Inorganica Chimica Acta 415 (2014) 14–21

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

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ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 6 February 2014
Accepted 11 February 2014
Available online 26 February 2014

Keywords:
Cadmium(II) complex
Methanolysis
Nitrile
1,4,7-Triazacyclononane
Crystal structure

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 methanolyzed 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 $[Cd(L^2)(DMF)Cl_2]\cdot CH_3CN$.

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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http://dx.doi.org/10.1016/j.ica.2014.02.021
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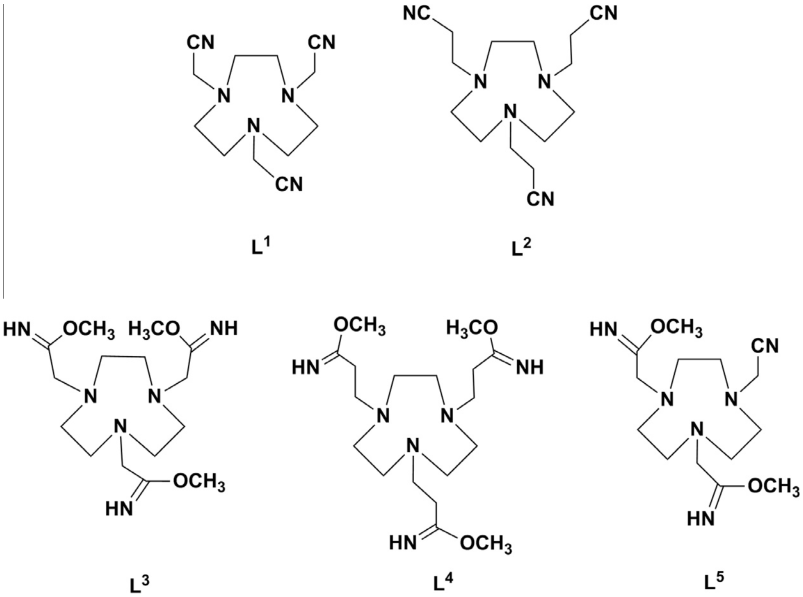
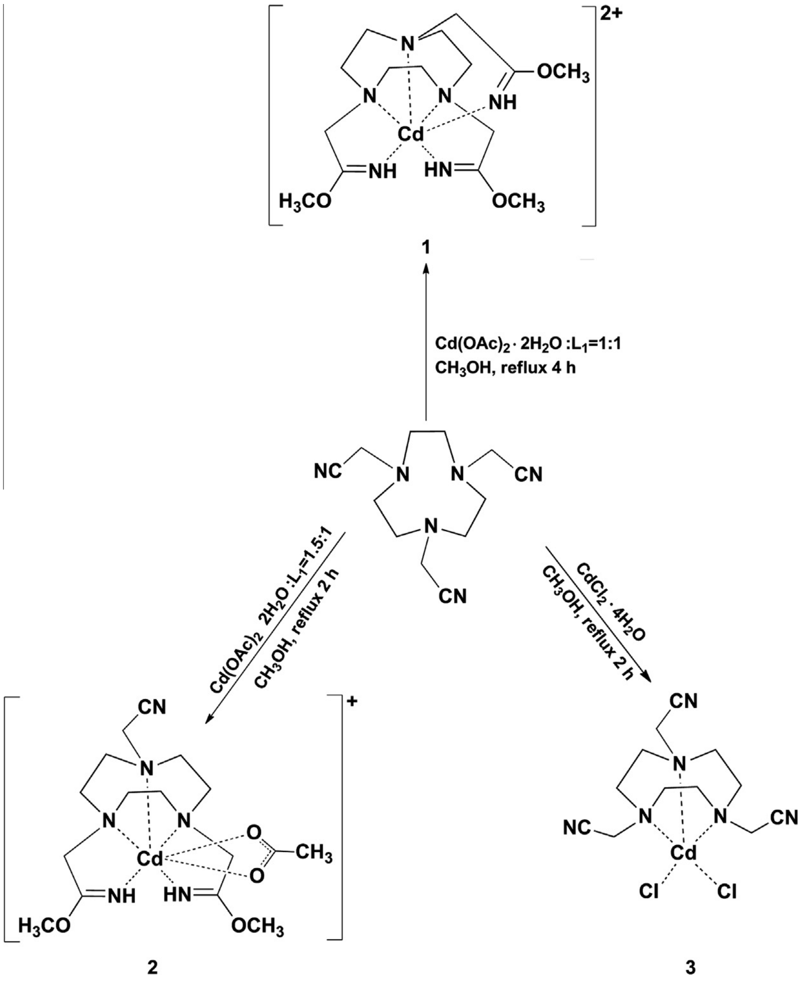
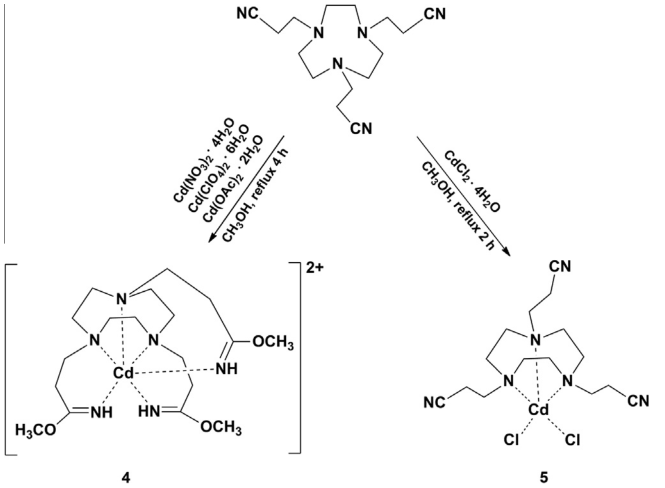


Scheme 1. Summary of triazamacrocyclic ligands with different pendant groups.



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



Scheme 3. Reactions of ligand L^2 and various Cd^{2+} salts with different counter anions.

In previous observations the closed-shell Zn^{2+} has shown excellent activating ability on metal-promoted nucleophilic addition of organonitriles [24,25], yet its congener Cd^{2+} has rarely been investigated in closely analogous reaction systems. With the aim to develop a feasible system to accomplish both complete or partial methanolysis of N-nitrile tri-functionalized tacn rings, Cd^{2+} center with larger ionic size was treated as a Lewis acid activator, in place of Cu^{2+}, to promote the nucleophilic addition of methanol towards two tacn derivatives containing nitrile pendant arms of different lengths, 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane (L^1) and 1,4,7-tris(cyanoethyl)-1,4,7-triazacyclononane (L^2) (Scheme 1). Fortunately, the methanolysis process of the pendant nitrile groups attached to triazamacrocyclic frameworks was strongly affected by the size and coordination nature of the anions present in Cd^{2+} salts, the length of the pendant arm and the reaction times. In the case of ligand L^1, the controllable transformation of two or three pendant $—CH_2CN$ groups into $—CH_2C(OMe){=}NH$ can be achieved by employing different amount of $Cd(OAc)_2{\cdot}2H_2O$ as the reaction promoter (Scheme 2). Meanwhile, all three pendant $—CH_2CH_2CN$ groups of L^2 reacted with methanol to yield a homo-functionalized triazamacrocycle L^4 under the mediation of Cd^{2+} salts with relatively bulky anions, and the partial conversion of the nitrile pendant arms of L^2 was not observed (Scheme 3). Synthesis, general characterization and crystal structures of Cd^{2+} complexes based on two original nitrile-functionalized tacn ligands as well as three tacn-derived imino ether ligands generated via methanolysis were described detailed in this paper.

2. Experimental

2.1. Materials and methods

Ligands 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane (L^1) and 1,4,7-tris(cyanoethyl)-1,4,7-triazacyclononane (L^2) were synthesized according to the literature methods [26]. Other chemicals and solvents were of analytical grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were measured on a Perkin-Elmer 240C analyzer. IR spectra were obtained as KBr discs with a Bruker Vector 22 FT-IR spectrophotometer in the 400–4000 cm^{-1} range. Positive ion ESI-MS spectra were recorded on the Bruker Esquire 3000 mass spectrometer. The molar conductance of all complexes were measured using a *Rex* DDS-307A conductivity meter.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

2.2. Synthesis of complex $[Cd(L^3)](ClO_4)_2{\cdot}H_2O$ (**1**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (26.7 mg, 0.10 mmol) and ligand L^1 (24.6 mg, 0.10 mmol) were dissolved in 20 mL methanol and refluxed with magnetic stirring for 4 h. Two equivalents of $NaClO_4$ were added and the solution was stirred for further 0.5 h. Then the mixture was cooled to room temperature and filtered off. The filtrate was left to evaporate in air at room temperature. After three weeks, colorless block-like crystals suitable for X-ray crystal structural determination were isolated (Yield: 9.2 mg, 14%). *Anal.* Calc. for $C_{15}H_{30}CdCl_2N_6O_{11}$: C, 27.56; H, 4.63; N, 12.86. Found: C, 27.42; H, 4.89; N, 13.02%. Positive ion ESI-MS: *m*/*z* 555.0 $[Cd(L^3)+ClO_4]^+$ and 455.1 $[Cd(L^3{-}H)]^+$. IR (KBr disk): ν 3372m, 1667s, 1090s cm^{-1}. Λ_m(DMF, 298 K): 183 S cm^2 mol^{-1}.

2.3. Synthesis of complex $[Cd(L^5)(OAc)](ClO_4)$ (**2**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (40.0 mg, 0.15 mmol) and ligand L^1 (24.6 mg, 0.10 mmol) were dissolved in 20 mL methanol and refluxed for 2 h. $NaClO_4$ (36.7 mg, 0.30 mmol) was added to the solution to facilitate the precipitation of the solid complex. After cooling, the solution was filtered off and evaporated at room temperature. Colorless prism crystals suitable for X-ray crystal structural determination were isolated one week later (Yield: 40.1 mg, 69%). *Anal.* Calc. for $C_{16}H_{29}CdClN_6O_8$: C, 33.06; H, 5.03; N, 14.46. Found: C, 33.36; H, 4.81; N, 14.48%. Positive ion ESI-MS: *m*/*z* 483.1 $[Cd(L^5)+OAc]^+$. IR (KBr disk): ν 3369m, 3244m, 2239w, 1661s, 1554m, 1112s cm^{-1}. Λ_m(DMF, 298 K): 107 S cm^2 mol^{-1}.

2.4. Synthesis of complex $[Cd(L^1)Cl_2]$ (**3**)

$CdCl_2{\cdot}4H_2O$ (25.5 mg, 0.10 mmol) was added to a methanol solution of ligand L^1 (24.6 mg, 0.10 mmol) and the resulting mixture was stirred under reflux for 2 h. During the reaction, a white precipitate formed. The product was filtered, washed with methanol for several times and dried under vacuum to afford a white powder (Yield: 36.9 mg, 86%). *Anal.* Calc. for $C_{12}H_{18}CdCl_2N_6$: C, 33.55; H, 4.22; N, 19.56. Found: C, 33.67; H, 4.57; N, 19.79%. IR (KBr disk): ν 2248w cm^{-1}. Λ_m(DMF, 298 K): 4.6 S cm^2 mol^{-1}.

2.5. Synthesis of complex $[Cd(L^4)](ClO_4)_2$ (**4**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (26.7 mg, 0.10 mmol) or $Cd(NO_3)_2{\cdot}4H_2O$ (30.8 mg, 0.10 mmol) and ligand L^2 (28.8 mg, 0.10 mmol) were dissolved in 20 mL methanol and refluxed for 4 h. After cooling, two equivalents of $NaClO_4$ was added and the solution was stirred under room temperature for further 0.5 h. Then the solution was filtered off to give a clear filtrate. Block-like colorless crystals suitable for X-ray crystal structural determination were obtained one week later by slow diffusion of diethyl ether into the filtrate (Yield: 54.3 mg, 78%). *Anal.* Calc. for $C_{18}H_{36}CdCl_2N_6O_{11}$: C, 31.07; H, 5.21; N, 12.08. Found: C, 31.15; H, 5.57; N, 12.36%. Positive ion ESI-MS: *m*/*z* 597.2 $[Cd(L^4)+ClO_4]^+$. IR (KBr disk): ν 3314m, 1646s, 1501w, 1090s cm^{-1}. Λ_m(DMF, 298 K): 171 S cm^2 mol^{-1}.

The complex can also be prepared by the reaction of ligand L^2 with $Cd(ClO_4)_2{\cdot}6H_2O$ in a 1:1 M ratio.

2.6. Synthesis of complexes $[Cd(L^2)Cl_2]{\cdot}0.5H_2O$ (**5**) and $[Cd(L^2)(DMF)Cl_2]{\cdot}CH_3CN$ (**5a**)

The preparing procedure of complex **5** is similar to that of complex **3** except that ligand L^2 was used in place of L^1. The reaction yielded a white powder (Yield: 40.4 mg, 84%). *Anal.* Calc. for $C_{15}H_{25}CdCl_2N_6O_{0.5}$ (**5**): C, 37.48; H, 5.24; N, 17.48. Found: C, 37.62; H, 4.97; N, 17.04%. IR (KBr disk): ν 2247m cm^{-1}. Λ_m(DMF, 298 K): 4.3 S cm^2 mol^{-1}.

A certain amount of solid complex **5** was dissolved in the mixed solvent of DMF and acetonitrile (1:1, v/v) to give a clear solution. By slow evaporation of solvent, block-like colorless crystals of complex **5a** suitable for X-ray crystal structural determination were obtained within two months. *Anal.* Calc. for $C_{20}H_{34}CdCl_2N_8O$ (**5a**): C, 37.48; H, 5.24; N, 17.48. Found: C, 37.62; H, 4.97; N, 17.04%. IR (KBr disk): ν 2248m, 1671s, 1643s cm^{-1}.

2.7. X-ray crystal structure determination

All diffraction intensity data were collected with a SMART-CCD II area detector diffractometer using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct method and subsequent Fourier difference techniques and refined on F^2 using full-matrix least-squares method (Bruker SHELXTL) [27]. All the non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were fixed geometrically and refined using riding models except the hydrogen atoms in imino ether groups and crystalline water molecules, which were located from the difference Fourier maps with N–H and O–H bond distances restrained to 0.86 and 0.85 Å, respectively, and with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atoms. Crystal data collection and refinement parameters are tabulated in Table 1. Selected bond distances and angles are listed in Table 2. Hydrogen bonds data are given in Table 3.

3. Results and discussion

3.1. Synthesis and characterization of Cd^{2+} complexes

In the present study, methanol was used both the reaction solvent and the protic nucleophile to promote the metal-mediated addition of methanol to the nitrile-functionalized macrocyclic ligands. Various Cd^{2+} salts with perchlorate, acetate, nitrate and chloride as counter anions were tried to accomplish the solvolysis of the nitrile functionalized macrocyclic ligands. Most of the reactions were carried out under refluxing conditions with the molar ratio of metal salts to ligand being 1:1 except for $Cd(OAc)_2{\cdot}2H_2O$ which was varied to control the extent of solvolysis of the pendant nitrile arms in macrocyclic ligands. Since in situ generated cadmium acetate or cadmium nitrate complexes with imino ether derivatives were not easy to isolate as solid, in these cases a sufficient amount of $NaClO_4$ was added to help the precipitation of the solid compounds. The absence of the free inorganic or organic base in this system implies that the activation of the nucleophilic methanol does not need the assistance of a base. Such situations are common in the addition of alcohols to Pt(IV)-organonitrile complexes but scarcely found for Pt(II)-mediated addition of alcohols to coordinated organonitriles [28,29].

Treating ligand L^1 with equimolar $Cd(OAc)_2{\cdot}2H_2O$ at refluxing temperature for 4 h followed by the addition of two equivalents of $NaClO_4$ afforded a white crystalline solid **1**. In IR spectra of complex **1**, the disappearance of the characteristic $\nu(C{\equiv}N)$ band of nitrile group and the emergence of the ν(N–H) and $\nu(C{=}N)$ stretching vibrations related to imino bond at 3372 and 1667 cm^{-1}, respectively, suggest that L^1 undergoes methanolysis in such a reaction system and a new macrocyclic derivative bearing only $=CH_2C(OMe){=}NH$ substituents is generated. The positive ion ESI-MS spectrum of this compound reveals two prominent signals at *m*/*z* 555.0 and 455.1, corresponding to two species $[Cd(L^3)+ClO_4]^+$ and $[Cd(L^3-H)]^+$, respectively. When the molar ratio of $Cd(OAc)_2{\cdot}2H_2O$ to L^1 was 1.5:1 or 2:1 and the reaction time was shortened to 2 h, another complex **2** was obtained. IR spectrum of this compound shows two stretching peaks around 2239 and 1661 cm^{-1} due to cyano and imino groups, respectively. A medium intensity band at 1554 cm^{-1} could be ascribed to $\nu_{as}(C{=}O)$ stretching of acetate group, showing acetate may be a component of the compound. The ESI-MS experiment provides unambiguous information that

Table 1
Crystal data collection and refinement parameters for complexes **1**, **2**, **4** and **5a**.

	Complex **1**	Complex **2**	Complex **4**	Complex **5a**
Empirical formula	$C_{15}H_{32}CdCl_2N_6O_{12}$	$C_{16}H_{29}CdClN_6O_8$	$C_{18}H_{36}CdCl_2N_6O_{11}$	$C_{20}H_{34}CdCl_2N_8O$
Formula weight	671.77	581.30	695.83	585.85
Temperature (K)	291(2)	293(2)	293(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	hexagonal	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*6(5)	*P*2(1)/*n*
a (Å)	14.040(3)	9.8481(11)	10.0350(10)	8.093(2)
b (Å)	11.580(2)	21.255(2)	10.0350(10)	16.878(5)
c (Å)	17.074(3)	11.1506(12)	49.030(6)	20.271(5)
α (°)	90.00	90.00	90.00	90.00
β (°)	106.340(2)	95.295(3)	90.00	94.256(5)
γ (°)	90.00	90.00	120.00	90.00
Volume ($Å^3$)	2663.9(8)	2324.1(4)	4275.9(8)	2761.3(12)
Z	4	4	6	4
Calculated density ($g\ cm^{-3}$)	1.675	1.661	1.621	1.409
Absorption coefficient (mm^{-1})	1.087	1.108	1.016	1.011
F (000)	1368	1184	2136	1200
Crystal size	0.30 × 0.26 × 0.24	0.35 × 0.28 × 0.22	0.42 × 0.40 × 0.19	0.30 × 0.24 × 0.22
θ range (°) for data collection	2.15–26.00	1.92–26.00	2.34–25.98	2.01–26.00
Limiting indices	$-15 \leqslant h \leqslant 17$	$-12 \leqslant h \leqslant 11$	$-10 \leqslant h \leqslant 12$	$-9 \leqslant h \leqslant 9$
	$-13 \leqslant k \leqslant 14$	$-26 \leqslant k \leqslant 21$	$-12 \leqslant k \leqslant 11$	$-20 \leqslant k \leqslant 18$
	$-21 \leqslant l \leqslant 14$	$-11 \leqslant l \leqslant 13$	$-60 \leqslant l \leqslant 57$	$-23 \leqslant l \leqslant 24$
Reflections collected/unique	13 714/5233 (R_{int} = 0.052)	12 426/4558 (R_{int} = 0.020)	23 059/5510 (R_{int} = 0.043)	14 458/5386 (R_{int} = 0.044)
Data/restraints/parameters	5233/0/328	4558/0/335	5510/1/346	5386/0/292
Goodness of fit on F^2	1.017	1.060	1.019	1.005
Final *R* indices [$I > 2(I)$]	R_1 = 0.0563	R_1 = 0.0577	R_1 = 0.0457	R_1 = 0.0450
	wR_2 = 0.1135	wR_2 = 0.1559	wR_2 = 0.1313	wR_2 = 0.0861
R indices (all data)	R_1 = 0.0824	R_1 = 0.0640	R_1 = 0.0490	R_1 = 0.0633
	wR_2 = 0.1184	wR_2 = 0.1585	wR_2 = 0.1329	wR_2 = 0.0887
Largest difference in peak and hole ($e\ Å^{-3}$)	0.836 and −0.808	0.560 and −0.525	0.383 and −0.923	0.694 and −0.882

the compound consists of a hetero-functionalized ligand L^5, which exhibits a peak at *m*/*z* 483.1 assignable to $[Cd(L^5)+OAc]^+$ ion. The reaction of $CdCl_2{\cdot}4H_2O$ and L^1 yielded a white powder **3** immediately, whose IR spectrum shows weak $\nu(C{\equiv}N)$ band at 2248 cm^{-1} and no peaks from imino ether functionality could be observed. The elemental analysis supports the formulation of $[Cd(L^1)Cl_2]$ for this compound. The low molar conductance data of the complex in DMF (4.6 S cm^2 mol^{-1}) suggests its non-electrolytic nature. Unprecedented, the reactions between L^1 and $Cd(ClO_4)_2{\cdot}6H_2O$ or $Cd(NO_3)_2{\cdot}4H_2O$ gave two white solids with poor solubility in methanol. IR characterization demonstrates that these solid complexes are not derived from the starting nitrile ligand or the tacn derivatives with imino ether pendant arms. Catalyzed cleavage of part of the nitrile pendant arms attached to tacn ring was conducted during the reaction process and CN^- group was detected in the final solid products. The further investigations on these interesting experimental results are undergoing in our group.

After mixing L^2 and various cadmium salts except $CdCl_2{\cdot}4H_2O$ in methanol, the ESI-MS spectra for each of the mixture solutions shows the corresponding peak of complex cation containing the homo-functionalized ligand L^4 (*m*/*z* 597.2, 560.2 and 557.1 for $[Cd(L^4)+ClO_4]^+$, $[Cd(L^4)+NO_3]^+$ and $[Cd(L^4)+OAc]^+$ ions, respectively). Whereas the IR spectra for all solid complexes obtained from above reactions do not exhibit the stretching bands attributed to the nitrile group. All these results manifest that either choosing metal salts with different counter ions or changing the molar ratio of cadmium salts to L^2 has been proved to be no effect on directing the partial methanolysis of this ligand and all pendant $-CH_2CH_2CN$ groups were turned into $-CH_2CH_2C(OMe){=}NH$ substituents. Not surprisingly, the treatment of L^2 with $CdCl_2{\cdot}4H_2O$ gave a neutral complex **5** based on the original ligand having a low conductance value, which was recrystallized from DMF/CH_3CN mixed solvent to produce a crystalline solid **5a**.

3.2. Crystal structure of complex 1

The single-crystal structure of complex **1** depicted in Fig. 1 confirms that the $-CH_2CN$ pendant arms of L^1 are totally transformed into $-CH_2C(OMe){=}NH$ functionalities under the mediation of Cd^{2+}, in agreement with the result obtained by IR and ESI-MS analysis. The coordination sphere around Cd^{2+} is slightly distorted from regular trigonal prismatic with the twist angle between the two opposite triangular faces, formed by three imino ether N atoms and

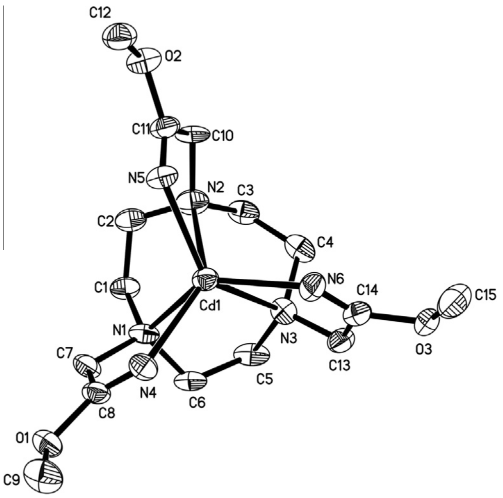


Fig. 1. The ORTEP representation of the cation $[Cd(L^3)]^{2+}$ in complex **1** (30% probability displacement ellipsoids). Perchlorate anions, crystalline water molecule and all hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances and angles for complexes **1**, **2**, **4** and **5a.**

*Complex **1***			
Cd1–N1	2.415(4)	Cd1–N2	2.472(5)
Cd1–N3	2.460(4)	Cd1–N4	2.244(4)
Cd1–N5	2.262(4)	Cd1–N6	2.228(5)
N6–Cd1–N4	103.59(18)	N6–Cd1–N5	102.81(17)
N4–Cd1–N5	105.59(16)	N6–Cd1–N1	138.35(16)
N4–Cd1–N1	72.76(15)	N5–Cd1–N1	118.32(16)
N6–Cd1–N3	71.63(16)	N4–Cd1–N3	117.30(16)
N5–Cd1–N3	136.94(15)	N1–Cd1–N3	73.82(15)
N6–Cd1–N2	117.25(19)	N4–Cd1–N2	138.77(17)
N5–Cd1–N2	71.89(16)	N1–Cd1–N2	73.08(16)
N3–Cd1–N2	73.53(16)		
*Complex **2***			
Cd1–N1	2.504(4)	Cd1–N2	2.470(4)
Cd1–N3	2.429(5)	Cd1–N5	2.323(5)
Cd1–N6	2.299(4)	Cd1–O3	2.522(4)
Cd1–O4	2.309(4)	C16-O3	1.232(7)
C16-O4	1.258(7)		
N5–Cd1–O4	83.00(15)	N5–Cd1–N6	99.89(16)
O4–Cd1–N6	105.75(15)	N5–Cd1–N3	137.80(16)
O4–Cd1–N3	139.20(14)	N6–Cd1–N3	72.09(15)
N5–Cd1–N2	71.39(15)	O4–Cd1–N2	141.46(13)
N6–Cd1–N2	106.63(15)	N3–Cd1–N2	71.71(14)
N5–Cd1–N1	114.64(15)	O4–Cd1–N1	93.08(13)
N6–Cd1–N1	142.49(14)	N3–Cd1–N1	72.51(13)
N2–Cd1–N1	73.17(13)	N5–Cd1– O3	134.25(15)
O4–Cd1–O3	53.53(13)	N6–Cd1–O3	81.50(14)
N3–Cd1–O3	86.59(14)	N2–Cd1–O3	152.44(12)
N1–Cd1–O3	84.43(12)		
*Complex **4***			
Cd1–N1	2.387(5)	Cd1–N2	2.369(5)
Cd1–N3	2.380(5)	Cd1–N4	2.266(5)
Cd1–N5	2.282(6)	Cd1–N6	2.248(6)
N6–Cd1–N4	93.8(2)	N6–Cd1–N5	94.7(2)
N4–Cd1–N5	93.6(2)	N6–Cd1–N2	106.5(2)
N4–Cd1–N2	159.6(2)	N5–Cd1–N2	85.67(19)
N6–Cd1–N3	85.72(19)	N4–Cd1–N3	105.9(2)
N5–Cd1–N3	160.4(2)	N2–Cd1–N3	75.45(19)
N6–Cd1–N1	159.94(18)	N4–Cd1–N1	84.29(19)
N5–Cd1–N1	105.4(2)	N2–Cd1–N1	76.33(18)
N3–Cd1–N1	75.69(19)		
*Complex **5a***			
Cd1–N1	2.461(3)	Cd1–N2	2.485(3)
Cd1–N3	2.400(3)	Cd1–O1	2.317(3)
Cd1–Cl1	2.5194(11)	Cd1–Cl2	2.5202(11)
O1–Cd1–N3	156.06(10)	O1–Cd1–N1	83.60(10)
N3–Cd1–N1	74.73(10)	O1–Cd1–N2	89.32(10)
N2–Cd1–N2	74.77(10)	N1–Cd1–N2	72.76(11)
O1–Cd1–Cl1	94.49(8)	N3–Cd1–Cl1	96.79(8)
N1–Cd1–Cl1	93.34(8)	N2–Cd1–Cl1	165.11(8)
O1–Cd1–Cl2	98.96(8)	N3–Cd1–Cl2	99.31(7)
N1–Cd1–Cl2	164.37(8)	N2–Cd1–Cl2	91.80(8)
Cl1–Cd1–Cl2	101.79(4)		

Table 3
Selected hydrogen bond parameters for complexes **1**, **2** and **4.**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
*Complex **1***[a]				
N4–H4···O12#1	0.86	2.02	2.831(6)	156
N6–H6···O12	0.86	2.54	3.230(6)	138
O12–H12D···O12#1	0.85	2.59	3.215(5)	132
*Complex **2***[b]				
N6–H6···O4#1	0.86	2.25	3.049(6)	155
*Complex **4***				
N4–H4C···O11	0.86	2.50	3.339(10)	164
N5–H5D···O13	0.86	2.43	3.186(10)	147
N6–H6D···O13	0.86	2.44	3.073(10)	131

[a] Symmetry transformations used to generate equivalent atoms in complex **1**: #1 $-x, 1-y, -z$.

[b] Symmetry transformations used to generate equivalent atoms in complex **2**: #1 $2-x, -y, 1-z$.

three macrocyclic backbone N atoms, respectively, being 14.9°. Cd^{2+} ion lies 0.931 Å above the triangular plane comprised of imino ether N atoms, 0.839 Å shorter than the distance of Cd^{2+} to another plane comprised of backbone N atoms. The average Cd–N (tacn backbone) bond length is 2.449 Å, similar to the values found in a Cd^{2+} complex incorporating a bis-tacn ligand [30]. The average Cd–N (imino ether) bond length (2.245 Å) is shorter relative to the former because of the large steric strain imposed by the small-sized tacn ring on Cd^{2+} center. The distances between coordinated imino N atoms range from 3.509 to 3.586 Å. The M–N–C–C–N five-membered chelating rings generated by $—CH_2C(OMe)═NH$ pendant arms are close to planarity with torsion angles about the central C–C bonds in the range from 20.8(9)° to 22.5(9)°. Each $[Cd(L^3)]^{2+}$ cation is hydrogen bonded to a water molecule via one imino N–H group and then two $[Cd(L^3)]^{2+}–H_2O$ species are joined together with the aid of O–H···O hydrogen bonds between two water molecules. The perchlorate anions are discrete units and balance the positive charge of $[Cd(L^3)]^{2+}$ species.

3.3. Crystal structure of complex **2**

Fig. 2 illustrates the molecular structure of the cation $[Cd(L^5)(OAc)]^+$ in complex **2**. The pentadentate triazamacrocyclic ligand L^5 with mixed $—CH_2C(OMe)═NH$ and $—CH_2CN$ pendant arms employs its three N donors of tacn backbone and two imino ether N donors to bind Cd^{2+} and the pendant $—CH_2CN$ group with weak coordination ability is not bound to the central metal. A bidentate acetate group completes the distorted seven-coordinate mono-capped trigonal prismatic arrangement around Cd^{2+}. One triangular base of the coordination polyhedron is made up of three backbone N atoms, and the other one consists of two imino ether N atoms and acetate O4 atom. The dihedral angle between these two planes is 17.2°. Acetate O3 atom occupies the capping position of the coordination sphere and deviates by 1.756 Å from the mean plane of N1, N2, N5 and O4. Cd–N (tacn backbone) bond lengths show no significant difference with those observed in complex **1**, but Cd–N (imino ether) bond lengths are a little longer compared to those in **1**. The distance of two imino N atoms coordinated to Cd^{2+} is 3.538 Å. Two Cd–O bonds to the chelating acetate are not equivalent and the lengths are 2.309(4) and 2.522(4) Å, respectively. Two adjacent cations are in contact with each other to form a dimer through pairs of intermolecular N–H···O hydrogen bonds between one imino group and the acetate O4 atom of the adjacent cation. The unique perchlorate ion is not involved in complexation and its oxygen atoms are disordered over two set of positions with site occupancy ratio of 0.74:0.26.

3.4. Crystal structure of complex **4**

X-ray diffraction analysis shows that the complex is chiral, crystallizing in the trigonal space group *P*6(5) with the Flack parameter of 0.09(3). The ORTEP drawing of the cation $[Cd(L^4)]^{2+}$ in complex **4** is present in Fig. 3. The longer imino ether pendant arms of L^4 compared to L^3 causes the N6 coordination environment about Cd^{2+} changing from trigonal prismatic to octahedral. The Flack parameter was refined close to zero, confirming the absolute structure of the molecule in the crystal is correct [31]. The five-membered chelating rings formed by the macrocycle backbone exhibit ($\lambda\lambda\lambda$) conformation and the orientation of the $—CH_2CH_2C(OMe)═NH$ pendant arms with respect to the parent macrocycle is clockwise, hence the isomer assumes a $\Delta(\lambda\lambda\lambda)$ conformation. Cd–N (imino ether) bond lengths (2.248(6)–2.283(6) Å) and Cd–N (tacn backbone) bond distances (2.369(5)–2.386(5) Å) are in the usual ranges. The separations between imino N atoms are in the range of 3.296 and 3.331 Å, obviously shorter than those in complexes **1** and **2**, suggesting that the longer $—CH_2CH_2C(OMe)═NH$ pendant arms would accommodate and bind the metal center more tightly. The uncoordinated perchlorate anion is joined to $[Cd(L^4)]^{2+}$ unit through N–H···O hydrogen bonding interactions.

3.5. Crystal structure of complex **5a**

As shown in Fig. 4, the neutral complex **5a** consists of two chloride ions and one DMF molecule, which occupy one triangular face of the octahedral Cd^{2+} ion. The remaining coordinating sites on the other side of Cd^{2+} are held by the facially capping tacn ring and Cd–N bond distances to tacn backbone (2.400(3)–2.485(3) Å) are comparable with those of complexes mentioned above, showing these metal–N coordination bonds are not heavily influenced by the factor whether the macrocyclic derivative is a cage-like chelator or a facially coordinating ligand. All three $—CH_2CH_2CN$ groups do not participate in metal binding, and each pendant arm directs away from the central metal ion and is approximately coplanar with its attached N atom. Two Cd–Cl bond lengths are nearly equal and match the values found in the related compounds containing Cd–Cl bond [32].

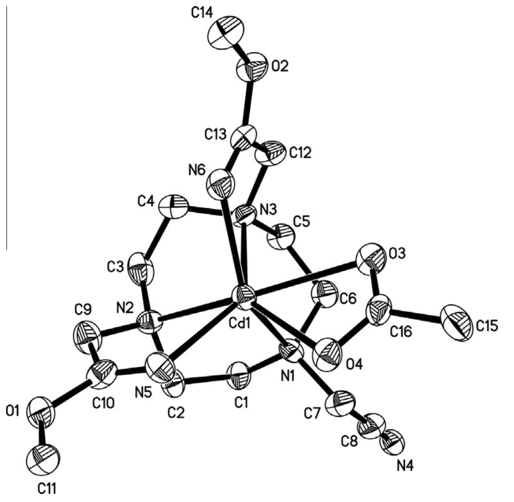


Fig. 2. The molecular structure of the cation $[Cd(L^5)(OAc)]^+$ in complex **2** (30% probability displacement ellipsoids). Perchlorate anion and all hydrogen atoms are omitted for clarity.

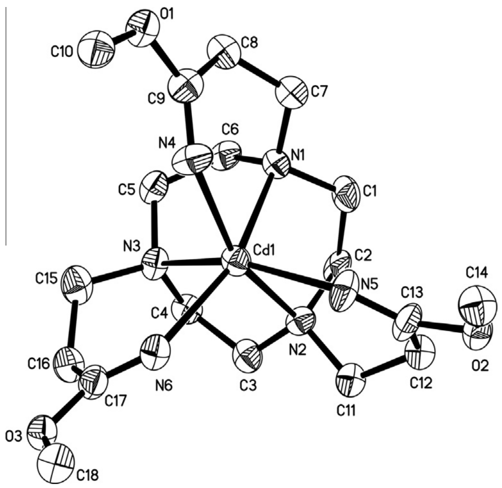


Fig. 3. The ORTEP drawing of the cation $[Cd(L^4)]^{2+}$ in complex **4** (30% probability displacement ellipsoids). Perchlorate anions and all hydrogen atoms are omitted for clarity.

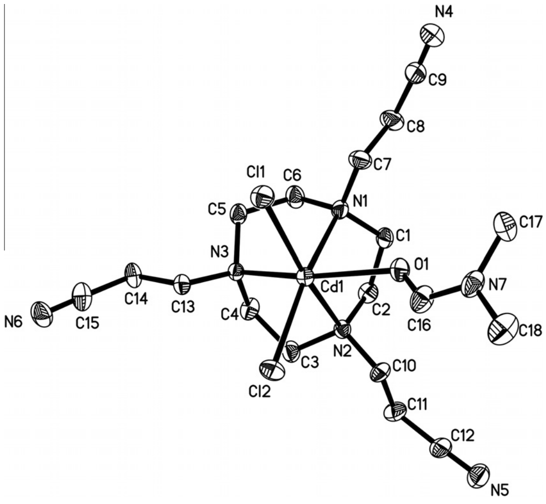


Fig. 4. The molecular structure of complex **5a** (30% probability displacement ellipsoids). All hydrogen atoms and crystalline solvent molecule are omitted for clarity.

3.6. Selective transformation of the triazamacrocyclic ligands bearing nitrile pendant arms

As mentioned above, the selective transformation of two or three pendant —CH_2CN groups of L^1 to —$CH_2C(OMe)$=NH substituents can be manipulated by changing the molar ratio of $Cd(OAc)_2 \cdot 2H_2O$ to ligand and the methanolysis reaction times. In this case, the coordinating nature of the bulky acetate anion may be considered as an important impact in determining the extent of methanolysis of pendant —CH_2CN groups. It is proposed when L^1 was added with $Cd(OAc)_2 \cdot 2H_2O$ at a molar ratio of 1:1, a large excess of solvent molecules will expel the acetate group from Cd^{2+} and the coordination sites opposite to the facially capping ligand L^1 are occupied by three methanol molecules. Then Cd^{2+}-activated methanol species are responsive to the stepwise methanolysis of three attached —CH_2CN groups in L^1. Upon addition of $NaClO_4$, complex **1** was in situ generated where Cd^{2+} ion is encapsulated into the cavity of the methanolysis product L^3. Once $Cd(OAc)_2 \cdot 2H_2O$ to ligand molar ratio was varied to 1.5:1, a bidentate acetate group can remain bound to Cd^{2+} and only two methanol molecules are accommodated in the coordination sphere around Cd^{2+}. As a result, two —CH_2CN pendant arms of L^1 undergo normal solvolysis reaction and the coordinated carboxylate group inhibits the conversion of the third one. In the presence of $NaClO_4$, the solid complex **2** was precipitated from the methanolic solution in which seven-coordinate Cd^{2+} center is chelated by an acetate group and a hetero-functionalized ligand L^5. Nevertheless, further increasing the amount of $Cd(OAc)_2 \cdot 2H_2O$ does not allow the binding of a second acetate on Cd^{2+} and thus the retaining of two —CH_2CN pendant arms of L^1 could not be achieved. As a comparison, the preliminary study on Zn^{2+}-containing system revealed that the variation in $Zn(OAc)_2 \cdot 2H_2O$ to L^1 molar ratio and reaction times cannot achieve the partial methanolysis of the macrocyclic ligand. Hence it is assumed that Zn^{2+} with smaller ionic radius cannot bind to a bidentate acetate ion when facially capped by L^1. Upon mixing $CdCl_2 \cdot 4H_2O$ and L^1, two small-sized Cl^- ions with more strong coordination ability are bound to Cd^{2+} along with the tridentate macrocyclic ligand L^1 to deposit a neutral compound **3** immediately and to avoid the solvolysis of the —CH_2CN pendant arms consequentially.

Different from L^1, treatment of perchlorate, nitrate and acetate salts of Cd^{2+} with ligand L^2 all afforded Cd^{2+} complexes of triazamacrocyclic derivative L^4 with three —$CH_2CH_2C(OMe)$=NH pendant arms. The change in the molar ratio of $Cd(OAc)_2 \cdot 2H_2O$ to ligand shows no remarkable effect on the methanolysis process of L^2 and only a single addition product L^4 could be obtained in our attempts. It seems probable that the bulky perchlorate or nitrate anions with weak coordination abilities cannot prevent the methanol molecules from coordinating to Cd^{2+} in the solution, which enables the complete solvolysis of three —CH_2CH_2CN pendant arms. The similar phenomena were also found for the reaction systems containing stoichiometric or excess amount of $Cd(OAc)_2 \cdot 2H_2O$ although the latter condition is considered to cause the partial solvolysis of the starting ligand. By comparing the non-bonding distances between imino N donors in **4** with those in **2**, it can be imagined that the macrocyclic intermediate containing two longer —$CH_2CH_2C(OMe)$=NH pendant arms originating from the methanolysis of L^2 can wrap up the metal center more tightly than L^5 and the larger steric hindrance induced by the prolonged pendant arms precludes the binding of an acetate group to Cd^{2+}, thus the preservation of the remaining nitrile group in such an intermediate becomes impossible. On the other hand, $CdCl_2 \cdot 4H_2O$ reacted with L^2 to give the expected complex **5** having the original ligand.

4. Conclusion

The closed-shell Cd^{2+} was chosen as a Lewis acid activator to promote the methanolysis of two tacn-derived compounds L^1 and L^2 with nitrile pendant arms of different lengths. Besides the pendant arm length, the size and coordination ability of the anions present in Cd^{2+} salts as well as the reaction times seem to influence the solvolysis process of the pendant nitrile groups attached to tacn to some extent. Greater curiosity has been raised in investigating the Cd^{2+}-mediated cleavage of pendant —CH_2CN group in L^1.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21027013, 21361004), the Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Guangxi Normal University), Ministry of Education of China (CMEMR 2012-A08, CMEMR 2013-C08).

Appendix A. Supplementary material

CCDC 971247, 250033, 260034 and 971248 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.02.021.

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