



# Cadmium(II) mediated addition of methanol to nitrile-functionalized 1,4,7-triazacyclononanes



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## ABSTRACT

The nucleophilic addition of methanol to two nitrile-functionalized triazamacrocyclic derivatives 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane ( $L^1$ ) and 1,4,7-tris(cyanoethyl)-1,4,7-triazacyclononane ( $L^2$ ) were systematically studied under the mediation of various  $Cd^{2+}$  salts with different counter anions. When  $L^1$  was reacted with  $Cd(OAc)_2 \cdot 2H_2O$  in refluxing methanol for 4 h at a ratio of 1:1, complete solvolysis of three pendant  $-CH_2CN$  groups of  $L^1$  was achieved and then a trigonal prismatic complex  $[Cd(L^3)]^{2+}$  with the resulting imino ether ligand  $L^3$  was in situ produced and crystallized upon the addition of stoichiometric  $NaClO_4$ . After raising the molar ratio of  $Cd(OAc)_2 \cdot 2H_2O/L^1$  to 1.5:1 or higher and shortening the reaction time to 2 h,  $L^1$  was methanolized selectively into  $L^5$ , incorporating two  $-CH_2C(OMe)=NH$  and one  $-CH_2CN$  pendant arms because an acetate can still bind to  $Cd^{2+}$  and limits the conversion of the remaining nitrile arm. By adding  $NaClO_4$ , a mono-capped trigonal prismatic complex  $[Cd(L^5)(OAc)](ClO_4)$  was easily precipitated from the methanolic solution. In contrast to  $L^1$ , perchlorate, nitrate, and acetate salts of  $Cd^{2+}$  were found to promote the transformation of  $L^2$  bearing longer  $-CH_2CH_2CN$  pendant arms into the entire solvolysis product  $L^4$  after refluxing for 4 h, which utilizes its three  $-CH_2CH_2C(OMe)=NH$  groups and tacn (tacn = 1,4,7-triazacyclononane) backbone to capture  $Cd^{2+}$  yielding an octahedral complex  $[Cd(L^4)]^{2+}$ . Additionally,  $L^1$  and  $L^2$  did not undergo methanolysis when treated with  $CdCl_2 \cdot 4H_2O$  and two neutral compounds  $[Cd(L^1)Cl_2]$  and  $[Cd(L^2)Cl_2] \cdot 0.5H_2O$  containing the original nitrile ligands were obtained. The latter was recrystallized from a DMF/ $CH_3CN$  solution to afford an octahedral solvent-coordinated complex  $[Cd(L^2)(DMF)Cl_2] \cdot CH_3CN$ .

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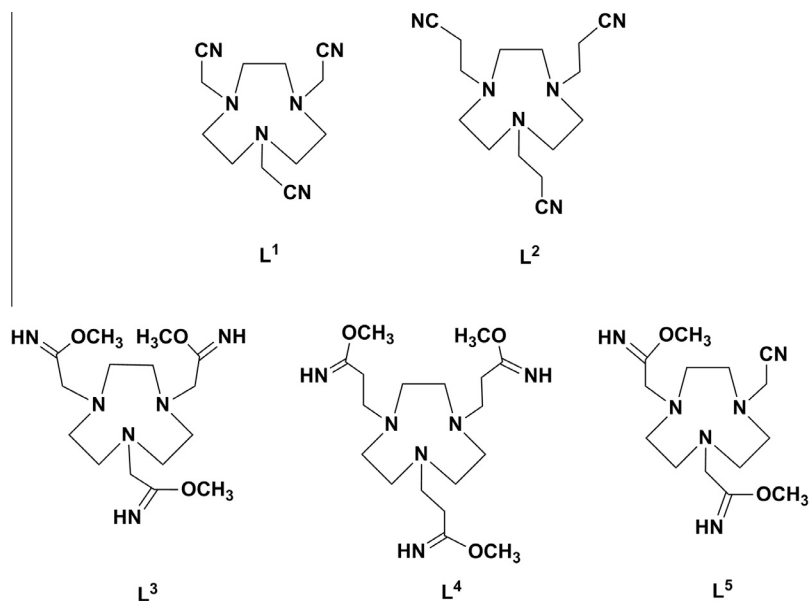
## 1. Introduction

Polyazamacrocycles with diversified functional pendant arms are quite pursued by researchers in recent years because of their wide uses in enzyme mimics, medicinal diagnostics and catalyzed oxidations [1–10]. Beside direct attachment of the pendant functional groups onto the secondary amine N atoms of the parent azamacrocycles [11–13], addition of nucleophilic reagents to the nitrile-functionalized polyazamacrocycles in the presence of metal ions has been found to be a convenient means to acquire azamacrocyclic derivatives bearing pendant amide, imino ether, amidine and heterocycle groups [14–19]. The metal-catalyzed or metal-mediated transformation shows some advantages over the traditional acid or base catalyzed ways, such as the moderately mild reaction conditions, without treatment of the troublesome acid

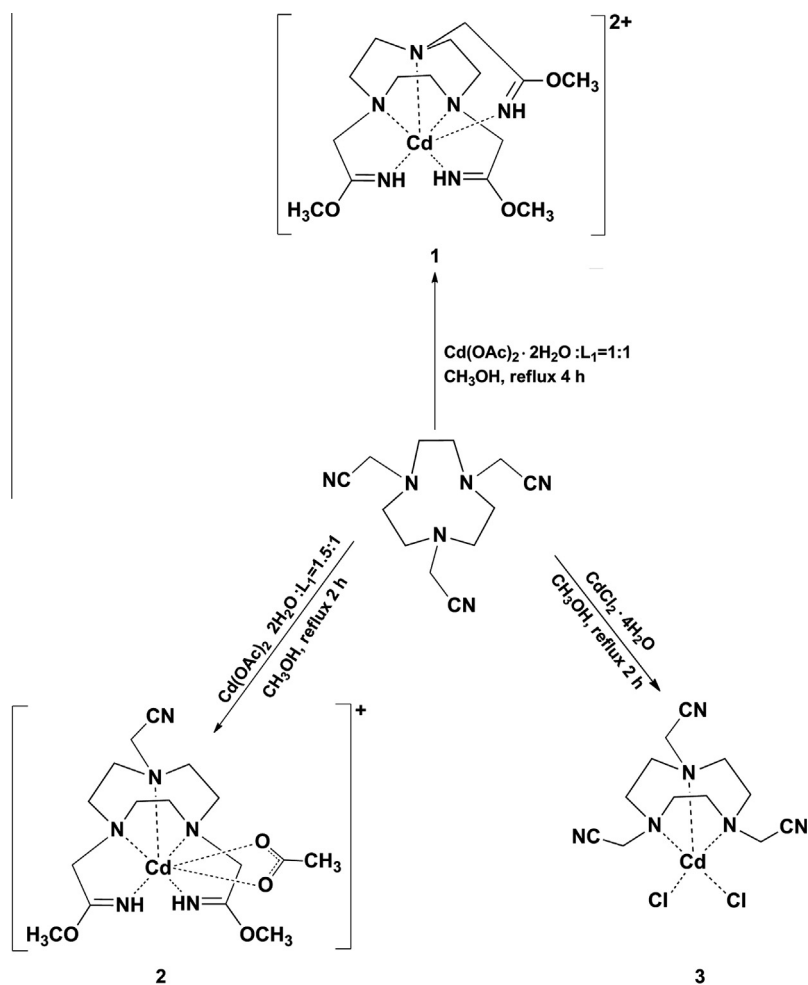
or base byproducts, stopping the transformation at a special stage [20,21]. In our previous published investigations, we have found a tri-substituted N-nitrile functionalized 1,4,7-triazacyclononane is stepwise hydrolyzed into the respective tri-amide species in the wet acetonitrile under the mediation of  $Zn^{2+}$  [22]. Tei et al. have reported that nitrile pendant arm derivatives of tacn upon chelating to  $Cu^{2+}$  may undergo the solvolysis in refluxing methanol to afford triazamacrocyclic compounds bearing imino ether functionalities [23]. Their study revealed that selective addition of methanol to one or two of three pendant nitrile groups can be realized by choosing the starting  $Cu^{2+}$  salts with different counter anions. However, in such a  $Cu^{2+}$ -containing system, complete solvolysis of all three nitrile groups attached to azamacrocycles was not fulfilled. The further studies about the nucleophilic addition of nitrile-functionalized tacn rings under the mediation of metals are necessary in consideration of the demands of looking for the convenient chemical procedures to obtain tacn derivatives with homo- or hetero- functional pendant arms.

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**Scheme 1.** Summary of triazamacrocyclic ligands with different pendant groups.



**Scheme 2.** Reactions of ligand  $L^1$  and various  $Cd^{2+}$  salts with different counter anions.

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