Study on Some Complex Salts of Malonic Acid

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Summary

A number of complex malonates of the general formulae $R_2[M^{II}(C_3H_2O_4)_2] \cdot x\, H_2O$ [where R = K, Na, and Tl(I); M(II) = Zn, Cd, Hg and Be] have been prepared by treating the freshly precipitated heavy metal hydroxide with a solution of alkali or thallous hydrogen malonate and submitting the resulting solution to crystallisation. The general behaviour of these compounds has been studied.

Introduction

In the previous communication[1]), it has been shown that malonic acid like oxlic acid, forms complex salts with trivalent heavy metal ions of the general formula $Tl_3[M(C_3H_2O_4)_3] \cdot H_2O$, where M-stands for trivalent metal ions, Al, Ga, Cr and Mn.

No systematic attempt has so far been made to obtain similar complex salts of the bivalent metals, although Britton[2]) and coworkers have investigated the composition of these complex salts by physico-chemical methods.

The praperation of quite a good number of such double or complex salts with oxalic acid has been reported. Thus Souchay and Lenssen[3]) prepared double oxalates of the alkali and some bivalent metalls e. g., Mn, Fe, Zn, Cd and Hg. Wyroubow[4]) obtained similar compounds with Be. In the present communication the preparation of complex malonates of the general formula. $R_2[M^{II}(C_3H_2O_4)_2] \cdot H_2O$ [R = Na, K or Tl and M^{II} = Zn, Cd, Hg and Be] has been reported and their properties described.

Experimental

The general method followed for preparation of complex malonates is described below. Requisite quantity of freshly precipitated heavy metal hydroxide was digested with a

[1]) T. N. Srivastava and S. P. Agrawal, J. prakt. Chem. **6**, 58 (1958).

[2]) H. T. S. Britton and M. E. D. Jarret, J. chem. Soc. London 1728 (1935).

[3]) A. Souchay and F. Lenssen, Ann. **102**, 42, 44, 46, 50; **103**, 314, 316, 31; **105**, 254, 255.

[4]) Wyroubow C. 1902, II, 631.

solution of alkali hydrogen or thallous hydrogen malonate. The undissolved hydroxide was removed by filtration and the filtrate was allowed to crystallize over concentrated sulphuric acid in a vacuum desiccator. The crystals were filtered on a filter pump, washed with water-alcohol mixture and finally with ether. The crystals thus, obtained were dried in a vacuum desiccator.

The complex malonates prepared as above were analysed for heavy metals (Zn, Cd, Hg and Be) after the decomposition of the complexes with strong sulphuric acid. The filtrate after proper treatment was utilised for the estimation of the monovalent ions (alkali metal and Tl). Potassium and sodium were estimated by LANGE FLAME Photometer, and thallium was determined as thallous chromate, Zinc and cadmium were determined as oxinates; mercury as sulfhide and beryllium as oxide.

The number of water molecules in these compounds was determined indirectly by finding out the loss in weight produced on heating these compounds to 110 °C. The fact that analysis of the compounds (after heating to 110 °C) always corresponded with the composition of anhydrous salts showed that the results obtained for the water content, were reliable.

The results of analyses of the various malonate complexes together with their salient properties are summarised below:

Potassium Zinc malonate:
Found: Zn 18.4, K 21.5 and H_2O 9.2%
$K_2[Zn(C_3H_2O_4)_2] \cdot 2\,H_2O$ requires Zn 18.7, K 22.4 and H_2O 9.4%.

Sodium Zinc malonate:
Found: Zn 20.0, Na 13.5, and H_2O 5.2%
$Na_2[Zn(C_3H_2O_4)_2]\,H_2O$ requires. Na 13.9, Zn 19.5 and H_2O 5.6%.

Thallous Zinc malonate
Found: Tl 57.8, Zn 9.4 and H_2O 5.8%
$Tl_2[Zn(C_3H_2O_4) \cdot 2\,H_2O$ requires Tl 57.3, Zn 9.1 and H_2O 5.2%.

All the zinc malonates are white crystalline solids, highly soluble in water (solubility of ptassium zinc malonate is 27% at 30 °C and 31.3% at 35 °C). All of them are stable upto about 250 °C but on further heating they get decomposed to zinc oxide. Potassium and thallous zinc malonates crystallisse more easily than the corresponding sodium salt.

Potassium cadmium malonate:
Found: Cd 28.0, K 19.4%.
$K_2[Cd(C_3H_2O_4)2]$ requires Cd 28.4; K 19.7%.

Sodium cadmium malonate
Found: Cd 27.7, Na 11.2, H_2O 8.8%
$Na_2[Cd(C_3H_2O_4)_2] \cdot 2\,H_2O$ requires Cd 28.0, Na 11.6 and H_2O 8.5%.

Thallous cadmium malonate:
Found: Tl(I) 54.0, Cd 15.2 and H_2O 4.5%
$Tl_2[Cd(C_3H_2O_4)_2] \cdot 2\,H_2O$ requires Tl (I) 53.6, Cd 14.8 and H_2O 4.7%.

The complex malonates of cadmium and monovalent metals (Na, K and Tl (I)) are similar to their zinc counterparts in their general appearance solubility and action of heat. (Solubility of Thallous cadmium malonate in water is 16% at 30 °C and 19% at 35 °C).

Potassium mercury malonate:
Found: K 14.5, Hg 37.2, H_2O 7.0%
$K_2[Hg(C_3H_2O_4)_2] \cdot 2\,H_2O$ requires K 15.0, Hg 36.6, H_2O 6.8%.

Sodium mercury malonate
Found: Na 9.8, Hg 47.2%
$Na_2[Hg(C_3H_2O_4)_2]$ requires Na 10.2, Hg 46.7%.

Thallous mercury malonate:
Found: Tl 48.8, Hg 25.5, H_2O 1.8%
$Tl_2[Hg(C_3H_2O_4)_2] \cdot 2\,H_2O$ requires Tl 49.2, Hg 24.12, H_2O 2.16%.

All the complex malonates of mercury are white crystalline solids, soluble in water and melt on heating. The melting points of sodium potassium and thallium mercury malonates are 196°, 170° and 216 °C respectively.

Potassium beryllium malonate:
Found: K 25.5, Be 3.6, H_2O 5.5%
$K_2[Be(C_3H_2O_4)_2] \cdot H_2O$ requires K 25.2, Be 2.9, H_2O 6.0%.

Sodium beryllium malonate:
Found: Na 16.1, Be 3.8, H_2O 5.9%
$Na_2[Be(C_3H_2O_4)_2]H_2O$ requires Na 16.6, Be 3.2, H_2O 6.3%.

Thallous beryllium malonate
Found: Tl 64.2, Be 1.8, H_2O 3.0%
$Tl_2[Be(C_3H_2O_4)_2] \cdot H_2O$ requires Tl 63.8, Be 1.4, H_2O 2.8%.

The properties of complex beryllium malonates are similar to their zinc and cadmium analogues.

Attempts to prepare the complex malonates of Lithium were, however, not successful, due to very high solubility of these salts.

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