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'*in situ*' Synthesis of a Trinuclear Nickel(II) Complex with a 40-Membered Macrocyclic Tricompartmental Hexadecaaza Dodecadentate Ligand Using Kinetic Template Reaction

H.C. RAI*, PRIYANKA† and A.K. GHOSH†
Department of Chemistry, B.R.A. Bihar University, Muzaffarpur-842 001, India
E-mail: hcrai@rediffmail.com

A novel nickel(II) complex with the ligand 4,5,24,25-tetramethyl-10,11:18,19:30,31:38,39-tetrabenzo-2,3,6,7,9,13,16,20,22,23,26,27,29,33,36,40-hexadecaazatricyclo[26,12,0,$0^{8,21}$]tetraaconta-1,3,5,7,10,12,16,18,21,23,25,27,30,32,36,38-hexadecaene has been synthesized with kinetic template reaction in which dibromo*bis*(biacetyldihydrazone) nickel(II) is allowed to condense with 13,14-exocyclicdioxo-1,5,8,12-tetraaza-2,3:10,11-dibenzo-cyclotetradeca-2,4,8,10-tetraenato(2-) nickel(II) in 1:2 molar ratio in DMF medium under nitrogen at 100 ºC. Characterization has been done with elemental analysis, conductivity and magnetic susceptibility measurements, electronic and vibrational spectral studies. The nickel(II) ions are in different stereochemical environments.

Key Words: Synthesis, Spectral, Macrocyclic complex, Compartmental ligand.

INTRODUCTION

Extensive studies on coordination compounds with macrocyclic ligands have been made and an elaborate, systematic and up-to-date account has been summarized in the reference book[1]. The works mostly relates to ligands encompassing one metal ion in its cavity. Recently dinuclear macrocyclic complexes have attracted attention for the last four decades since Robson introduced the term 'binucleating ligands' to such complexes[2]. These molecules are well known to manifest cooperating phenomenon in their magnetochemical and electrochemical behaviour[3-5]. Though structurally diverse coordination complexes engulfing two or more metal ions are relatively rare. Consequently in continuation of our earlier interest in the field[6-8] we in the present communication report a novel nickel(II) complex with a 40-membered macrocyclic ligand which has 16 nitrogen atoms (12 azomethine and 4 amido) enclosing three nickel(II) ions.

EXPERIMENTAL

Salicylaldehyde, biacetyl, hydrazine hydrate hydrochloride, ethylenediamine and nickel(II) salts are all Aldrich reagents.

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†Department of Chemistry, Sido Kanhu Murmu University, Dumka-814 101, India.

Preparation of dibromo*bis*(butane-2,3-dionedihydrazone)nickel(II): It was prepared as per literature procedure[6]. Biacetyl (1.7 g, 0.02 mol) in alcohol was treated dropwise with an alcoholic solution of nickel(II) bromide hexahydrate (3.2 g, 0.01 mol). The resulting mixture was warmed to boiling and hydrazine hydrate (2.0 g, 0.04 mol) was added dropwise with constant stirring when a bluish violet precipitate was readily obtained. It was refluxed on a hot water bath for nearly two hours. The compound was filtered after cooling, washed with alcohol followed by ether and analysed after drying.

The precursor complex $[Ni(BDH)_2Br_2]$ was also prepared by traditional method using biacetyldihydrazone (BDH) prepared by literature procedure[9,10] and nickel(II), bromidehexahydrate. The yield in the '*in situ*' process was *ca.* 48 % whereas in the traditional method it was only 26 %.

The complex 13,14-exocyclicdioxo-1,5,8,12-tetraaza-2,3:10,11dibenzo-cyclotetradeca-2,4, 8,10-tetraenato (2-) nickel(II) has been prepared by the method reported in literature[11].

1,2-Dioxo ethane-1,2-diamine, ethylenediamine and nickel(II) acetate dihydrate are allowed to condense in DMF solution at 100 ºC in atmosphere of nitrogen in the molar ratio 1:1:1 an yellowish green crystals crystallize out on cooling (**Scheme-I**).

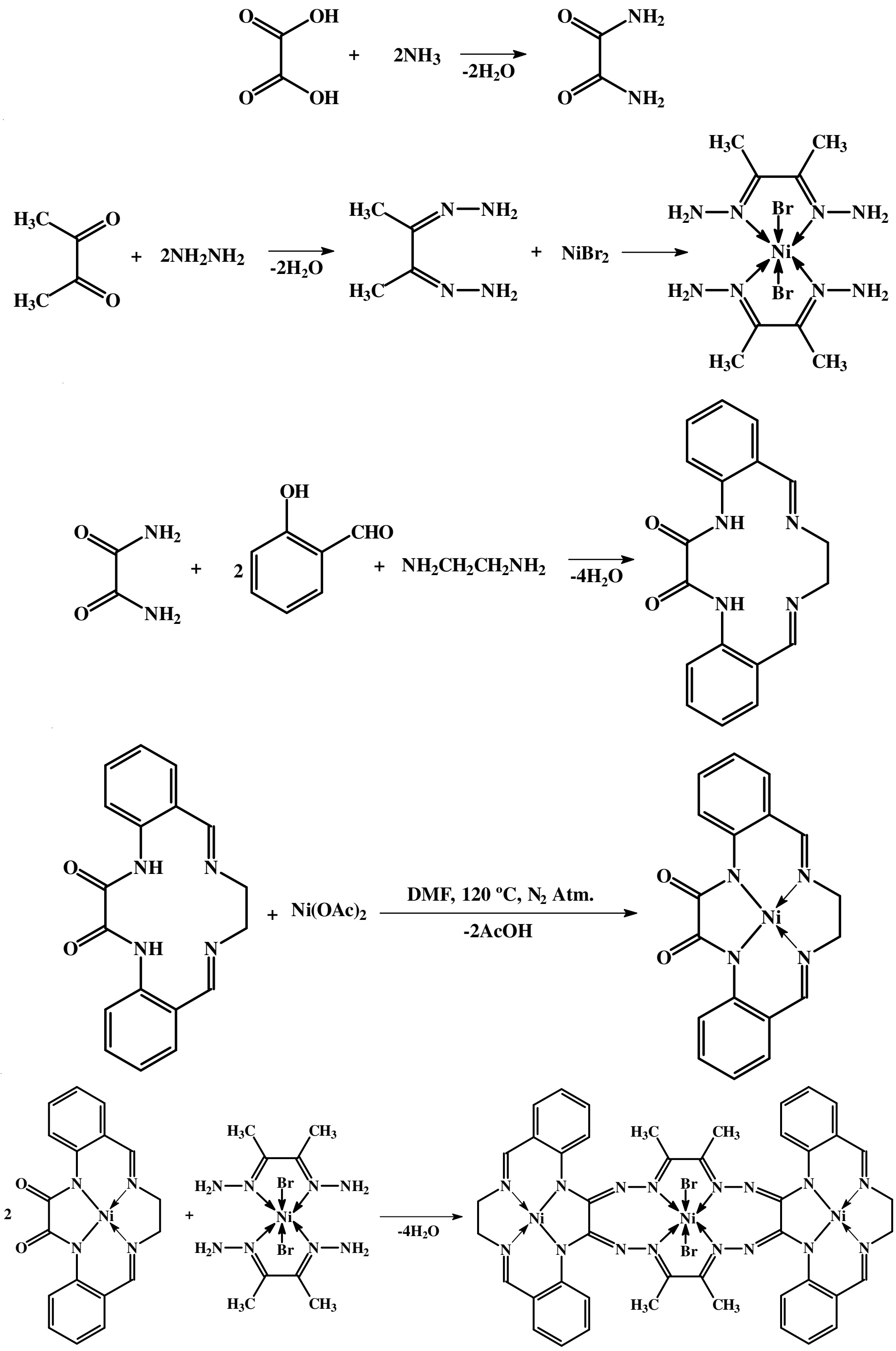
Finally blue and green crystals were allowed to undergo condensation in 1:2 molar ratio in DMF solution at 100 ºC in atmosphere of nitrogen. The resulting solution was cooled and slow evaporation under vacuum produced beautiful red crystals which were dried *in vacuo* and analyzed. Analytical results have been recorded in Table-1.

RESULTS AND DISCUSSION

On the basis of elemental analysis, stoichiometry of the macrocyclic precursors, bichelate non macrocyclic precursor and tricyclomacrocyclic complex have been found to be $[Ni(C_{18}H_{14}N_4O_2)]$, $[Ni(C_8H_{20}N_8)Br_2]$ and $[Ni_3(C_{44}H_{40}N_{16})Br_2]$, respectively.

In order to the structural problems elucidation, infrared and electronic spectra of the precursors and tricyclomacrocyclic complex were recorded respectively on Shimadzu 160 A and Beckman-20 spectrophotometers. Conductivity and magnetic susceptibility have also been measured on Systronics conductometer model-303 and Guoy balance, respectively. Low value of molar conductivity in the range 10-15 ohm cm^{-2} mol^{-1} indicate the precursor and macrocyclic complex to be non-electrolytic in nature. The magnetic moment of macrocyclic precursor $[Ni(C_{18}H_{14}N_4O_2)]$ indicated to be diamagnetic. Electronic spectrum with a broad band with low intensity at 20000 cm^{-1} suggests the stereochemistry to be square planar. Non-macrocyclic precursor $[Ni(C_8H_{20}N_8)Br_2]$ have μ_{eff} = 3.15 BM indicating it to be octahedral in nature. The electronic spectra is also in good agreement with the literature[7].

The μ_{eff} of tricyclomacrocyclic complex has been found to be 3.8 BM and is presumed to be due to central octahedral and terminal square planar environment of Ni(II) ions. The excess value is most presumably due to TIP contribution.


O
OH
O
OH
+
2NH3
-2H2O
O
NH2
O
NH2
H3C
O
H3C
O
+
2NH2NH2
-2H2O
H3C
N—NH2
H3C
N—NH2
+
NiBr2
H3C
CH3
H2N—N
Br
N—NH2
Ni
H2N—N
Br
N—NH2
H3C
CH3
O
NH2
O
NH2
+
2
OH
CHO
+
NH2CH2CH2NH2
-4H2O
O
NH
N
O
NH
N
O
NH
N
O
NH
N
+
Ni(OAc)2
DMF, 120 °C, N2 Atm.
-2AcOH
O
N
N
Ni
O
N
N
2
O
N
N
Ni
O
N
N
+
H3C
CH3
H2N—N
Br
N—NH2
Ni
H2N—N
Br
N—NH2
H3C
CH3
-4H2O
N
N
Ni
N
N
H3C
CH3
N—N
Br
N—N
Ni
N—N
Br
N—N
H3C
CH3
N
N
Ni
N
N

Scheme-I

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complexes	Colour	Elemental analysis (%): Found (calcd.)				
		Ni	C	H	N	Br
[Ni($C_{18}H_{14}N_4O_2$)]	Green	15.62 (15.64)	56.92 (57.29)	3.70 (3.71)	14.83 (14.84)	
[Ni($C_8H_{20}N_8$)Br_2]	Blue	13.15 (13.19)	21.43 (21.47)	4.46 (4.47)	24.98 (25.05)	35.75 (35.79)
[Ni_3($C_{44}H_{40}N_{16}$)Br_2]	Red	15.64 (15.67)	46.70 (46.76)	3.52 (3.54)	19.82 (19.84)	14.13 (14.17)

Infrared spectra: The intense and strong band in the region 3400-3200 cm^{-1} in the spectra of non macrocyclic precursor is absent in the spectra of tricyclomacrocycle due to condensation and uncoordinated NH_2 group with the exocyclic carbonyl function of cyclic precursor during macrocyclization. The strong band at 1700 cm^{-1} in the spectra of cyclic precursor is also absent in the spectra of macrocycle.

A strong band of medium intensity is present in the ir spectra of all the complexes precursor as well as tricyclomacrocycle in the range 1630-1640 cm^{-1} and can be assigned to ν(C=N). A pair of strong bands appear in the spectra of macrocycles which are absent in the spectrum of the free ligand. They appear in the regions 470-450 cm^{-1} and 570-520 cm^{-1} are tentatively assigned[12] to ν(Ni-N) and ν(Ni-O). The bands at 1060-1050 and are assigned to N-N stretching vibrations of the hydrazide moiety. These bands in all the complexes shift to the higher wave number side confirming involvement of one of its N-atom in bonding with the metal ions.

On the basis of above information, the structure as shown in Fig. 9 has been assigned to tricyclomacrocyclic complex.

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