Nickel(II) Macrocyclic Complexes: Salts of 1,3,6,9, 11,14-Hexaazaacyclohexadecanenickel(II)

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A novel series of nickel(II) macrocyclic complexes of the type, NiLX₂ (where X = Cl⁻, Br⁻, I⁻, NO₃⁻ and ClO₄⁻) with the cyclic ligand L = 1,3,6,9,11,14-hexaazaacyclohexadecane, has been synthesized by the action of formaldehyde on bis(diethylenetriamine)nickel(II) salts. They are obtained as shining yellow diamagnetic crystals and have been characterised by IR, PMR and electronic spectral studies.

An important aspect of amine complexes is their interaction with carbonyl groups leading to macrocycles¹ and clathrochelates². During the course of our studies on macrocyclic complexes a series of new nickel(II) macrocyclic complexes has been synthesized with the cyclic ligand, 1,3,6,9,11,14-hexaazaacyclohexadecane, by metal ion template synthesis involving the reaction of formaldehyde with bis(diethylenetriamine)nickel(II) complexes of the type NiL₂X₂ (where X = Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻ and L = diethylenetriamine).

The parent paramagnetic and bluish violet [Ni(dien)₂]X₂ H₂O complexes, when reacted withaq. formaldehyde in 1:2 molar ratio gradually change their colour and the rate of colour change is enhanced on warming. The resulting solution on standing overnight at 0°C yields diamagnetic shining yellow or orange crystals, which analyse for Ni(C₂H₄N₈)₂X₂ H₂O. On the basis of IR and PMR data, discussed in the sequel, the compounds have been found to be the macrocyclic complexes, (1,3,6,9,11,14-hexaazaacyclohexadecane)nickel(II) X₂ H₂O, (Ni[16]ane N₄)X₂ H₂O (see structure I).

The IR spectra of the macrocyclic complexes are strikingly different from those of [Ni(dien)₂]X₂ H₂O in the OH and NH stretching frequency regions. The stretching and bending vibrations of water persist in the macrocycle and are observed ~3450, 3390 and 1610 cm⁻¹ respectively. On the other hand, the νNH₂ and δNH₂ of the parent complexes are observed in the region 3400-3200 and 1560 cm⁻¹ respectively and disappear in the macrocycles. Several new bands appear in the macrocyclic complexes at 1210, 1180, 825 and 695 cm⁻¹. The first two bands are due to the deformation vibrations of the methylene groups as a result of ring formation and the last two bands arise due to the wagging mode of secondary NH groups.

A medium intensity band ~1140 cm⁻¹ in the parent complexes disappears in the macrocyclic complexes and two new sharp bands appear at 1125 and 1130 cm⁻¹ due to γC-N-C of non-coordinated secondary amines. Apart from this, another band observed for the original complex at 1250 cm⁻¹ arising out of NH₄ rocking mode disappears in the macrocycle.

PMR spectra of the complexes in D₂O at room temperature exhibit two multiplets centered at 82.66 and 3.22 which have been attributed to the -CH₂-CH₂-protons of the seven and five-membered rings respectively and a sharp singlet at ~3.74 due to the methylene groups. A complex pattern of NH proton resonances are observed at ~4.00-6.00. This provides evidence in favour of the structure(I).

All these complexes show electronic transition at 22, 720 cm⁻¹ which arise due to the transition 1A₁g → 1A₂g under D₄h symmetry and a strong charge transfer band near 44,000 cm⁻¹. Further investigations are in progress and will be communicated in due course.

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References