

INTRODUCTION

Addition compounds of thiourea with metal salts had been known to exist even before the postulation of the theory of coordination by Werner. A very wide and assorted variety of metals like mercury, lead, copper, iron, aluminium, etc., had been complexed with thiourea by earlier workers like Maly, Rosenheim, Claus, Meyer and others. Beilstein's handbook of organic chemistry¹ gives a more or less complete anthology of the early work in the field of metal thiourea complexes. It appears, however, that these authors, beyond identifying this new type of addition compounds and assigning molecular formulae to them, did not go any further. The purpose of the present work is to give a unified account of the metal thiourea complexes in terms of their properties and constitution.

The metal thiourea complexes have found extensive use in the qualitative and quantitative estimation of metals and a brief summary of such work is given below under three heads.

(a) Colour Reactions :

- (i) Estimation of bismuth².
- (ii) Estimation of copper, cadmium and mercury³.
- (iii) Microchemical test for thallium⁴.
- (iv) Colorimetric determination of osmium⁵, ruthenium⁶ and molybdenum⁷.

- (v) Photometric determination of palladium⁸ and tin⁹.
- (vi) Qualitative detection of cobalt¹⁰.

(b) Precipitation Reactions :

- (i) Gravimetric estimation of lead¹¹, cadmium¹², silver¹³, bismuth¹⁴, thallium¹⁵, etc., by the precipitation of thiourea complex.
- (ii) Separation of cations as sulphides¹⁶.

(c) Other Reactions :

- (i) As a sulphuretting reagent for certain cations used in the separation of metals e.g., separation of cadmium from zinc¹⁷, zinc from mercury and silver¹⁸.
- (ii) For sulphuration of metals like arsenic, antimony and mercury¹⁹.

Polarographic behaviour of the complexes of mercury²⁰, copper²¹, lead and cadmium²² with thiourea have been studied recently.

Physical studies on metal thiourea complexes.

Only very few investigations of metal thiourea complexes by physical methods like X-ray diffraction, absorption spectroscopy etc., are recorded in the literature. Structural elucidation by X-ray diffraction of $\text{CuCl} \cdot 3 \text{CS}(\text{NH}_2)_2$ ²³ and $\text{PbCl}_2 \cdot 2\text{CH}_4\text{N}_2\text{S}$ ^{23A}, a

crystallographic study of a palladium complex²⁴ and infra red absorption studies on a few thiourea complexes of Pt, Pd and Zn²⁵ are a few instances. Siddhanta and Banerjee (unpublished result, private communication) have made magnetic studies on copper complexes of substituted thioureas. The present work reports some studies on the magnetic behaviour of thiourea complexes of Mn, Co and Ni (vide infra).

Beilstein's anthology¹ of metal thiourea complexes show certain important characteristics of this series of compounds. Large number of metal ions, especially of the non-transitional elements, have a tendency to form a series of complexes with thiourea in which the metal ion seems to have varying coordination numbers. For example, the following complexes of mercuric ion with thiourea are reported : (i) $\text{HgCl}_2 \cdot 4\text{CH}_4\text{N}_2\text{S}$; (ii) $\text{HgCl}_2 \cdot 2\text{CH}_4\text{N}_2\text{S}$; (iii) $\text{HgSO}_4 \cdot 3\text{CH}_4\text{N}_2\text{S}$; (iv) $\text{HgI}_2 \cdot \text{CH}_4\text{N}_2\text{S}$ and (v) $3\text{HgO} \cdot 2\text{CH}_4\text{N}_2\text{S} \cdot 3\text{H}_2\text{O}$. Further, compounds of the type $2\text{CoSO}_4 \cdot 3\text{CH}_4\text{N}_2\text{S}$ and $2\text{NiCl}_2 \cdot 7\text{CH}_4\text{N}_2\text{S}$ have been reported where fractional molecules of thiourea are being attached to one metal ion and this will necessitate the introduction of bridge structures in the constitution of these complexes. In the early work, molecular formulae have been assigned mostly on the basis of the estimation of either the metal or the thiourea content though an analysis for both seems to be necessary for accurate work. Much of the previous work is the outcome of

analysing the compounds crystallised from solutions of the two components viz. salt and thiourea in aqueous or nonaqueous medium. One can reasonably doubt whether the compounds thus obtained are pure compounds or are really mixtures. This emphasis on the isolation of a really pure complex becomes very important since a number of metals form a series of complexes with thiourea and the probability for a mixture to be taken as a pure complex is considerable. In compounds where fractional molecules of thiourea are involved per metal ion, the unambiguity in the purity of the complex has to be established before a structural assignment can be attempted. So, it becomes clear that the first step in the systematic study of the chemistry of metal thiourea complexes is the fixing up of the number and formulae of the definite single chemical entities present in any metal salt-thiourea system. Physical studies like magnetic measurements and X-ray diffraction will have to follow such studies.

The number and formula of definite single addition compounds formed from two components can be settled finally and unequivocally only by studying the phase equilibrium of the system. In the present study, therefore, phase equilibrium studies of three component systems viz. metal salt-thiourea-water at a fixed temperature have been made. The usefulness of such studies and the construction of phase diagram is not only restricted to the unambiguous

identification of solid complexes, but also to know exactly the conditions of their formation in the solid state. In certain favourable cases, the solubility relations help us in getting a qualitative and even a semi-quantitative idea of what is happening in solution (Chapters 8, 9 and 10).

Literature records such phase equilibrium studies in two systems of thiourea (1) Thiourea-ammonia-water²⁶ and (2) sodium chloride-thiourea-water²⁷. The former system revealed the existence of two complexes (a) $\text{NH}_3 \cdot \text{CH}_4\text{N}_2\text{S}$ and (b) $3\text{NH}_3 \cdot \text{CH}_4\text{N}_2\text{S}$ whereas the latter showed none.

The common methods of investigation of the inorganic complexes such as conductivity, calorimetry, potentiometry, etc., have not been extensively put to use in metal thiourea complexes. The thermometric investigation of cadmium chloride-thiourea-water system²⁸ and the conductometric and viscometric work on the system, thiourea-sodium chloride-water²⁹ are two instances of such studies.

An interesting outcome of the present work is the elucidation of the theory of solubility of polar nonelectrolytes in polar solvents like water, by which the phenomena of "salting out" and "salting in" have found a new interpretation (Chapter 9). A good deal of new light has been thrown on the phenomenon of solubility in general and a qualitative theory to explain the

influence of polar nonelectrolytes on the solubility of electrolytes has been proposed (Chapter 9).