

Synthesis, characterization and spectroscopy of two new macrocyclic Schiff base Cd(II) complexes

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Abstract

In this paper we report the synthesis and characterization of two new mononuclear Cd(II) macrocyclic Schiff base complexes [CdL_{23pydfp}(NO₃)], (1), [CdL_{33pydfp}(NO₃)], (2). [1+1] cyclocondensation of L_{23py} = N-(2-pyridylmethyl)-N-(3-aminopropyl)-1,3-diaminoethane, L_{33py} = N-(3-pyridylmethyl)-N-(3-aminopropyl)-1,3-diaminopropane and 2,6-diformyl-4-methylphenol, dfp, in the presence of Cd(NO₃)₂·4H₂O in equimolar ratios gave two new macrocyclic complexes. Resulting complexes were characterized by NMR, IR, mass spectroscopy and elemental analysis. Spectroscopy results show nitrogen and oxygen atoms of macrocyclic ligand with N₄O donor set, one nitrate molecule (with two donor oxygen atoms) is coordinated to the Cd(II) center in each complex. So, the cadmium center is seven coordinated.

Keywords: Schiff base; macrocyclic; cadmium; ligand.

Introduction

Many variously shaped polydentate chelating ligands have been prepared in the past and successfully used in the selective coordination of metal ions. The properties arising from this aggregation were investigated in detail by different physicochemical procedures and also were adequately reviewed [1–18]. These systems were acyclic or cyclic in nature, planar or tridimensional in their framework, and this depends on the designed structure (discrete, ordered, porous, helicoidal, 1D, 2D or 3D polymeric, etc.) to which they give rise, and the specific functions they must perform or the peculiar properties they must achieve. Compartmental ligands, i.e. compounds with two (or more) coordination

chambers in close proximity, represented a relevant evolution, owing to their capability of providing different, well selective recognition of charged and/or neutral species at their adjacent chambers. These systems quite often are Schiff bases (or the related reduced derivatives), obtained by condensation of appropriately designed and prepared formyl- (or keto-) and primary amine precursors [19]. It has been reported that the most recent results achieved by the acyclic compartmental systems have been classified into [1+1] acyclic, [1+ 1], [1+2] or [2+1] end-off, [2+1] or [1+2] side-off and [3+1] or [1+3] polypodal systems. The [1+1] acyclic ligands are obtained by reaction of one equivalent of formyl- or keto-derivative with an

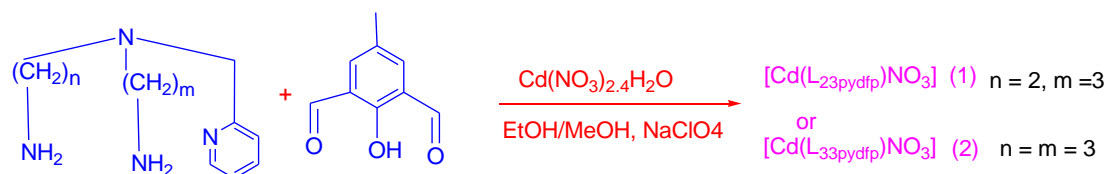
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equimolar amount of a primary amine. Several of these precursors, except those containing additional donor groups at the appropriate positions (i.e. 3-methoxy-3-ethoxy-, 2-hydroxybenzaldehyde, 3-formylsalicylic acid), are not strictly compartmental; nevertheless, they can serve as dinucleating or polynucleating ligands through their phenolate and alcoholate oxygen atoms. More relevant through quite specific self-assembling reactions, they can give rise to heteropolynuclear systems capable of acting as single molecule magnets (SMM). Some examples which are reported demonstrate that preorganization of the ligand, as occurs in the compartmental systems, although quite useful, is not a necessary requisite for obtaining organized polynuclear systems. Self-organization of different, organic and inorganic components can produce quite sophisticated supra molecular architectures. When the formyl- or the amine-precursors contain an additional pendant group with donating atoms, the mentioned condensation reaction gives rise to [1+1] asymmetric end-off ligands, which contain two adjacent dissimilar coordination chambers appropriately designed to verify the

different stereochemistry and properties of the dinuclear complexes obtained according to the coordination moiety of the two chambers. Thus, these ligands were progressively modified in order to provide [5 + 5], [5 + 6], [6 + 5] and [6 + 6] adjacent chambers and to verify the parameters affecting the stereochemistry of the resulting complexes. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from the appropriate amines for transition metal ion complexes has come from the realization that the coordinated ligands around the central metal ions in natural systems are unsymmetrical [20-40]. We have recently reported the synthesis and characterization of a number of Cd(II) [21-23] and Schiff base complexes. Herein, we report the synthesis and characterization of two new macrocyclic [1+1] Cd(II) complexes with two new synthesized asymmetric tripodal tetraamine ligands L_{23py} and L_{33py} (Scheme 1). The resulting synthesized Cd(II) complexes in this work were characterized by elemental analysis, IR, mass and NMR spectroscopy.



Scheme 1. Synthetic routes of compounds 1 and 2

Experimental

Apparatus

Hydrated metal salts were obtained from Aldrich and were used without further purification. The tripodal ligand L_{23py} and L_{33py} were prepared as their hydrochloride salt via literature method [24]. IR spectra were measured on a

Perkin Elmer FT-IRGX spectrophotometer. Mass spectra were measured on a Bruker micro TOFQ. NMR spectra were measured on a Bruker DPX 300 spectrometer.

Synthesis

Preparation of $[CdL_{23pydfp}(NO_3)]$, **1**

$L_{23py} \cdot 3HCl$ (0.11 g, 0.35 mmol) and NaOH (0.04 g, 0.99 mmol) were mixed and heated under reflux for 30 min in absolute ethanol (15 ml). The NaCl which formed upon cooling was filtered off. The filtrate was added to a mixed solution of 2,6-diformyl-4-methylphenol (0.05 g, 0.33 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.06 g, 0.33 mmol) in dry MeOH (40 ml) with continuous stirring, and the solution color gradually changed from brown to deep white. The mixture was stirred at room temperature for 72 h, then $NaClO_4$ (0.09 g, 0.66 mmol) was added. The solution was filtered and the filtrate was reduced to ca 10 cm³. A white purified powder was obtained by slow diffusion of Et₂O vapor into this solution. Yield: 68%. Anal. Calc. for $C_{20}H_{23}CdN_5O_4$: C, 47.15; H, 4.52; N, 11.00. Found: C, 46.96; H, 4.49; N, 10.84%. IR (KBr, cm⁻¹): 1657, (ν C=N Schiff base), 1534 (ν C=N pyridine), 1602 (ν C=C), 1091, 622 (ν ClO₄⁻). Accurate mass spectrometry (FAB-MS) $m/z = 448.092$ $[Cd(L_{23pydfp})]^+$, $C_{20}H_{23}CdN_4O$ requires 449.090; ¹H NMR (DMSO-d₆, ppm, 300 MHz, py = pyridine): δ 2.56 (m, 2H), 2.82 (s, 3H) 3.76 (t, 2H), 3.84 (t, 2H) 3.88 (t, 2H), 3.94 (t, 2H) 4.54 (s, 2H, CH₂-Py), 8.12 (d, 2H), 8.29 (m, 4H) 8.76 (s, 2H, with two satellite peaks in the ratio 1:6:1 relative to the main signal ³J(^{111/113}Cd-1H) = 41.38.

Preparation of $[CdL_{33pydfp}(NO_3)]$, **2**

$L_{33py} \cdot 3HCl$ (0.12 g, 0.33 mmol) and NaOH (0.04 g, 0.99 mmol) were mixed and heated under reflux for 30 min in absolute ethanol (15 ml). The NaCl which formed upon cooling was filtered off. The filtrate was added to a mixed solution of 2,6-diformyl-4-methylphenol (0.05 g, 0.33 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.06 g, 0.33 mmol) in

dry MeOH (40 ml) with continuous stirring, and the solution color gradually changed from brown to deep white. The mixture was stirred at room temperature for 72 h, then $NaClO_4$ (0.09 g, 0.66 mmol) was added. The solution was filtered and the filtrate was reduced to ca 10 cm³. A white purified powder was obtained by slow diffusion of Et₂O vapor into this solution. Yield: 73%. Anal. Calc. for $C_{21}H_{25}CdN_5O_4$: C, 48.13; H, 4.76; N, 13.33. Found: C, 47.94; H, 4.56; N, 13.11%. IR (KBr, cm⁻¹): 1654, (ν C=N Schiff base), 1538 (ν C=N pyridine), 1606 (ν C=C), 1092, 628 (ν ClO₄⁻). Accurate mass spectrometry (FAB-MS) $m/z = 462.108$ $[Cd(L_{33pydfp})]^+$, $C_{21}H_{25}CdN_4O$ requires 463.106; ¹H NMR (DMSO-d₆, ppm, 300 MHz, py = pyridine): δ 2.53 (m, 4H), 2.72 (s, 3H) 3.74 (t, 4H), 3.79 (t, 4H) 4.51 (s, 2H, CH₂-Py), 8.11 (d, 2H), 8.63 (m, 4H) 8.82 (s, 2H, with two satellite peaks in the ratio 1:6:1 relative to the main signal ³J(^{111/113}Cd-1H) = 41.48.

Result and discussion

Synthesis and Characterization

Compounds **1** and **2** (Figure. 1) were prepared through full condensation of $L_{23py} = N$ -(2-pyridylmethyl)- N -(3-aminopropyl)-1,3-diaminoethane and $L_{33py} = N$ -(3-pyridylmethyl)- N -(3-aminopropyl)-1,3-diaminopropane and 2,6-diformyl-4-methylphenol, dfp, in the presence of $Cd(NO_3)_2 \cdot 4H_2O$ in equimolar ratios. The resulting compound was characterized by IR, elemental analysis, mass and NMR spectroscopy (Figure 2). The condensation of both primary amino groups is confirmed by the lack of N-H stretching split band at 3150–3450 cm⁻¹ and the presence of strong C=N (Schiff-base) stretching band at 1630–1660 cm⁻¹. The sharp band at 3250–3260 cm⁻¹ can be assigned to secondary N-H.

Broad intense bands at *ca* 1080–1100 cm^{-1} due to ClO_4^- shows no splitting, indicating the absence of coordination of ClO_4^- . The mass is consistent with its structure and formulation. The clear intense peaks associated to $[\text{Cd}(\text{L}_{23\text{pydfp}})]^+$ and $[\text{Cd}(\text{L}_{33\text{pydfp}})]^+$ are

observable in the mass spectra of cadmium complexes (Figures 3 and 4).

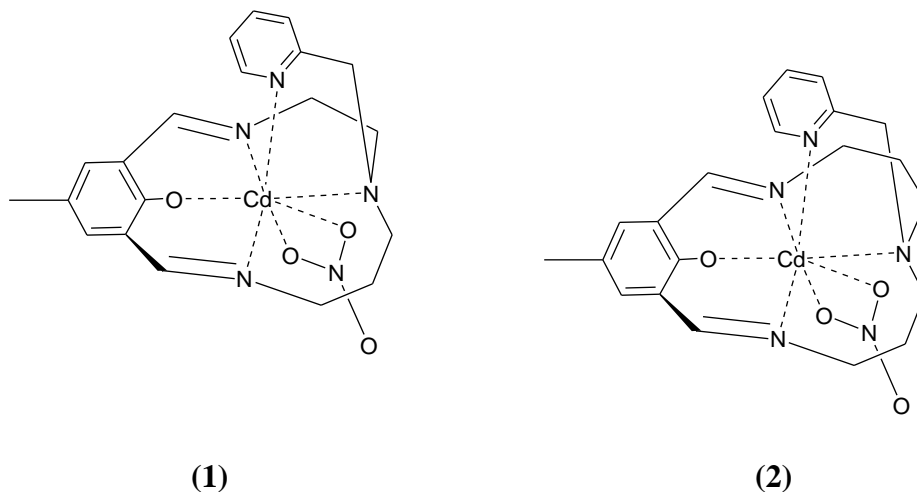


Figure 1. The structure of complexes **1** and **2**

It should be noted that the experimental isotopic patterns are confirmed with those found in theoretical study. If the weight and/or isotopic patterns are different, it will mean the proposed structure isn't correct and it needs to prepare the crystal to get X-ray. According to Figs. 3 and 4 the weight and patterns of experimental study is confirmed with theoretical study. The patterns of appropriate formula will be getting with mwtwin software easily.

NMR spectrum

The ^1H NMR spectrum of the cadmium complex confirms the formation of a fully condensed Schiff base complex. It is interesting that the ^1H NMR spectrum of this complex shows two

kinds of protons for the methylene group adjacent to the tertiary nitrogen atom. In addition to the above observations the ^1H NMR spectrum of the cadmium complex synthesized here, which shows that the signal corresponding to the imine proton displays two satellite peaks ($^3J = 44.43$ Hz) with intensities in the ratio 1:6:1 due to coupling with the neighboring $^{111/113}\text{Cd}$ nucleus (^{111}Cd , 12.81%; ^{113}Cd , 12.22%) (Figure 2). The very similar magnetogyric ratio of ^{113}Cd and ^{111}Cd , -5.93303 and -5.6720×10^{-7} rad/Ts, respectively, lead to satellite overlap at the collection frequency. It should be noted that there are several reports of $^{111/113}\text{Cd}-^1\text{H}$ heteronuclear coupling [21-23, 25-29].

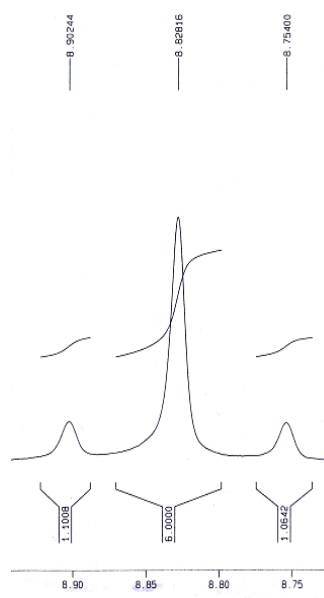
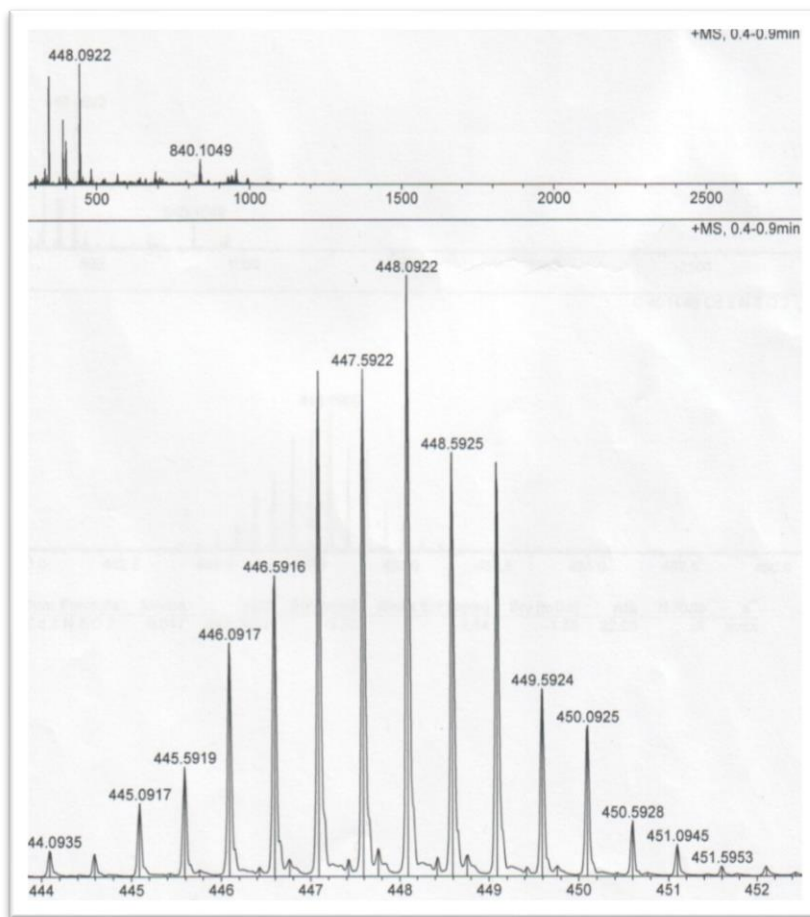
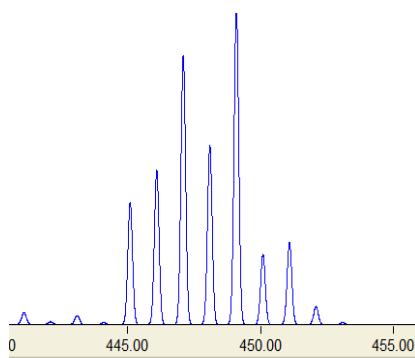


Figure 2. Observed satellites for CH=N hydrogen resonances in ¹HNMR complex **2**

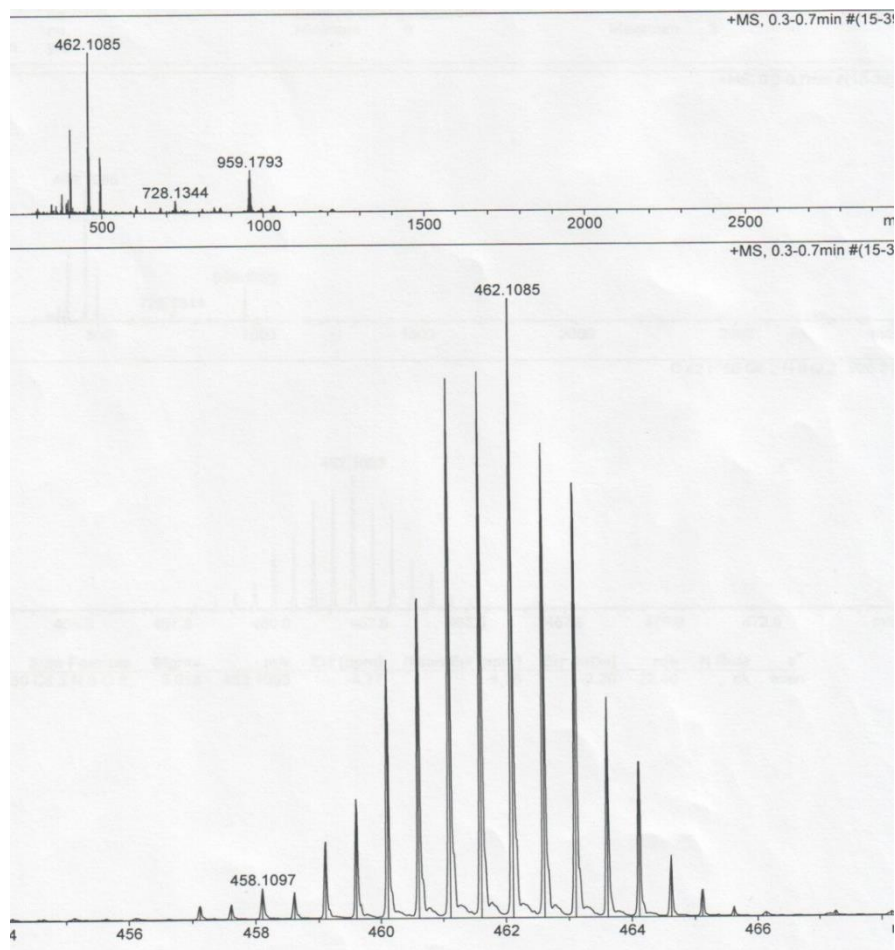


(a)

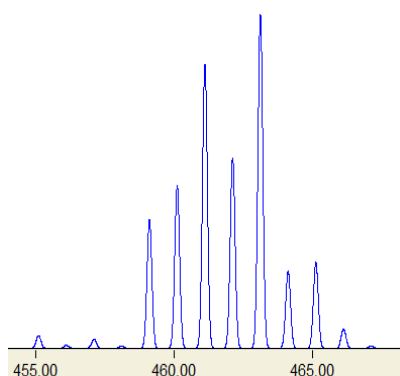


(b)

Figure 3. A comparison of observed isotopic pattern (a) and calculated isotopic pattern (b) for $[\text{Cd}(\text{L}_{23}\text{pydip})]^+$



(a)



(b)

Figure 4. A comparison of observed isotopic pattern (a) and calculated isotopic pattern (b) for $[Cd(L_{33}pydfp)]^+$

Conclusion

In this paper we have reported the synthesis and structure of two new Cd(II) macrocyclic Schiff base. Both

ligands are N4O donor and all donor atoms are coordinated to the central metal ions. In addition, we have studied

the NMR and mass spectroscopy of reported complexes.

The spectra of complexes confirm with the proposed structures.

Acknowledgments

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