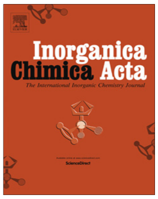
Inorganica Chimica Acta 479 (2018) 203–212

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Research paper

A new macrocyclic ligand salt, 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane dihydrobromide dehydrate $[H_2L_{B¢}]Br_2·2H_2O$ and some of its metal complexes – Synthesis, characterization and antimicrobial studies

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ARTICLE INFO

Article history:
Received 4 January 2018
Received in revised form 17 April 2018
Accepted 20 April 2018
Available online 23 April 2018

Keywords:
Transition metal(II) complexes
Azamacrocyclic ligand
Spectroscopic studies
Crystal structure
Antimicrobial activities

ABSTRACT

The reaction of an isomeric ligand L_B (a C-chiral isomer of 3,10-C-*meso*-Me$_8$[14]ane) with dibromoxylene resulted in an unstable N-pendent ligand salt, $[(H_2L_{B¢}\text{-}2H)(\text{-}CH_2\text{-}C_6H_4\text{-}CH_2\text{-}OH)_2]\ Br_2·CH_3OH·H_2O$, which on recrystallization yielded a stable supramolecular ligand salt $[H_2L_{B¢}]Br_2·2H_2O$.The structure of the new ligand salt was confirmed by X-ray crystallography. The solid state structure of ligand shows that $L_{B¢}$ is protonated at the N2 and N2A nitrogen atoms and the methyl groups of L_B and $L_{B¢}$ have the same axial and equatorial positions with slight changes in bond angles and bond lengths. The overall charge balance is provided by two bromide anions. In the solid state $[H_2L_{B¢}]Br_2·2H_2O$ shows that the 3, 10 methyl groups are at axial positions and the 5,12 methyl groups at equatorial positions. $L_{B¢}$ undergoes complexation with different metal salts to form the corresponding metal complexes $[M(L_{B¢})X_m]Y_n·xH_2O$, ($M = Cu^{2+}$, Ni^{2+}, Co^{3+}, Zn^{2+}, Cd^{2+} or Pd^{4+}; X & Y = ClO_4^-, NO_3^-, Br^-, Cl^-, SCN^-; m, n & x = 0, 1, 2). The metal complexes were characterized on the basis of elemental analyses; IR, UV–Vis and ^{1}H NMR spectroscopy, magnetic and conductance data. These complexes showed different electrolytic behavior in different solvents. The antibacterial and antifungal activities of the ligand $L_{B¢}$ and its complexes toward different phytopathogenic bacteria were investigated.

1. Introduction

The azamacrocyclic chemistry has drawn an incredible attention in the research world for its spellbinding and fastest growing areas of experimental chemistry. For the importance of different macrocyclic ligands, their N-pendent derivatives and their metal complexes as pharmacological agent [1–4], they got the top most pressing matter not only in the general field of chemistry but also in the field of medicinal chemistry. Tetraaza-macrocyclic chemistry has focused its light in the region of coordination chemistry, as well as in analytical [5] and industrial [6] fields. Considering the multifarious importance of macrocyclic chemistry, scientists have reported unique work on macrocyclic ligands as well as their N-pendent derivatives and their metal complexes [7–24]. In this context it can be noted that several complexes of the isomeric ligand L_B = 3,10-C-meso-Me$_8$[14]ane [18,25] and its N-pendent derivatives [26–28] have been reported in the literature. So it appeared interesting to see whether a similar type of an N-pendent ligand, $(L_B\text{-}2H)(\text{-}CH_2\text{-}C_6H_6\text{-}CH_2Br)_2$ could be prepared by the interaction of L_B with dibromoxylene. However a less stable *N*-pendent ligand, $[(H_2L_{B¢}\text{-}2H)(\text{-}CH_2\text{-}C_6H_4\text{-}CH_2\text{-}OH)_2]$ $Br_2·CH_3OH·H_2O$ (revealed by its mass spectrum and microanalysis) was in fact obtained. On recrystallization, however, a supramolecular ligand salt, 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane dihydrobromidedihydrate, $[H_2L_{B¢}]Br_2·2H_2O$ resulted (Scheme 1). The structure of $[H_2\ L_{B¢}]Br_2·2H_2O$ has been confirmed by X-ray crystallography. This ligand salt undergoes complexation with copper(II), nickel(II), zinc(II), cadmium(II), cobalt(III) and palladium(IV) to form the corresponding metal complexes. All these complexes have been characterized by different analytical and spectroscopic analyses. The synthesis, characterization, antibacterial and antifungal potential of these compounds are reported herein.

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https://doi.org/10.1016/j.ica.2018.04.041
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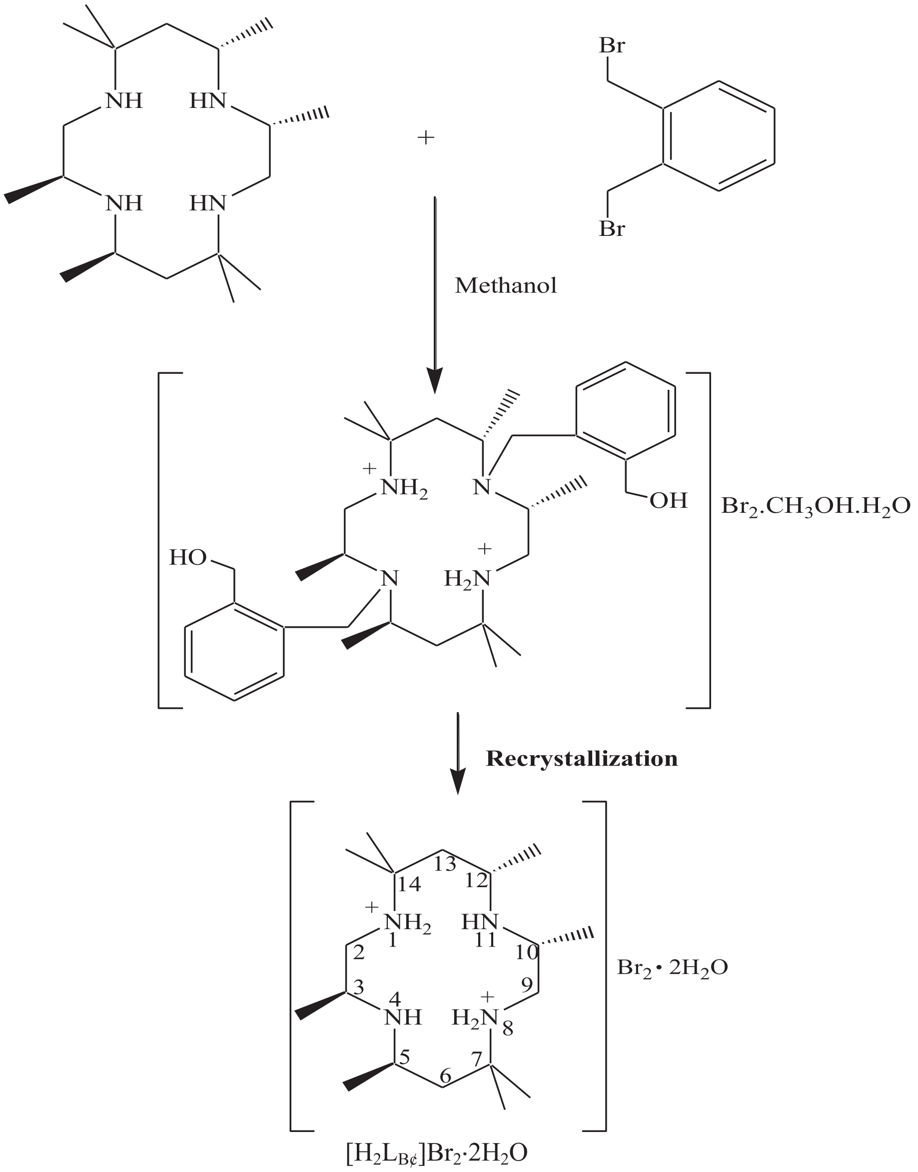

Scheme 1. Synthesis of N-pendent ligand and ligand salt.

2. Results and discussion

2.1. Ligand

On attempting the preparation of the N-pendent derivative of L_B with dibromoxylene, a less stable N-pendent ligand salt, $[(H_2L_{B¢}\text{-}2H)(\text{-}CH_2\text{-}C_6H_4\text{-}CH_2\text{-}OH)_2]Br_2{\cdot}CH_3OH{\cdot}H_2O$ (Scheme 1) resulted, but the analytical data of recrystallized product fit well with the ligand salt of formula, $[H_2L_{B¢}]Br_2{\cdot}2H_2O$. This observation demonstrates that the pendent arms break down on recrystallization as well as on aging, indicating it as the less stable product. This ligand salt showed differences in solubility from the parent ligand L_B in some common solvents like water, chloroform, xylene, methanol and DMSO. The elemental analysis fits well with the molecular formula assigned for the ligand salt. The infrared spectrum of the ligand salt shows $\nu_{N\text{–}H}$, $\nu_{C\text{–}H}$, $\nu_{C\text{–}C}$ and ν_{CH3} bands at 3124, 2980, 1143 and 1382 cm^{-1} respectively in the expected region. Further, the spectrum displays ν_{OH} band at around 3369 cm^{-1} and the δ_{H2O} band at 1625 cm^{-1} which indicates the presence of water of crystallization. The mass spectrum of the fresh product reveals the following mass spectral pattern (Table 1 & Scheme S1).

The mass spectrum of the ligand salt (prior to crystallization) with the N-pendent moiety exhibits the highest *m*/*z* value at 778.75, corresponding to its molecular ion $[(H_2L_{B¢}\text{-}2H](\text{-}CH_2\text{-}C_6H_4\text{-}CH_2\text{-}OH)_2]Br_2{\cdot}CH_3OH{\cdot}H_2O\}$. The base peak corresponds to the molecular ion of the parent ligand, L_B. However the X-ray structure determination of the crystallized product confirms that the original molecular composition of the fresh product becomes rearranged during the crystallization to form $(H_2L_{B¢}){\cdot}Br_2{\cdot}2H_2O$. Mass

Table 1
Intensities of mass spectral peaks of $[(H_2L_{B¢}\text{-}2H](\text{-}CH_2\text{-}C_6H_4\text{-}CH_2\text{-}OH)_2]$ $Br_2{\cdot}CH_3OH{\cdot}H_2O$.

Peaks at *m*/*z*	Fragments	Intensities
778.75	$C_{36}H_{66}N_4Br_2O_4$	3.45%
710.64	$C_{34}H_{54}N_4Br_2O_4$	8.54%
510.40	$C_{34}H_{54}N_4Br_2O_4$	4.34%
461.76	$C_{28}H_{53}N_4O$	17.52%
415.69	$C_{26}H_{47}N_4$	21.43%
313.32	$C_{18}H_{40}N_4$	100%
157.35	$C_9H_{21}N_2$	3.54%