STUDIES ON MIXED AND SUBSTITUTED TETRAHALO-COBALTATES (II) AND NICKELATES (II)

BY

RADHEYSHYAM PRASAD

SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

JANUARY, 1981

CERTIFICATE

This is to certify that thesis entitled "Studies on Mixed and Substituted Tetrahalocobaltates(II) and Nickelates(II)", being submitted by Mr. Radheyshyam Prasad to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Radheyshyam Prasad has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

(N.K. Jha)
Professor,
Department of Chemistry,
Indian Institute of Technology, Delhi,
New Delhi 110 016.

ACKNOWLEDGEMENTS

I take this opportunity to express my sincere gratefulness to Professor N.K. Jha for giving me a chance to work with him on this problem and for his inspiring guidance throughout the course of this investigation. I am highly indebted to him for the encouragement and interest he has shown in my personal welfare.

My deep sense of gratitude is also due

to Professors R.P. Gandhi, R.D. Dua, J.C. Ahluwalia, G.V. Jere and B.L. Khandelwal who were always helpful to me,

to Professor R.C. Aggarwal (B.H.U., Varanasi), Dr. U.R.K. Rao (B.A.R.C., Bombay), Dr. L.K. Mishra (P.U., Patna) and Dr. S.M. Prasad (R.U., Ranchi) for certain help during the course of experimental work,

to my friends, especially Dr. A. Saxena, Dr. (Miss) A. Kumari, Dr. S.M. Kaushik, Mr. C.S.R. Murthy, Mr. S.S. Mishra, Mr. A. Mishra and Mr. R.V. Jasra for their kind help.

My humble regards are also due to my parents and relatives who always encouraged and assisted me to pursue higher studies.

The patience and understanding shown by my wife, Kiran, is thankfully acknowledged.

Finally, I wish to thank Mr. Bala Dutt Phuloria for his help during spectral recording, Mr. N.L. Arora for fine tracing and Mr. S.L. Aneja for excellent typing.

Radheyshyam

(Radheyshyam Prasad)

ABSTRACT

The present investigation reports the isolation and characterization of

(i) mixed tetrahalonickelates(II), (halo = chloro or bromo),

(ii) substituted mixed tetrahalocobaltates(II) and nickelates(II), (halo = chloro, bromo or iodo)

and(iii) diisothiocyanatodihalocobaltates(II) and nickelates(II), (halo = chloro, bromo or iodo)

by conductance, electronic (visible and near i.r.), i.r. and far i.r. spectral studies and magnetic susceptibility measurements.

Molar conductance measured at a fixed concentration in nitromethane suggests the electrolyte type as manifest in the molecular formula of the respective complexes. The electronic spectra have been interpreted on the basis of T_d symmetry in case of mixed tetrahalonickelates(II), e.g. $(NiCl_2Br_2)^{2-}$, C_{2v} symmetry in case of diisothiocyanatodihalocobaltates(II) and C_{3v} symmetry in case of substituted mixed tetrahalocobaltates(II) and nickelates(II). For some of the complexes ligand field parameters 10 Dq, B' and β and for only a few the crystal field splitting parameter D_τ have been calculated. The magnetic moments generally fall within the range expected for a tetrahedral and pseudotetrahedral Co(II) and Ni(II) complexes. Low temperature magnetic susceptibility data (reported only for two of the complexes) do not indicate any significant magnetic interaction. Bands in the i.r. (in case of thiocyanato complexes) and far i.r. regions have been assigned.

Unit cell dimensions of one of the compounds $[(C_2H_5)_4N][Ni(PPh_3)Cl_2Br]$ were determined by single crystal Weissenberg photographs. Other few complexes with the formulation $[(C_2H_5)_4N][M(PPh_3)X_2Y]$ (where M = Co or Ni; X and Y = Cl, Br or I) were found to be isomorphous to the above compound by x-ray powder diffraction study.

CONTENTS