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

BY

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SUBMITTED

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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.

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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 $(MnX_2Y_2)^{2-}$ (X and Y are Cl, Br or I), and $(MnCl_{4-n}Br_n)^{2-}$ (n=1 or r),

(ii) mixed isothiocyanatohalomanganates(II), $[Mn(NCS)_2X_2]^{2-}$ (X = Cl, Br or I), and $[Mn(NCS)_nCl_{4-n}]$ (n = 1 or 3),

(iii) substituted tetrahalomanganates(II) $R(MnX_3L)$ (where R = $(C_2H_5)_4N$, $(n\text{-}C_3H_7)_4N$, $(C_6H_5)_4P$ or $(C_6H_5)_4As$; X = Cl or Br and L is a neutral donor - triphenylphosphine or quinoline),

(iv) substituted mixed tetrahalomanganates(II) species of the type $(MnX_2YL)^-$ (where X and Y are Cl, Br or I and L = triphenylphosphine or quinoline)

and (v) mixed pentahalomanganates(II) of the type $R_3(MnX_2Y_3)$ (where R = $(C_2H_5)_4N$, $(n\text{-}C_3H_7)_4N$ or $(n\text{-}C_4H_9)_4N$; 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. $(MnX_2Y_3)^{2-}$ is in fact $(MnX_2Y_2)^{2-}.Y^-$. Molar conductance measured at a fixed concentration in nitromethane suggests the electrolyte type as manifest in the molecular formula of the complexes.

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