

NOTE

32- and 34-Membered Macrocyclic Trinuclear Nickel(II) Complexes

H.C. RAI*, A. KUMAR and VEENA KUMARI

*Department of Chemistry**L.S. College, Muzaffarpur-842 001, India*

An interesting group of 32- and 34-membered macrocyclic trinuclear nickel(II) complexes have been isolated by synergic template condensation of bis-(dihydrazone) nickel(II) bromide complexes with a suitable dialdehyde nickel(II) bromide complex in molar ratio 1 : 2.

Dialdehydes and dihydrazone nickel(II) bromide complexes have been prepared as reported earlier¹⁻³. Chemicals used were mainly from Aldrich. Standard procedures were adopted for obtaining physico-chemical data. Analyses agreed well with the proposed formulations. The reaction sequence can be represented as shown in Fig. 1.

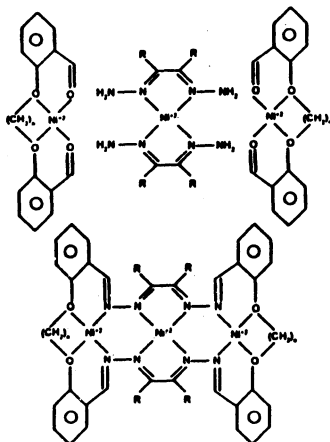
R = H, CH₃, Phenyl or furyl, n = 2, 3

Fig. 1

The important attributes of the spectra of the trinuclear macrocycles are the disappearance of the NH₂ stretching vibrations of the precursor dihydrazones in the region 3300–3200 cm⁻¹ and the carbonyl stretching vibrations of the dialdehydes observed near 1680 cm⁻¹. The spectra show the persistence of the ν(C=N) of the α-diimine groups of the dihydrazone complexes and it is the only band of its kind observed in the vicinity of 1600 cm⁻¹. The lone ν(C=N) band implies that all the imine groups of the macrocyclic ligand are equienergetic which

appears to be the consequence of their coordination with the metal ions and high degree of electron delocalization on the macrocyclic molecular frame; the asymmetric and symmetric ethereal C—O—C vibrations appear near 1250 and 1050 cm^{-1} respectively.

Besides these structurally important features, vibrational bands of the phenyl groups, furyl groups, CH_3 and CH_2 vibrations in each kind of macrocycles are discernible. The spectral data are self-consistent with macrocyclization and support the structure as proposed.

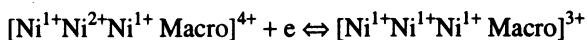
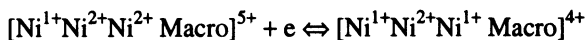
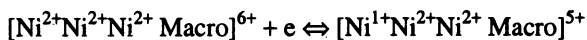
All the metal ions encased within the macrocyclic cavity are in spin-free state and the magnetic moment per metal ion is found to be about 3.0 B.M. The electronic spectra manifest tetragonal distortion about the metal ion. They show electronic transitions near 8,700, 11,000, 17,000 and 28,000 cm^{-1} . These transitions are assigned to ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$, ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}$, ${}^3\text{B}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{B}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ alongwith charge transfer bands under D_{4h} symmetry.

The ligand field parameters D_t , D_{qxy} and D_{qz} have been estimated. The ligand field parameters are reminiscent of considerable π -bonding along the macrocyclic plane and the axial ligand field is not transferable.

The complexes undergo reduction in three well defined steps. Each redox step is reversible and is accompanied by one-electron transfer. The thermodynamic parameters $E_{1/2}$ are observed in the ranges -0.85 to -1.19 , -0.99 to -1.43 and 1.13 to -1.160 respectively. The analysis of the polarographic data shows that the $E_{1/2}$ values are dependent on the structural parameters of the macrocyclic ligands, namely, on the macrocyclic ring size and on the substituents pendant on the macro-ring⁴⁻⁶.

The $E_{1/2}$ values in each step of reduction are found to be less cathodic for the larger ring (34-membered). Similarly the $E_{1/2}$ values are found to be most cathodic for the methyl substituents on the macro-ring and become anodic with H, phenyl and furyl groups.

The redox processes are thus believed to accompany the stepwise redox equilibria as under:



In the intermediate steps the metal ions occur in ambivalent oxidation states.

REFERENCES

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