

**TEMPLATE SYNTHESIS OF NEW TYPE OF MACROCYCLIC MOLECULE DERIVED FROM PYRIDINE-2, 6-DICARBOXALDEHYDE AND 1,2-BIS(2-AMINOETHOXY)ETHANE**

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**ABSTRACT**

The cyclic (2+2) template condensation of pyridine-2,6-dicarboxaldehyde with 1,2-bis(2-aminoethoxy) ethane using  $\text{Pb}(\text{SCN})_2$  as the metal source gave dinuclear lead (II) complex,  $\text{Pb}_2\text{L}_1(\text{SCN})_4$  (**1**), where  $\text{L}_1$  is tetra-Schiff-base macrocycle. Treatment of **1** with  $\text{NaBH}_4$  in methanol gave a metal-free reduced macrocycle  $\text{L}_2$  which has been characterized by  $^1\text{H}$ NMR and ESI-MS spectroscopy.

Key words: Macrocylic molecules, Spectroscopic studies, 1, 2-bis(2-aminoethoxy) ethane, Schiff-base

**INTRODUCTION**

Macrocylic ligands are widely recognized as molecules that can bring out the full potential of adapted metal ions. Several excellent examples of universal ligands such as crown ethers (Gokel *et al.* 2004), porphyrins (Hambright 1971) and saturated (or unsaturated) macrocylic polyamines (Kimura 1992, Busch 1978, Zhang *et al.* 1997), their chemical properties and functions as metal complexes have been systematically heightened by the facile and diversified chemical modification of their macrocylic frameworks. Therefore, the design and study of macrocylics with desirable properties is still a notable achievement. The template condensation reaction lie at the heart of macrocylic chemistry (Curtis 1968) and have been widely used for synthesis of macrocylic complexes where, the transition metal ions are used as templating metal agents (Niasari *et al.* 2006). Macrocylic metal chelating agents is useful for detecting tumor lesions (Kosmos *et al.* 1992). Prompted by these facts, in the present paper, synthesis and characterization of reduced macrocylic molecule derived from pyridine-2,6-dicarboxaldehyde and 1,2-bis(2-aminoethoxy) ethane have been discussed. Macrocylic molecule has been characterized using  $^1\text{H}$ NMR and ESI-MS spectroscopy.

**EXPERIMENTAL**

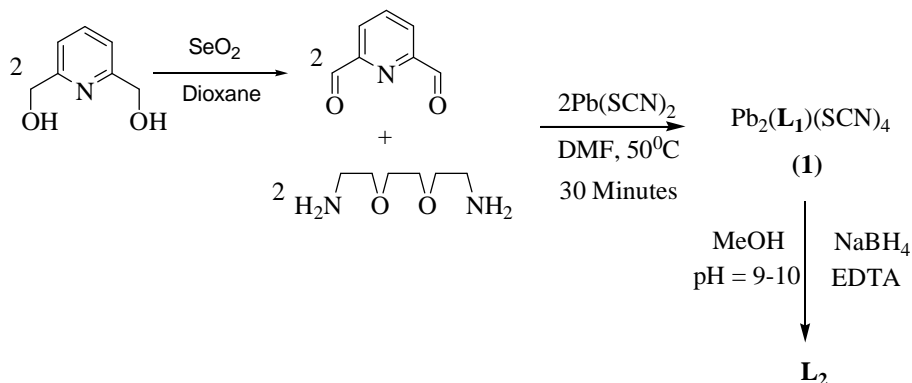
All chemicals were of analytical reagent grade and used without further purification. All measurements were performed at room temperature ( $25 \pm 2^\circ\text{C}$ ). NMR spectra were measured

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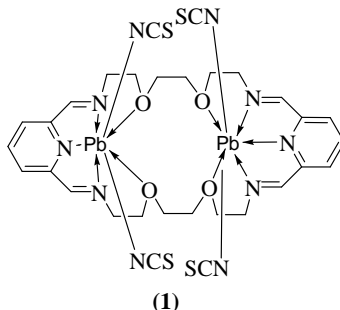
on Bruker Avance<sup>III</sup>-400 with CDCl<sub>3</sub> as solvent. The positive-ion ESI-mass spectrum of complexes was recorded with a Quattro micro API spectrometer made by Waters.

8.122 gm (0.073 mol) of SeO<sub>2</sub> was added to 10.186 gm (0.073 mol) of 2, 6-bis-(hydroxymethyl) pyridine in distilled dioxane (≈ 200 mL). The reaction mixture was refluxed with stirring at 101<sup>o</sup>C for 5 hours. The oxide residue was separated from the solution by vacuum filtration on a filtered glass funnel. The light yellow filtrate was concentrated in a rotary evaporator, and then the crude product was dissolved in minimum amount of chloroform and passed through a short (ca. 12 cm long, ca. 4 cm diameter) silica gel column. About 95% of crystalline light pink compound was obtained after evaporation of chloroform. Calc. for C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>N: C, 62.22; H, 3.73; N, 10.29 %. Found: C, 61.50; H, 4.39; N, 10.25%. IR (KBr): ν(C=O) 1716 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ ppm): 10.17 (singlet, 2Ha) 8.18 (doublet, 2Hb), 8.08(triplet, Hc).



Scheme 1. L<sub>1</sub> is Schiff base ligand and L<sub>2</sub> is reduced macrocycle.

Pb(SCN)<sub>2</sub> (0.438 g, 0.00136 mol) and 2,6-pyridinedicarboxaldehyde (0.183 g, 0.00136 mol) were placed in a round bottle-flask containing 10 ml of N,N-dimethylformamide (DMF). After complete dissolution of both the reagents, a solution (0.201 g, 0.00136 mol) of 1,2-bis(2-aminoethoxy) ethane was added dropwise.

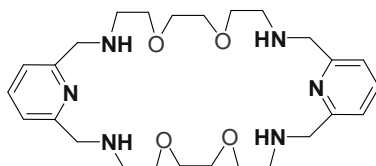


After 30 minutes stirring at 50<sup>0</sup>C, the yellow reaction mixture was filtered off. Then diffusion of diethyl ether to the filtrate gave a yellow colored crystalline compound. Yield 72%, Calc. for C<sub>30</sub>H<sub>34</sub>O<sub>4</sub>N<sub>10</sub>Pb<sub>2</sub>S<sub>4</sub>: C, 31.30; H, 3.04; N, 12.17 %. Found: C, 31.34; H, 3.04; N, 12.12 %. IR (KBr):  $\nu(\text{SCN})$  2013 cm<sup>-1</sup> and 2032 cm<sup>-1</sup>.

About 9 equivalent of NaBH<sub>4</sub> was added to compound **1** in a appropriate volume of methanol and stirred vigorously for about 2.5 hours. Then standard (Mandal *et al.* 1986, Mandal *et al.* 1987) demetallation technique using H<sub>4</sub>EDTA (ethylenediaminetetraacetic acid) chelator and extracting with chloroform, quantitatively gave the metal-free reduced macrocycle **L**<sub>2</sub> as a pale yellow oil. Yield: 30%. ESI-MS:  $m/z$  503.3 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz,  $\delta$  ppm): 7.52-7.57 (a, triplet), 7.17 (b, doublet), 3.89 (c, doublet), 3.61-3.70 (e + f, triplet), 2.83 (d, triplet), 2.19 (g, singlet).

## RESULTS AND DISCUSSION

The elemental analysis data of compound **1** point out the presence of Schiff-base type macrocyclic molecule **L**<sub>1</sub>. In Pb<sub>2</sub>L<sub>1</sub>(SCN)<sub>4</sub> two strong bands appeared at 2013 and 813cm<sup>-1</sup> because of SCN<sup>-</sup>-centered absorption (Nakamoto).



The strong bands at 1620-1660 and 1580-1600 are assigned to  $\nu(\text{C}=\text{N})$  and the highest-energy pyridine ring vibration, respectively (Drew *et al.* 1977 and Drew *et al.* 1978).

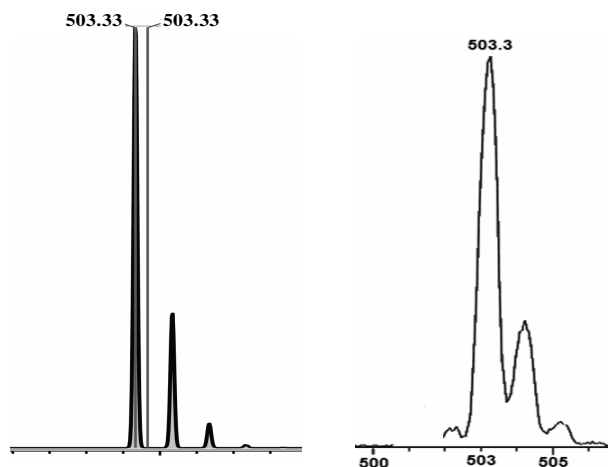


Fig. 1. Calculated (left) and measured (right, in MeCN) isotope patterns of macrocyclic molecule ion **L**<sub>2</sub>H<sup>+</sup>.

On  $\text{NaBH}_4$  reduction of compound 1 and removal of  $\text{Pb}^{2+}$  by EDTA titration gave the reduced macrocyclic molecule  $\text{L}_2$ . The formation of macrocyclic molecule was confirmed by ESI-MS spectrometry. The  $m/z$  value for the macrocyclic molecules appeared at 503.3. Measured and calculated isotope patterns of the  $\text{L}_2\text{H}^+$  are shown in Fig. 1.

The  $^1\text{H}$ NMR spectra of macrocycle  $\text{L}_2$  measured in  $\text{CHCl}_3$  is shown in Fig. 2. Author notes that the chemical shift of pyridine ring proton (a and b) is at high field (lower  $\delta$ -value).

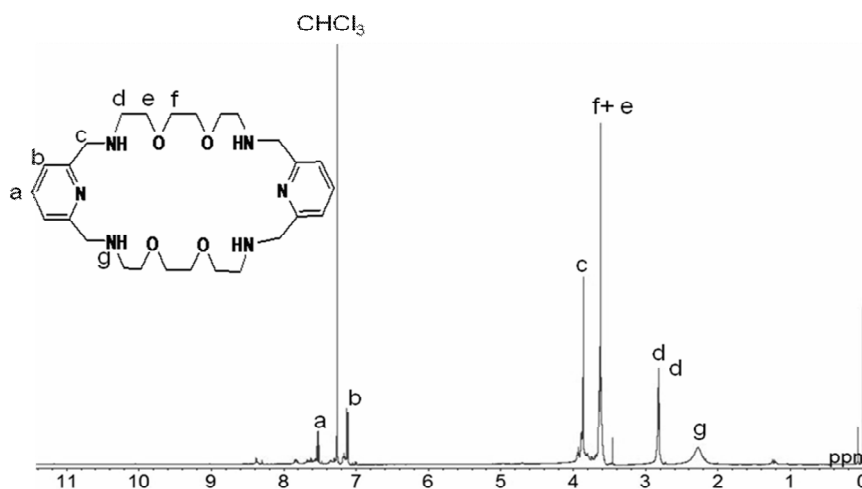


Fig. 2.  $^1\text{H}$ NMR spectra of macrocycle  $\text{L}_2$  measured in  $\text{CHCl}_3$ .

The strong aldehydic singlet peak had disappeared whereas a doublet of  $-\text{CH}_2$ -proton appeared. The presence of  $-\text{NH}-$  at  $\delta$  2.19 points out to reduced schiff-base macrocycle.

## CONCLUSION

An efficient template synthesis of  $\text{Pb}_2\text{L}_1(\text{SCN})_4$  (1) is reported. The macrocyclic molecule  $\text{L}_1$  showed di-nucleating in case of smaller ion  $\text{Pb}^{2+}$ . Both infrared frequencies of  $\text{SCN}^-$  in complex 1 show the bonding through nitrogen atom. In addition, metal free macrocyclic molecule  $\text{L}_2$  can be easily gained in a moderate yield through this template synthesis of complex 1.

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