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ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (1): Pg. 347-349

Synthesis Methods of Metal Chelates β -ketoesters - (A Critical Review)

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(Received: November 16, 2010; Accepted: December 13, 2010)

abstract

A critical review of various methods reported in the literature for the synthesis of β -ketoesterato complexes is furnished. A vast majority of the synthetic methods for metal β -ketoesterato employ neutral β -ketoester as the starting material. This is reacted with various types of substrates such as alkoxides, salts or oxides of metals and in some cases also with the metal powder. Trans esterification has been resorted to frequently.

Key words: Synthesis and β -ketoesterato complexes and Trans esterification.

INTRODUCTION

Studies on metal chelates of β -ketoesters have been mostly extensions of similar studies on complexes of β -diketones. Probably, the lower stability of the β -ketoesterato complexes would have frustrated many a systematic and concerted efforts of ardent researchers. The earliest report of an ethyl acetoacetate complex is credited to Emmert and Jarczynski.

Many of the complexes β -ketoesters are mixed ligand complexes containing halogen, water of heterocyclic base as co-ligand(s) or are alkoxy or oxo complexes. Complexes of the mixed type are expected when the coordination number of the metal ion is not twice its oxidation number. When

the former number is more than twice the later, neutral ligands get coordinated and if less than twice, the coordination sphere contains extra negative ligands for electroneutrality.

Methods of synthesis

By-Trans-esterification

This method involves the reflexing of the metal chelate of a β -ketoester in an excess of the appropriate higher alcohol for 3 to 16 hours depending on the nature of the metal. The resulting solution is then concentrated to isolate the transformed metal chelate, which is then recrystallised from the corresponding alcohol.

The β -ketoester chelates of $\text{Cu}^{2,3}$, Al^2 and Be^2 undergo facile trans-esterification reaction

leading to metal chelates of other β -ketoesters. In view of the difficulty of preparing metal chelates of β -ketoesters directly, this indirect method of synthesis is beneficial.

Using Metal alkoxides

Metal alkoxides constitute a very useful class of starting materials for the synthesis of metal β -ketoesterates. In this method, the metal alkoxides, usually isopropoxide, ethoxide or methoxide, is mixed with the β -ketoester and refluxed for 4-5 hours at 100-140°C. The reaction is usually carried out in a hydrocarbon medium such as benzene, xylene or ligron. By varying the stoichiometric ratio, different types of products can be isolated. The reactions are exothermic. After collecting the liberated alcohol azeotropically, the metal complexes are obtained by concentrating the solution under reduced pressure.

By this method, β -ketoester (mostly ethylacetoacetate) complexes of U⁴, Ga⁵, Ta⁶, Sm⁷, Al^{8,9}, (Ti,Zr)^{10,11}, (La, Pr, Nd)¹², Zn¹³, Sb¹⁴, (Gb,Er)¹⁵ have been synthesized. To avoid possible transesterification, the metal alkoxide should be properly chosen. Since such caution doesn't seem to have been exercised in most cases, purity of the product is in doubt.

Using Metal salts of mineral acids

The aqueous solution of the metal salt is mixed with an ethanolic solution of the ligand and the complex is precipitated by buffering the mixture with sodium acetate or by controlling the pH by adding alcoholic KOH, ammonia, sodium carbonate, triethyl amine or urea. When a heterocyclic base is to be present as a co-ligand, a liberal excess of it is included in the reaction mixture. Rarely, concentration of the reaction mixture is necessary to cause crystallisation of the complex.

Solvent such as benzene, carbon tetrachloride or neat ketoester are used for those metal halides and β -ketoesters soluble in them. Complexes of V¹⁶, Ti¹⁷, W¹⁸, Ni¹⁹, Ga⁵, Fe²⁰, (Ca, Ba, Al)⁸, (Cu, Co)²¹, Zn²³, Mn²⁴ and Be²⁵ have been prepared by this method. Instead of halides, the metallic sulphates (Cu²⁶, Fe¹) and nitrates (Co²⁷, U²⁸) also have been used for preparing metal β -ketoesterates.

The existence of metal complexes in a solvent so extremely acidic as liquid HF, in which the complexing agents themselves must exist largely in cationic form, is of practical and theoretical importance²⁹. Ethyl acetoacetate though formed copper complex in HF, there was no evidence for complex formation with other metals²⁹.

Using Metallic oxides and hydroxides

The metal β -ketoesterates of Ca³⁰ and Pb³¹ could be obtained from their oxides in an inert solvent as benzene or xylene. The metal β -ketoesterates of alkaline earth metals³² have been obtained from their hydroxides in the absence of solvents. This method has the advantage of introducing minimum amount of impurity.

Using pure metals

The β -ketoesterates of Cu³³ and Mg³⁴ could be obtained through direct reaction of the metal powder with the ketoester.

Method of purification of the samples obtained by various route involved recrystallisation from any one of the following suitable solvents: benzene, ethanol, chloroform, carbon tetrachloride, carbon disulphide or petroleum ether.

CONCLUSION

Among β -ketoesters, ethyl acetoacetate is the most frequently studied ligand. The continued interest³⁵ in the study of β -ketoesterato complexes appears to be mainly due to their diverse applications in areas such as spectral studies, gas chromatography, solvent extraction, column and thin layer chromatography, nmr shift reagents, laser technology, stabilizers for chlorine containing polymers, wood preservatives, varnish composition, fungicides and as initiators in polymerisation reactions.

ACKNOWLEDGEMENTS

The author is grateful to UGC, New Delhi, for the award of a fellowship and Prof. N. Thankarajan, former Head, Department of Chemistry, University of Calicut for initiating his interest in β -ketoesterato complexes.

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