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Dithiolate complexes: Synthesis and thermal behavior

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Abstract

In this brief review general method of synthesis of dithiolate ligands, their complexes and thermal behaviour has been presented. Thermal degradation of metal dithiolates generally gives metal or metal sulfide as an end product. Sometimes oxide of metal forms. In some cases increase in mass take place due to oxidation of decomposition product.

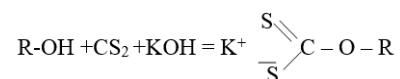
Keywords: Synthesis, dithiolate, thermal behavior

Introduction

Dithiolate ligands are very versatile reagent finding diverse application. In the past decades large number of dithiolate ligands were synthesized and complexes have been prepared from these ligands. Overall literature is vast. General method of preparation of some dithiolate ligands, complexes and their thermal behaviour have been reviewed herein.

Preparation of xanthates

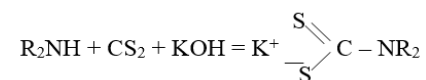
Xanthate salts are prepared by reaction of alcohol with CS₂ and a base generally aqueous.



Various kinds of xanthates are derived from different alcohols.

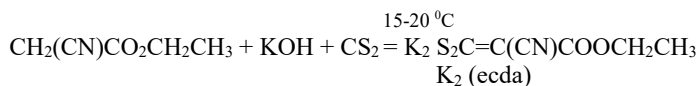
Preparation of Dithiocarbamates

Dithiocarbamates are prepared from various primary or secondary amines by reacting these with CS₂ and a base, eg NaOH, KOH etc.

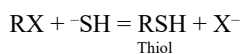


Ligands are xanthates, dithiocarbamates, trithiocarbonate and various other dithiolates. Method of preparation of some of these is reviewed below.

Several dithiolates are prepared from diethylmalonate, ethylcyanoacetate type of esters^[1]. By reacting these compounds with CS₂ and a base in appropriate solvent under suitable conditions dithiolate salts can be prepared. Potassium 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate is obtained by following reaction.



Acetylacetone fails to give corresponding dithiolate salt if reacted with CS₂ and base. Thiol compounds can be prepared by reacting sodium sulfhydryde (obtained from NaOH and H₂S) with alkyl halide.



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Alkyl halide used for this purpose is primary or secondary. In tertiary halides predominant competing reaction is elimination reaction leading to formation of alkene. Various other dithiolates are prepared by adopting different procedures. Potassium trithiocarbonate is obtained as red solution in dmf by reacting CS₂ and KOH. Potassium monothiooxalate is derived from ester diethyloxalate by reacting it with potassium dissolved in ethanol and solution saturated with H₂S [2]. Maleonitriledithiolate, a very important planar 1,2-type of dithiolate, is synthesized from sodium cyanide and CS₂ in dmf [3,4].

Synthetic route to complexes

Homoleptic metal complexes of these ligands have been prepared by reacting metal and ligand in appropriate ratio and precipitating the complex using coordinatively saturated bigger salts, eg quarternary ammonium salts, arsonium salts etc. Heterobimetallic complexes are prepared similarly through tetrathiometalate route. Sulfide clusters can also be prepared through tetrathiometalate species [5].

Thermal behavior

Metal dithiolate complexes show semiconductance properties. On thermal decomposition metal dithiolates generally yields metal sulfide as final product. These complexes have potential to be used as precursor material for sulfides for use in photovoltaic material and nano particles.

In dithiolates, like other complexes, water of crystallization is lost around 100 °C whilst coordinated water is released at much higher temperature around 180 °C. steps in which thermal decomposition take place may be many depending on presence of various decomposable moieties and structural features of the complex.

Thermal behaviour of xanthate esters have been reported much earlier. The decomposition leads to formation of alkene at elevated temperature which is known as Chugaev elimination. Metal xanthates simply yield Metal or Sulfide of the metal. Pyrolysis of gold xanthate complexes give gold metal around 200 °C [6]. Solvent thermolysis of indium xanthate furnishes β -In₂S₃ nano particles [7]. Thermal decomposition of mixed ligand bimetallic complexes of shift bases and xanthate result into formation of metal sulfide as an end product [8]. Metal dithiocarbamate complexes decompose similarly giving metal or metal sulfide. Thermolysis of dialkyldithiocarbamate complexes of In(III) give metal or sulfide of metal depending upon presence of alkyl group [9]. Mixed ligand complexes of Zn, Cd with dithiocarbamate and diimine bases show two decomposition steps corresponding to presence of two kinds of ligands. In these complexes, cadmium complex show higher stability in comparison to its Zn analog [10]. N-methyl-N-Phenyldithiocarbamate Zn, Cd, Hg give sulfide of metal by single weight loss [11]. Mixed ligand complex of Zinc with dithiocarbamate and diimine ligand produced α -ZnS at 350 °C [12]. Formation of stable metal thiocyanate or cyanate intermediate as decomposition product of shift bases dithiocarbamate complexes with various metals have been reported [13]. Dithiocarboxylato complexes of various metal, like Indium and other metals have been studied. Tris (dithiocarboxylato) In(III) give β -In₂S₃ [14]. Solvothermal pyrolysis of Zn, Cd and Hg give metal Sulfide nano particles whilst heating in furnace produces metal sulfides

with cubic or hexagonal packing [15]. Bimetallic complex may give ternary metal sulfide material as an end product of thermal decomposition [16]. Some times thermal behaviour of complexes are far from being strait forward. Metal oxide formation may take place from oxygen present in nitrogen under which decomposition study is carried out. In some cases increase in mass take place due to oxidation of decomposition product.

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