Macrocyclic Complexes: Part IX—Metal Ion Directed Template Condensation of a \(1\)Hexaaaza Macrocyclic Complex of Nickel(II)

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Received 27 March 1984; accepted 25 May 1984

A macrocyclic complex of nickel (II) with hexaazacyclotetradecane([14]N\(_6\)ane) has been isolated through a stepwise metal ion assisted template synthesis by the action of formaldehyde and ammonia on bis-(diaminoethane)nickel (II) perchlorate. The synthesis and quadratic bonding of the macrocycle to the metal ion are evidenced from magnetic, electronic, IR and PMR spectral data.

Tetraaza macrocyclic complexes have generated considerable interest in the past decade. For 3d metal ions, extensive investigations have been made with 12- to 16-membered macrocycles, specially pertaining to their spectral, magnetic, thermodynamic and redox chemistry. Tetraaza macrocyclic complexes have generated considerable interest in the past decade. For 3d metal ions, extensive investigations have been made with 12- to 16-membered macrocycles, specifically pertaining to their spectral, magnetic, thermodynamic and redox chemistry. Tetraaza macrocyclic complexes have generated considerable interest in the past decade. For 3d metal ions, extensive investigations have been made with 12- to 16-membered macrocycles, specifically pertaining to their spectral, magnetic, thermodynamic and redox chemistry.

We have now prepared another saturated unsubstituted hexaaaza but quadricoordinated macrocyclic ligand, 1,4,7,9,12,15-hexaazacyclohexadecane([16]N\(_6\)ane), which on complexation with nickel(II) gives complexes with rarely encountered 5,7,5,7-chelate ring sequence. We have now prepared another saturated unsubstituted hexaaaza 14-membered macrocyclic, 1,3,6,8,10,13-hexaazacyclocotetradecane([14]N\(_6\)ane), complex of nickel (II) by a successive and stepwise metal ion assisted template condensation.

A hot solution of bis-(1,2-diaminoethane)nickel (II) perchlorate, either in methanolic or in aqueous medium, when added dropwise to a mixture of formaldehyde and ammonia solutions (in 2:1 molar ratio) gave a bright green solution. The solution on standing produced a shining diamagnetic orange yellow crystalline substance which has been characterized to be complex (1) with the ligand 1,4,6,8,11-pentaazaundecane. The aqueous solution of complex (1) on being refluxed with a slight excess of the required quantity of formaldehyde and ammonia for 50 hr, at a moderate to high dilution, produced the macrocycle. The solution on being concentrated and allowed to stand gave the diamagnetic bright yellow crystalline complex (2) with the macrocyclic ligand 1,3,6,8,10,13-hexaazacyclotetradecane. Elemental analyses of (1) and (2) agree with the assigned stoichiometries. The electronic spectra of complexes (1) and (2) show bands at 22,700 and 23,200 cm\(^{-1}\) respectively which have been assigned to the transitions \(^{1}A_{1g} \rightarrow ^{1}A_{2g}\) under planar \(D_{4h}\) symmetry.

The IR spectrum of (1) shows two strong bands at 3305 and 3240 cm\(^{-1}\) corresponding to asymmetric and symmetric stretching vibrations of NH\(_2\) groups and a weak band at 3120 cm\(^{-1}\) due to secondary amine NH stretching mode. The deformation vibrations of NH\(_2\) groups of (1) appear at 1590 cm\(^{-1}\). It exhibits several new bands at 1350, 1310, 920 and 860 cm\(^{-1}\) that do not appear in the present bis/tris-(1,2-diaminoethane)nickel (II) perchlorates. The successor macrocyclic complex (2) is free from the asymmetric and symmetric stretching and deformation vibrations of the NH\(_2\) groups. Except the band at 920 cm\(^{-1}\) appearing in (1), the rest of the new bands occur in (2) also, and an additional band appears at 795 cm\(^{-1}\). These bands originate from the new ring modes, methylene groups and the wagging mode of secondary NH groups.

The PMR spectrum of the diamagnetic complex (1) shows resonances at (\(\tau\) scale) 7.50 and 6.90 ppm that occur as triplets, and a third signal at 6.1 ppm as a singlet. The triplets originate due to inequivalent protons of the ethylene, \(-\text{CH}_2-\text{CH}_2-\), groups and the singlet is assigned to the methylene protons. The relative areas under the peaks are in the ratio 1:1:1 and thus characterize the product. A broad and weak N-H peak is observed in the range 5-4 ppm. In sharp contrast, the macrocycle gives a pair of signals as singlets at 7.47 and 5.1 ppm with equal areas under the peaks. The former absorption arises due to the protons of the ethylene groups that have assumed equivalence and the down field absorption originates from the methylethylenic protons. It is striking that the signals due to methylethylenic protons of (2) appear at more down field positions in comparison with the positions of the corresponding signals for (1); this seems to arise from the macrocyclic effect.

Thus, chemical, magnetic and spectral data point exclusively to structures (1) and (2), and their stepwise successivesynthesises are indicative of the dominating influence of coordination geometry of the template metal ion. Further investigations are in progress and the results will be communicated in due course.
References