Axial addition reactions on diastereoisomeric [Ni(Me8[14]ane)](ClO4)2 and antifungal activities

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The importance of the polyaaza macrocyclic ligands and their metal complexes are now well recognized due to their high thermodynamic stability, kinetic inertness, structural similarities to natural macrocyclic complexes like vitamin B12, haemoglobin, chlorophyll etc. which play multifarious role in our biological system. The fourteen membered biogenic tetraazamacrocycles and their complexes have taken a considerable position for their wide variety of applications. They are applicable in magnetic resonance imaging (MRI), pharmacological, radioimmunotherapy, analytical and industrial field. This contribution focuses on the synthesis and characterization of diastereoisomeric nickel(II) complexes of isomeric octamethyl tetraazacyclotetradecanes. Condensation of 1,2-diaminopropane with acetone yields the stereospecific 3,10-C-meso isomer of the macrocycle 3,5,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me8[14] diene. This on reduction with NaBH4 yields three isomeric Me8[14]anes. i.e. Me8[14]aneA (LA), Me8[14]aneB (LB) and Me8[14]aneC (LC). The isomeric Me8[14]anes, designated by LA, LB and LC, on reaction with nickel(II) acetate tetrahydrate and subsequent addition of LiClO4 .3H2O yield yellow or orange-yellow square planar [NiL](ClO4)2 diastereoisomers. It has been possible to isolate two N-chiral diastereoisomers for each ligand such as [NiLAα](ClO4)2 & [NiLAβ](ClO4)2 for LA, [NiLBα](ClO4)2 & [NiLBβ](ClO4)2 for LB and [NiLCα](ClO4)2 & [NiLCβ](ClO4)2 for LC. Three diastereoisomeric square planar nickel(II) diperchlorate complexes, [NiL´](ClO4)2 (L´= LAα, LBα or LCα) undergo axial ligand addition reactions with NO3-, Cl-, Br- and SCN- to yield six coordinate octahedral derivatives trans-[NiL´(X)x(Y)y](H2O)z (X= Cl, Br, NO3, SCN; Y= ClO4 x= 1 or 2; y= 1 or 0 and z = 0, 1 or 2). The products have been characterized on the basis of analytical, spectroscopic, magnetic and conductance data. All the derivatives are unstable in open air except [NiLCa(NCS)2] and revert back to original square planar complexes. One structure, namely [NiLBa](ClO4)2 , has been confirmed by X-ray crystallography. The monoclinic unit cell comprises two complex cations and four perchlorate anions so that the Ni atom is located on a crystallographic center of symmetry. Antifungal activities of the ligands, square planar Ni(II) complexes and their addition products have been investigated against some phytopathogenic fungi.


Keywords: Axial addition, Nickel(II) complexes, Antifungal Activities