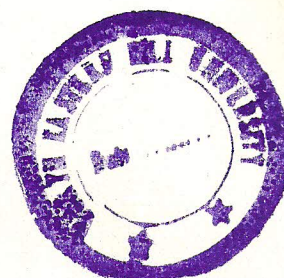


STUDIES ON THE COMPLEXES OF NICKEL (II),
NICKEL (III), COBALT (II) AND RUTHENIUM (II)
WITH SOME MONODENTATE LIGANDS

(Abstract)

by

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Thesis submitted in fulfilment of the requirement of the degree of
DOCTOR OF PHILOSOPHY

to



THE NORTH-EASTERN HILL UNIVERSITY
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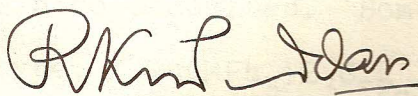
ABSTRACT

C E R T I F I C A T E

I certify that the thesis entitled "Studies on the Complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) with some **Monodentate** Ligands" submitted by Mr. Kali Prasad Sarma for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph. D. Degree. This work has not been submitted for any Degree of any other university.

Date : 9/12/83

Place: Shillong


(R. K. PODDAR)

Signature of the Supervisor

The thesis deals with the synthesis and study of the physical properties, reactivity and structural aspects of the complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) with some monodentate ligands.

Chapter I, describes the synthesis and some of the physical and chemical studies on some ruthenium(II) complexes containing both strong and weak donor ligands. These complexes are of the type $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$ (M = P or As). On the basis of the above studies, it is proposed that the complexes have a distorted square pyramidal structure. To study the ease of substitution of benzaldehyde in $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$, reactions with some weak donor ligands, viz. pyridine, DMF, DMSO, acetonitrile and carbondisulphide are also described. Some new complexes obtained, are of the type, $[\text{Ru}(\text{MPh}_3)\text{L}_3\text{Cl}_2]$ (when M = As, L = py or DMF; when M = P, L = DMF) and $[\text{Ru}(\pi\text{-CS}_2)(\text{PPh}_3)\text{Cl}_2]$. Some ruthenium(II) carbonyl complexes of the type $[\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2]$ (M = P or As) are also synthesized and structural assignments for the complexes have been made with the help of physical and chemical studies.

Chapter II, describes the synthesis and studies on nickel(II) complexes of the type, $[\text{Ni}(\text{PPh}_3)\text{XCl}_2]$,

$[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$ (X = Cl, Br, SCN or NO_3). On the basis of physical measurements and chemical reactions, it is proposed that the complexes have a dimeric structure with a distorted tetrahedral environment around the nickel atom with Chloro-bridges. Low value of magnetic moments of these complexes is probably due to antiferromagnetic interaction between two nickel atoms of the dimer through chloro-bridges. Evidence of chloro-bridges is obtained from far infrared spectra too. Reactions of the above mentioned dimeric complexes with triphenylphosphine resulted in the formation of the complexes of the type, $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$ (X = Br, NO_3 or NCS). A distorted tetrahedral structures for $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$ (X = Br or NO_3) and a square planar structure for $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$ is proposed.

Chapter III of the thesis deals with the synthesis of a novel nickel(III) complex, viz. $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$ by the oxidation of $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$ with nitrosyl chloride or chlorine. With the help of magnetic and e. s. r. studies and some chemical reactions the oxidation state of the metal is confirmed to be +3. With the help of other physical measurements a distorted tetrahedral geometry around nickel(II) is proposed. This complex is found to act as a catalyst in the oxidation of triphenylphosphine to

triphenylphosphine oxide and as an oxidant for the oxidation of cyclohexanol to cyclohexanone.

In Chapter IV, syntheses of some cationic nickel(II) complexes, viz. $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2^{+}[\text{Y}_3]_2^{-}$ (when $\text{X} = \text{Cl}$, $\text{Y}_3 = \text{Br}_3$; when $\text{X} = \text{Br}$, $\text{Y}_3 = \text{Br}_3$ or IBr_2) and their physical and chemical behaviours studied. The presence of trihalide anions is confirmed with the help of uv spectral data, where a very strong band ($\epsilon \simeq 5 \times 10^4$) in the u.v. region is observed due to $\sigma \rightarrow \sigma^*$ transition. Magnetic moments of these complexes correspond to that of nickel(II) tetrahedral complexes. On the basis of various physical studies, these complex cations are proposed to have dimeric structures having distorted tetrahedral environment around nickel(II) with chlorobridges.

Chapter V describes the preparation of nickel(II) thiocyanate by a convenient one-step method and its various physical properties in solid and in solution. Nickel(II) thiocyanate has been used as a precursor for the synthesis of some new and some reported compounds, containing nickel thiocyanate and other donor atoms such as oxygen, nitrogen or phosphorus. New compounds synthesized are, $\text{NiL}_2(\text{SCN})_2$ ($\text{L} = \text{OPPh}_3$, OAsPh_3 or N_2H_4), $[\text{Ni}(\text{bipy})_3]^{+}(\text{SCN})_2^{-}$, $[\text{NiL}_4(\text{NCS})_2]^{+}(\text{NCS})_2^{-}$ (where $\text{L} = \text{dimethylamine}$ or triethyl

amine). The physical properties of the above mentioned compounds have been studied to know their structures and mode of bonding of thiocyanate to the metal.

In Chapter VI, complexes of nickel(II) and cobalt(II) containing both strong and weak donor ligands, viz. $[\text{Ni}(\text{PPh}_3)_2\text{L}_2\text{X}_2]$ and $[\text{Co}(\text{PPh}_3)\text{LX}_2]$ (L = DMF or DMSO; X = Cl or Br) have been synthesized and characterized with the help of various physical data, including infrared and electronic spectra, magnetic and conductivity measurements. On the basis of physical studies mentioned above, it is proposed that the nickel(II) complexes have distorted trigonal bipyramidal geometry in the solid state and a tetrahedral geometry in solution (when one molecule of DMF or DMSO is lost in the solution) and the cobalt complexes have a distorted tetrahedral geometry around the metal ion.

Part of the work presented in the thesis is published in the following Journals:

Chapter II

1. Reaction of Nitrosylchloride with $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]^{+7}$
(X = Cl, Br, SCN, NO_3)

Kali Prasad Sarma and Raj K. Poddar
Trans. Metal Chemistry, 8, 31-33 (1983).

2. Mixed Ligand Complexes of Nickel(II).

Kali Prasad Sarma and Raj K. Poddar
Trans. Metal Chemistry, 8, 225 (1983).

Chapter III

3. Synthesis and Studies on Dichloroiodotriphenylphosphine oxide Nickel(III).

Kali Prasad Sarma and Raj K. Poddar
Polyhedron, 2, 672 (1983).

Chapter V

4. A Convenient Method of Preparing Nickel(II) Thiocyanate and Its Use in Synthesis.

Kali Prasad Sarma and Raj K. Poddar
Trans. Metal Chemistry, (in press).

Chapter VI

5. Mixed Ligand Complexes of Nickel(II) and Cobalt(II).

Kali Prasad Sarma and Raj K. Poddar

J. Coordination Chemistry, 12, 237 (1983).

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