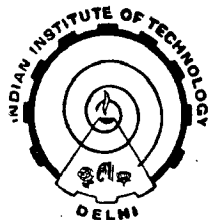


**STUDIES ON MIXED AND SUBSTITUTED TETRAHALOMANGANATES(II)  
AND MIXED PENTAHALOMANGANATES(II)**

BY  
**BAIDYANATH THAKUR**

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



DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, DELHI  
**SEPTEMBER, 1985**

*Dedicated  
to  
My Parents*

C E R T I F I C A T E

This is to certify that the thesis entitled "Studies on Mixed and Substituted Tetrahalomanganates (II) and Mixed Pentahalomanganates (II)", being submitted by Mr. Baidyanath Thakur to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bona fide research work carried out by him. Mr. Thakur 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-110016

## ACKNOWLEDGEMENTS

I sincerely express the deep sense of gratitude to Professor N.K. Jha, who welcomed me as a doctoral student and took incessant pains to supervise my research work; without which the thesis would not have attained the present form.

I am also grateful to Professors B.L. Khandelwal, R.D. Dua, J.C. Ahluwalia, R.P. Gandhi, G.V. Jere and R.C. Agrawal (B.H.U., Varanasi) for their help and encouragement during my research work.

I cannot restrain myself from thanking Prof.Y.Thakur (Head, Chemistry Department, L.N. Mithila University, Darbhanga), Dr. Ashutosh Mishra, Assistant Professor, Mechanical Engineering Department, I.I.T. Delhi) and Dr. G.K. Jha (Physics Department, L.N. Mithila University, Darbhanga) for their valuable advice to take up research work at I.I.T. Delhi.

My sincere thanks are due to Dr. Radheyshyam Prasad (Chemistry Department, St. Columba's College, Hazaribag, Bihar) who not only helped me in the final preparation of the manuscript but also added flavour to the material.

Helps from Drs. G.S. Singh (Physics Department, R.U., Ranchi), Ramadhar Singh, S.K. Gupta (N.P.L., Delhi), A. Mishra,

C.S.R. Murthy and Mrs. Amrita Kumari, are thankfully acknowledged.

I am truly indebted to my friends, D.M. Joshi, A.C. Mishra, Amitabh Ghosh, R.K. Jha and A. Arora for their kind help at various stages of the work. I cannot really ignore the forbearance of the members of my family.

I am also thankful to University Grants Commission, India for awarding Teacher Fellowship under the 'Faculty Improvement Programme' and authorities of C.M. Science College, Darbhanga and L.N. Mithila University, Darbhanga for the sponsorship.

Last but not the least, fine tracing by Sri N.L.Arora and excellent typing by Sri S.L. Aneja, deserve my heart-felt thanks.

*Baidyanath Thakur*  
(Baidyanath Thakur)

## ABSTRACT

The present investigation reports the isolation and characterization of different types of halomanganate(II) derivatives which are listed below:

(i) mixed tetrahalomanganates(II) species of the types  $(\text{MnX}_2\text{Y}_2)^{2-}$  (X and Y are Cl, Br or I), and  $(\text{MnCl}_{4-n}\text{Br}_n)^{2-}$  (n=1 or 2),

(ii) mixed isothiocyanatohalomanganates(II),  $[\text{Mn}(\text{NCS})_2\text{X}_2]^{2-}$  (X = Cl, Br or I), and  $[\text{Mn}(\text{NCS})_n\text{Cl}_{4-n}]^{2-}$  (n = 1 or 3),

(iii) substituted tetrahalomanganates(II)  $\text{R}(\text{MnX}_3\text{L})$  (where R =  $(\text{C}_2\text{H}_5)_4\text{N}$ ,  $(n\text{-C}_3\text{H}_7)_4\text{N}$ ,  $(\text{C}_6\text{H}_5)_4\text{P}$  or  $(\text{C}_6\text{H}_5)_4\text{As}$ ; X = Cl or Br and L is a neutral donor - triphenylphosphine or quinoline),

(iv) substituted mixed tetrahalomanganates(II) species of the type  $(\text{MnX}_2\text{YL})^-$  (where X and Y are Cl, Br or I and L = triphenylphosphine or quinoline)

and (v) mixed pentahalomanganates(II) of the type  $\text{R}_3(\text{MnX}_2\text{Y}_3)$  (where R =  $(\text{C}_2\text{H}_5)_4\text{N}$ ,  $(n\text{-C}_3\text{H}_7)_4\text{N}$  or  $(n\text{-C}_4\text{H}_9)_4\text{N}$ ; X and Y are Cl, Br or I).

These complexes have been characterized by elemental analyses, melting points, magnetic susceptibility measurements, i.r. and far i.r., electronic spectral studies and molar conductance measurements.

The magnetic moment values fall within the usual range expected for high spin tetrahedral/pseudotetrahedral manganese(II) complexes. The observed bands in the i.r. spectra (in case of complexes containing thiocyanate) and far i.r. spectra (for all of the complexes) have been assigned on the basis of tetrahedral geometry around Mn(II). The bands in the electronic spectra (uv-visible) have also been assigned tentatively on the basis of tetrahedral geometry. On the basis of the far i.r. and electronic spectral study it has been concluded that the mixed pentahalomanganates(II) are in fact double salts containing tetrahedral Mn(II) e.g.  $(\text{MnX}_2\text{Y}_3)^{2-}$  is in fact  $(\text{MnX}_2\text{Y}_2)^{2-} \cdot \text{Y}^-$ . Molar conductance measured at a fixed concentration in nitromethane suggests the electrolyte type as manifest in the molecular formula of the complexes.

## LIST OF FIGURES

<u>Fig. No.</u>	<u>Caption</u>
1.	IR spectra of (a) $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_2\text{Cl}_2 \right]$ and (b) $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_2\text{Br}_2 \right]$ .
2.	IR spectrum of $\left[ \left( n\text{-C}_3\text{H}_7 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_2\text{I}_2 \right]$ .
3.	IR spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_3\text{Cl} \right]$ .
4.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{MnCl}_2\text{Br}_2 \right]$ .
5.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{MnBr}_2\text{I}_2 \right]$ .
6.	Far i.r. spectrum of $\left[ \left( n\text{-C}_3\text{H}_7 \right)_4\text{N} \right]_2 \left[ \text{MnCl}_2\text{I}_2 \right]$ .
7.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{MnClBr}_3 \right]$ .
8.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_2\text{Cl}_2 \right]$ .
9.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_2\text{Br}_2 \right]$ .
10.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_2 \left[ \text{Mn}(\text{NCS})_3\text{Cl} \right]$ .
11.	Far i.r. spectrum of $\left[ \text{C}_6\text{H}_5 \right)_4\text{As} \right] \left[ \text{MnCl}_3(\text{Ph}_3\text{P}) \right]$ .
12.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right] \left[ \text{MnBr}_3(\text{Ph}_3\text{P}) \right]$ .
13.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right] \left[ \text{MnCl}_2\text{Br}(\text{Ph}_3\text{P}) \right]$ .
14.	Far i.r. spectrum of $\left[ \left( n\text{-C}_3\text{H}_7 \right)_4\text{N} \right] \left[ \text{MnBr}_2\text{IQ} \right]$ .
15.	Far i.r. spectrum of $\left[ \left( n\text{-C}_4\text{H}_9 \right)_4\text{N} \right] \left[ \text{MnCl}_2\text{IQ} \right]$ .
16.	Far i.r. spectrum of $\left[ \left( \text{C}_2\text{H}_5 \right)_4\text{N} \right]_3 \left[ \text{MnCl}_2\text{Br}_3 \right]$ .
17.	Far i.r. spectrum of $\left[ \left( n\text{-C}_3\text{H}_7 \right)_4\text{N} \right]_3 \left[ \text{MnCl}_2\text{I}_3 \right]$ .

<u>Fig. No.</u>	<u>Caption</u>
18.	Energy level diagram of $Mn^{2+}$ in tetrahedral ligand field.
19.	Electronic spectrum of $[-(C_2H_5)_4N]_2[MnCl_2Br_2]$ .
20.	Electronic spectrum of $[(n-C_3H_7)_4N]_2[Mn(NCS)_2I_2]$ .
21.	Electronic spectrum of $[(C_6H_5)_4P][MnCl_3(Ph_3P)]$ .
22.	Electronic spectrum of $[(n-C_4H_9)_4]_3[MnBr_2I_3]$ .

## LIST OF TABLES

<u>Table No.</u>	<u>Title</u>
I	Elemental analyses and melting points.
II	Room temperature magnetic data.
III	IR spectral data ( $4000-400\text{ cm}^{-1}$ ) of the mixed isothiocyanatohalomanganates(II).
IV	Correlation between change of symmetry and number of i.r. active vibrations.
V	Far i.r. spectral data ( $350-50\text{ cm}^{-1}$ ) of mixed and simple tetrahalomanganates(II).
VI	Far i.r. spectral data ( $350-50\text{ cm}^{-1}$ ) of mixed isothiocyanatohalomanganates(II).
VII	Far i.r. spectral data ( $350-100\text{ cm}^{-1}$ ) of substituted tetrahalomanganates(II).
VIII	Far i.r. spectral data ( $350-100\text{ cm}^{-1}$ ) of substituted mixed tetrahalomanganates(II).
IX	Far i.r. spectral data ( $350-50\text{ cm}^{-1}$ ) of mixed pentahalomanganates(II).
X	Electronic spectral data.
XI	Molar conductance data of $\sim 10^{-3}\text{M}$ solutions in nitromethane.

## CONTENTS

	Page
CERTIFICATE	.. (i)
ACKNOWLEDGEMENTS	.. (ii)
ABSTRACT	.. (iv)
LIST OF FIGURES	.. (vi)
LIST OF TABLES	..(viii)
CHAPTER I	
INTRODUCTION	.. 1
1.1 Simple tetrahalo- and tetraiso-	
thiocyanatomanganates(II)	.. 1
1.2 Mixed tetrahalomanganates(II)	.. 17
1.3 Substituted tetrahalomanganates(II)..	17
1.4 Substituted mixed tetrahalo-	
manganates(II)	.. 18
1.5 Pentahalomanganates(II)	.. 18
Applications	.. 19
Scope of the present work	.. 20
References	.. 23
CHAPTER II	
PREPARATIVE INVESTIGATION	.. 37
2.1 Introduction	.. 37
2.2 Purification of the reagents	
and solvents	.. 38
2.2.1 Reagents	.. 38
2.2.2 Solvents	.. 39
2.3 Preparation	.. 41
2.3.1 Mixed tetrahalomanganates(II)..	41

	Page
2.3.2 Diisothiocyanatodihalo- manganates(II): $R_2[Mn(NCS)_2X_2]$ and tri/monoisothiocyanato- mono/trichloromanganates(II): $E_2[Mn(NCS)_nCl_{4-n}]$	.. 44
2.3.3 Substituted tetrahalo- manganates(II): $R[MnX_3L]$	.. 46
2.3.4 Substituted mixed tetrahalo- manganates(II): $R[MnX_2YL]$	.. 48
2.3.5 Mixed pentahalomanganates(II): $R_3[MnX_2Y_3]$	.. 49
2.4 Analyses	.. 51
2.4.1 Analyses of halogens	.. 51
2.4.2 Analysis of thiocyanate	.. 52
2.4.3 Analysis of manganese	.. 52
2.4.4 Analyses of carbon and hydrogen	.. 52
2.5 General properties	.. 53
2.6 Discussion	.. 61
References	.. 65
CHAPTER III STRUCTURAL STUDIES	.. 66
3.1 Magnetic moments	.. 66
3.1.1 Introduction	.. 66
3.1.2 Experimental	.. 68
3.1.3 Results and discussion	.. 70
References	.. 75
3.2 Infrared spectra	.. 76
3.2.1 Introduction	.. 76
3.2.2 Experimental	.. 76

	Page
3.2.3 Results and discussion ..	77
3.2.3(i) IR spectra of mixed iso-thiocyanatohalomanganates(II)..	77
3.2.3(ii)Far i.r. spectra ..	86
(a) Mixed tetrahalomanganates(II)..	86
(b) Mixed isothiocyanatohalomanganates(II) ..	95
(c) Substituted tetrahalomanganates(II) ..	103
(d) Substituted mixed tetrahalomanganates(II) ..	108
(e) Mixed pentahalomanganates(II)..	116
References ..	125
3.3 Electronic spectra ..	128
3.3.1 Introduction ..	128
3.3.2 Experimental ..	132
3.3.3 Results and discussion ..	132
Mixed tetrahalomanganates(II)..	133
Mixed isothiocyanatahalomanganates(II) ..	144
Substituted and substituted mixed tetrahalomanganates(II)..	145
Mixed pentahalomanganates(II)..	146
References ..	148
3.4 Conductance measurements ..	149
3.4.1 Introduction ..	149
3.4.2 Experimental ..	150
3.4.3 Molar conductance ..	150
3.4.4 Results and discussion ..	156
References ..	158

	Page
CHAPTER IV SUMMARY AND FURTHER SCOPE OF THE WORK ..	159
4.1 Summary ..	159
4.2 Further scope of the work ..	161
LIST OF PUBLICATIONS ..	163
BIO-DATA ..	164