



## Mini-review

## In situ rearrangement of polyamines in the presence of different metal ions



Smita Satapathi

Department of Chemistry, A.K.P.C. Mahavidyalaya, Bengai, Hooghly, PIN-712 611, India

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## ABSTRACT

Synthetic methods, structural features, in situ rearrangement pattern and exciting properties of some model compounds are described in this short review.

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## 1. Introduction

We know that the use of simple polyamines and tripodal polyamines [1–4] as blockers is an efficient way for assembling metal centers in close proximity ensuring electronic communication through their chelation [5,6]/congregation [7,8] motifs. The active amine hydrogens on

their frameworks are useful in the construction of supramolecular assemblies through hydrogen bonding [9–11]. Literature shows that, in the presence of metal ions, some polyamines through in situ ligand rearrangement [12–22] give novel metal–ligand frameworks of the otherwise unavailable and inaccessible ligands. Such reactions not only can play a vital role in crystal engineering of functional coordination compounds but also may serve as a new bridge between coordination chemistry and synthetic organic chemistry.

E-mail address: [smitasatapathi@gmail.com](mailto:smitasatapathi@gmail.com).

The advantages of the in situ ligand rearrangement reactions are as follows: (i) These reactions are efficient as there was no need for ligand synthesis; (ii) these reactions are able to ensure the sufficient growth of large single crystals; and (iii) these are generally environmentally friendly [23,24]. Several important in situ metal–ligand rearrangements of different organic ligands including carbon–carbon bond formation [25,26], hydroxylation [27,28], alkylation [29], cycloaddition [30], hydrolysis [31–33], aminizing reactions and deaminizing coupling reactions [12–22], acylation [34,35], decarboxylation [36] etc. are well known. Among them in situ metal–ligand rearrangement of polyamines in the presence of different metal ions through aminizing reactions (AR) and deaminizing coupling reactions (DCR) [12–22] (Scheme 1) is a very important research field in both coordination chemistry and organic chemistry. However the actual mechanism of the rearrangement reaction is still unclear so far. The aim of the present review is to give an overview of such type of metal–ligand rearrangement to form novel coordination compounds and elucidation of probable reaction mechanisms.

## 2. Synthetic methods

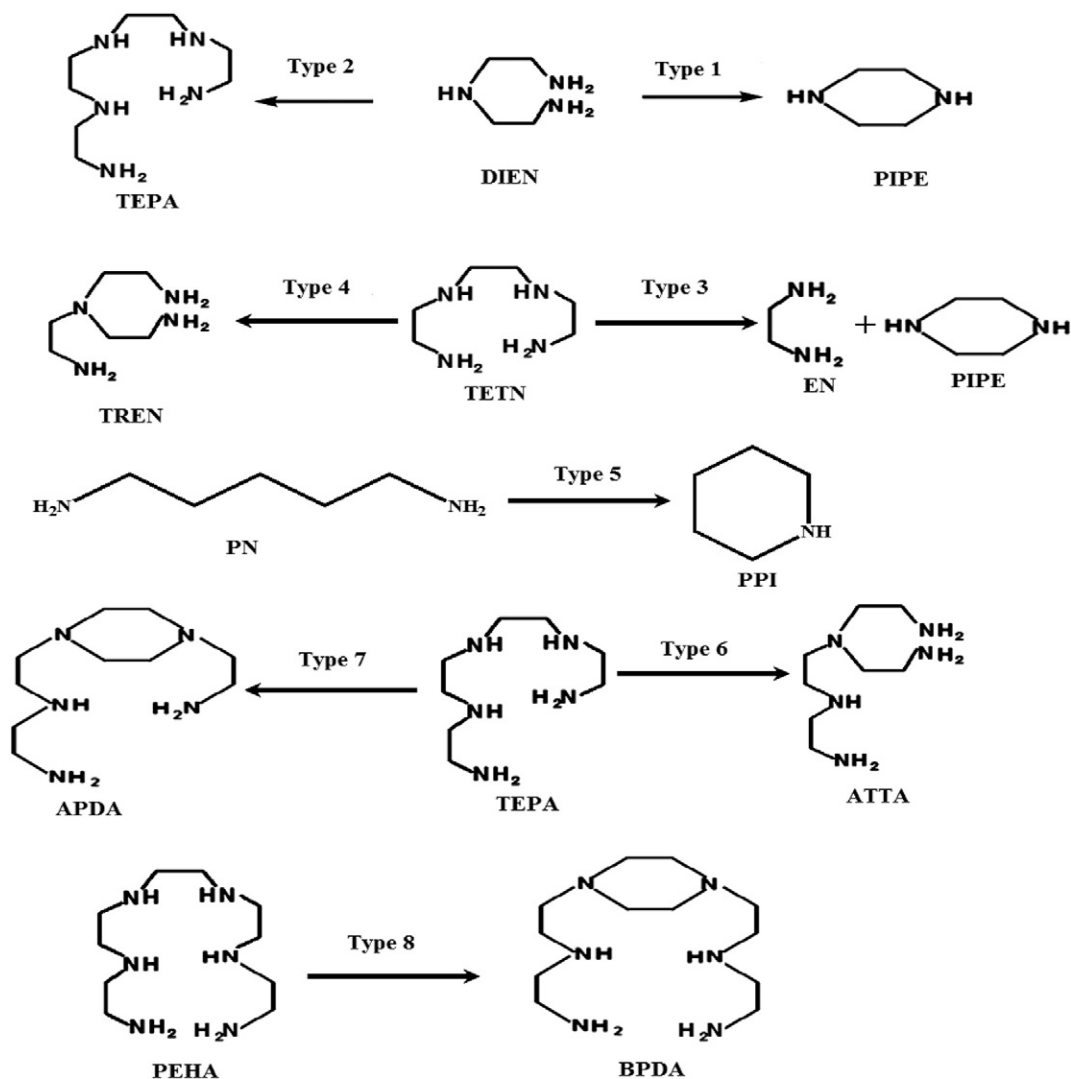
In situ metal–ligand reactions are generally conducted in open air and under mild conditions. On the contrary, solvothermal/hydrothermal reactions [12–21] are usually performed in a sealed

solution at elevated high temperature and pressure. Syntheses of a number of novel complexes through hydro(solvo)thermal [12–21] and nonhydro(solvo)thermal [22] in situ metal–ligand rearrangement reactions of polyamine will be discussed now one by one.

### 2.1. Preparation through hydro(solvo)thermal in situ metal–ligand rearrangement reaction

A common scheme (Scheme 2) is used to show the syntheses of several novel compounds at a glance through hydro(solvo)thermal in situ metal–ligand rearrangement reactions.

Compound **1** can be obtained [12] by using  $\text{GeO}_2$ , S, and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 1:3:1 molar ratio in DIEN/ $\text{H}_2\text{O}$  solution ( $V/V = 4/1$ ) in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heating it at 180 °C for 6 days and finally cooling it to room temperature. Purple crystals of **1** were filtered, washed with ethanol and diethyl ether, dried and stored under vacuum. For the preparation of compound **2** [13], initially a mixture of  $\text{V}_2\text{O}_5$  and  $\text{As}_2\text{O}_3$  in 1:1 molar ratio was stirred in distilled water forming an orange solution. Then 5.5 mmol of DIEN was added drop wise with stirring turning the color to kelly green. Further,  $\text{Zn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and 2,2'-BPY in 2:1 molar ratio were added to it and stirred for 30 min. The resulting



**Scheme 1.** In situ rearrangements of different polyamines. [EN = ethylenediamine, DIEN = diethylenetriamine, PN = 1,5-pentanediamine, TETN = triethylenetetramine, TEPA = tetraethylenepentamine, PEHA = pentaethylenhexamine, PIPE = piperazine, PPI = piperidine, TREN = N,N,N-tris(2-aminoethyl)amine, ATTA = 4-(2-aminoethyl)-triethylenetetramine, APDA = N-(2-aminoethyl)-piperazine-1,4-diethylamine, BPDA = N,N'-bis(2-aminoethyl)piperazine-1,4-diethylamine].

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