

MIXED HALOCOBALTATES(II) -- A PREPARATIVE  
AND STRUCTURAL STUDY

BY

AKHILESH SAXENA  
CHEMISTRY DEPARTMENT

SUBMITTED

IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

DECEMBER, 1976.

CERTIFICATE

This is to certify that the thesis entitled 'Mixed Halocobaltates(II)-- A Preparative and Structural Study' being submitted by Mr. Akhilesh Saxena 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. The results reported in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

Mr. Saxena has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis.

  
( N. K. Jha )

Thesis Supervisor  
Asstt. Professor  
Department of Chemistry  
Indian Institute of Technology  
New Delhi-110029  
INDIA

## ACKNOWLEDGEMENTS

I wish to express my deep sense of gratitude to Dr.N.K. Jha, Assistant Professor, Chemistry Department, Indian Institute of Technology, Delhi, for his valuable guidance during the course of this work.

To Dr. D.M. Adams, Chemistry Department, University of Leicester, U.K., by whose courtesy I could get far i.r. spectra of some of the complexes, I am grateful and more so to Dr.P.K. Pandey, X-ray Laboratory, Indian Institute of Petroleum, Dehradun, India, who rendered me all the possible assistance for recording the X-ray powder diffractograms of some of the compounds.

Among my colleagues, I am especially thankful to Miss Amrita and Mr. Radhay Shyam to whom I could always look for help.

It was a pleasant experience to work with Mr. Bala Dutt Phuloria, STA, who helped me in recording the spectra of the compounds. Co-operation by other members of the supporting staff is sincerely acknowledged.

I am thankful to the I.I.T. Delhi and the C.S.I.R., India, for the financial help. Laboratory facilities provided by I.I.T.Delhi are also gratefully acknowledged.

  
(A. SAXENA)

## ABSTRACT

This work reports the isolation and characterization of some mixed halocobaltates(II) (halo = chloro, bromo, iodo). Electronic spectral (visible and near i.r.), far i.r. ( $400-100\text{ cm}^{-1}$ ), magnetic moment and conductance studies have been carried out to get an insight into the structural aspects of these complexes. While the mixed tetrahalocobaltates(II) have been found, as expected, to be tetrahedral, the mixed tri- and the pentahalocobaltates(II) have also revealed a tetrahedral environment around Co(II). Pentahalocobaltates(II) have been formulated as double salts containing a tetrahalocobaltate(II) species and for trihalocobaltates(II) a linear chain structure with bridging halogens has been favoured over a possible dimeric unit structure.  $10Dq$ ,  $B'$  and  $\lambda'$  values have been calculated. Assignment of the bands in the far i.r. region has been done. An attempt has been made to explain the abnormally high and abnormally low magnetic moment values found (at room temperature) for pentahalocobaltates (II) and trihalocobaltates(II), respectively, in view of their containing a tetrahedrally surrounded Co(II). Molar conductance values measured at a fixed concentration in acetonitrile to characterize these complexes have been shown to lead to deceptive results. For trihalocobaltates(II), Debye-Hückel-Onsager equation shows them to be, at least in solution, (1:1) electrolytes. Unit cell dimensions for some of the complexes have been found out from X-ray powder diffraction patterns.

## CONTENTS

	<u>Page No.</u>
1. List of figures.	i
2. List of tables.	iii
3. Chapter 1                      Introduction	1-28
1.1 Trihalocobaltates(II)	1
1.2 Tetrahalocobaltates(II)	7
1.3 Pentahalocobaltates(II)	20
1.4 Hexahalocobaltates(II)	24
1.5 Dinuclear Halocobaltates(II)	25
1.6 Applications of halocobaltates(II)	26
1.7 Scope of the present work	27
4. Chapter 2                      Preparative Investigations	29-48
2.1 Introduction	29
2.2 Purification of reagents and solvents	29
2.3 Preparation	31
2.3.1 Pentahalocobaltates(II)	31
2.3.2 Tetrahalocobaltates(II)	35
2.3.3 Trihalocobaltates(II)	36
2.4 Analysis	36
2.5 General properties	38
2.6 Discussion	39

CONTENTS  
(Continued)

	<u>Page No.</u>
5. Chapter 3            Structural Studies	49-190
3.1 Electronic spectra	49
3.1.1 Introduction	49
3.1.2 Experimental	50
3.1.3 Calculation of ligand field parameters	51
3.1.4 Results and Discussion	52
(I) Tetrahalocobaltates(II)	53
(A) Pure Tetrahalocobaltates(II)	53
(B) Mixed Tetrahalocobaltates(II)	63
(C) Ligand field parameters	68
(D) Average ligand field approximation	72
(E) Solution spectra	72
(II) Pentahalocobaltates(II)	74
(A) Pure Pentahalocobaltates(II)	79
(B) Mixed Pentahalocobaltates(II)	80
(C) Ligand field parameters	82
(D) Average ligand field approximation	88
(E) Solution spectra	89
(III) Trihalocobaltates(II)	90
(A) Diffuse reflectance and nujol mull spectra	90
(B) Ligand field parameters	94
(C) Average ligand field approximation	95
(D) Solution spectra	96

CONTENTS  
(Continued)

Page No.

(IV)	Search for ${}^4T_2(F) \xleftarrow{\nu_1} {}^4A_2(F)$ transition.	97
(V)	Effect of the outer-sphere cation on the d-d electronic transition.	99
(VI)	A comparison of $\nu_2$ , $\nu_3$ and $10Dq$ values of tetra- and pentahalocobaltates(II).	101
3.2	Infrared Spectra	124
3.2.1	Introduction	124
3.2.2	Experimental	124
3.2.3	Results and Discussion	125
(A)	4000-400 $\text{cm}^{-1}$ region	125
(B)	400-100 $\text{cm}^{-1}$ region	125
(i)	Tetrahalocobaltates(II)	125
(ii)	Pentahalocobaltates(II)	131
(iii)	Trihalocobaltates(II)	138
3.3	Magnetic Moments	146
3.3.1	Introduction	146
3.3.2	Experimental	146
3.3.3	Treatment of data	146
3.3.4	Results and Discussion	148
(i)	Tetrahalocobaltates(II)	148
(ii)	Pentahalocobaltates(II)	151
(iii)	Trihalocobaltates(II)	156

CONTENTS  
(Continued)

	<u>Page No.</u>
3.4 Conductance Measurements	160
3.4.1 Introduction	160
3.4.2 Experimental	161
3.4.3 Treatment of data	162
3.4.4 Results and Discussion	165
3.5 X-ray powder diffraction	177
3.5.1 Experimental	177
3.5.2 Results and Discussion	177
6. Chapter 4 Summary and Further Scope of Work	191-195
4.1 Summary	191
4.2 Further Scope	195
7. References	196-211
8. Bio-data of the author.	212