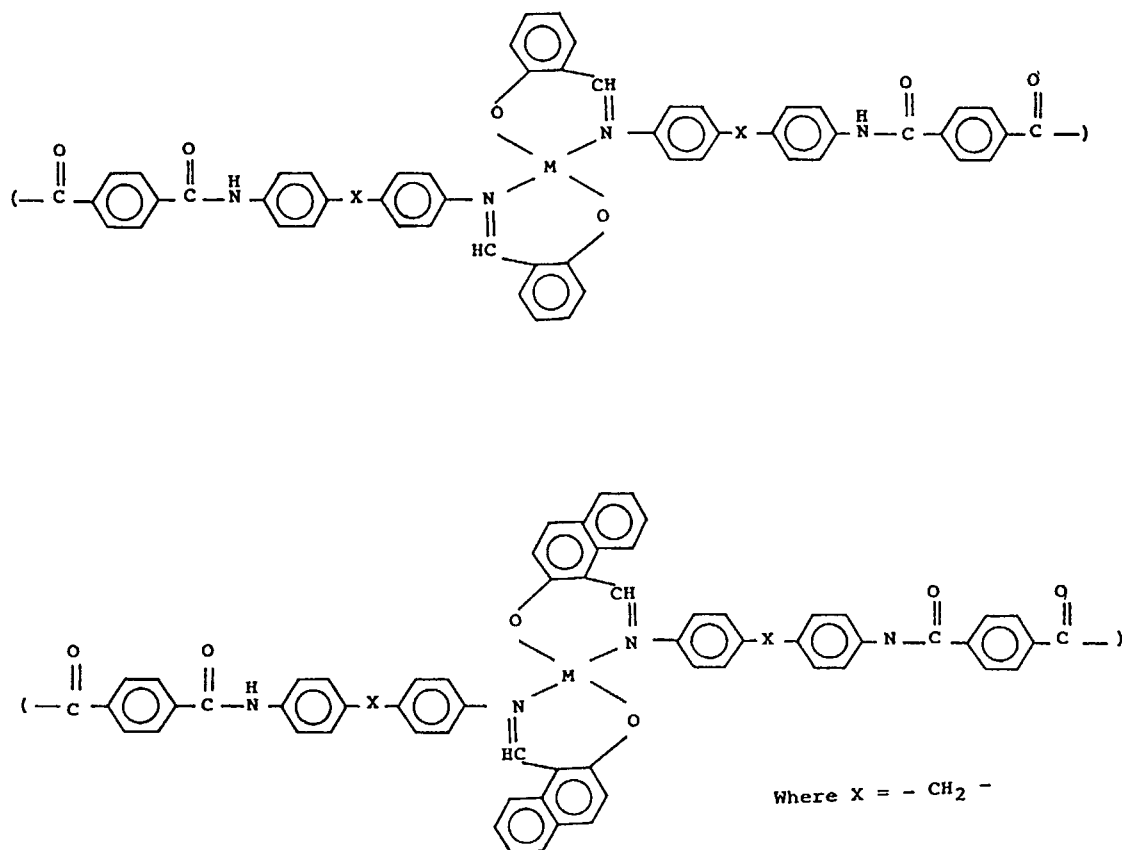


Figure 3 Proposed structures for the coordination polymers.

Table IV Analytical data of PMDTA–Metal Coordination Polymers Prepared Heterogeneously in Dimethylacetamide

No.	Compound	Elemental Analysis ^a			
		%C	%H	%N	%M
1	PMDTA–Co(II)–SAL [C ₃₂₀ H ₂₄₂ N ₂₈ O ₃₂ Co(II) ₃] · 18H ₂ O ^b	70.0	5.1	7.2	3.2
		70.0	4.6	7.8	3.0
2	PMDTA–Ni(II)–SAL [C ₃₂₀ H ₂₄₂ N ₂₈ O ₃₂ Ni(II) ₃] · 18H ₂ O	70.0	5.0	7.2	3.1
		69.9	4.7	7.4	2.9
3	PMDTA–Cu(II)–SAL [C ₃₂₀ H ₂₄₂ H ₂₈ O ₃₂ Cu(II) ₃] · 18H ₂ O	69.8	5.0	7.1	3.4
		70.0	4.5	7.6	3.2
4	PMDTA–Co(II)–NAPHTHAL [C ₃₄₄ H ₂₅₄ N ₂₈ O ₃₂ Co(II) ₃] · 18H ₂ O	71.3	5.0	6.8	3.1
		70.1	4.7	7.7	3.1
5	PMDTA–Ni(II)–NAPHTHAL [C ₃₄₄ H ₂₅₄ N ₂₈ O ₃₂ Ni(II) ₃] · 18H ₂ O	71.3	5.0	6.8	3.0
		70.9	4.8	7.4	3.0
6	PMDTA–Cu(II)–NAPHTHAL [C ₃₄₄ H ₂₅₄ N ₂₈ O ₃₂ Cu(II) ₃] · 18H ₂ O	71.2	5.0	6.8	3.3
		70.5	4.7	7.4	3.0

^a For each compound, the upper values represent theoretical analysis and the lower values show the results obtained experimentally.

^b Theoretical compositions are calculated according to assumed structures given in Figure 1(c) and nine water molecules are taken per repeat unit of the ligand.

through Schiff's base structure formation by interaction of terminal amino groups of PMDTA and metal–aldehyde complexes,

2. Introduction of ring structure as a result of coordination that increases the stiffness of polyaramide chain.
3. Increase in the aromatic character within the polyaramide chain due to the introduction of chelate rings with aromatic nuclei.

On the basis of the stoichiometry of the coordination polymers obtained from analytical results and IR studies, thermal stabilities, and magnetic moments values, the structures proposed for PMDTA coordination polymers are shown in Figure 3.

Application Aspect

The reported reaction for the synthesis of coordination polymers was also conducted in a heterogeneous medium in order to see whether the films, fibers, or sheets of polyaramide can be reacted with the metal–aldehyde to improve upon their thermal stability. The very fine particles of the polyaramid, PMDTA, were suspended in a solution of the metal–aldehyde complex in dimethylacetamide. This mixture was refluxed for 24 h with constant stirring. The resulting colored mass was filtered and washed thoroughly with the hot DMF followed by alcohol

and then dried. To our utmost surprise, the analytical results (Table IV) are almost the same as those obtained in the case of a complexation reaction in the dissolved condition. In heterogeneous medium, amino groups present on the surface of particles will react only with the metal–aldehyde complex to form Schiff's base complex. Therefore, free amino groups present on the surface of polyaramid film, sheet, or fibers may be complexed in the reported way to enhance their thermal stability.

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