XCV.—*Dithiomalonates.*

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It has been shown (Jones and Tasker, *Trans.*, 1909, **95**, 1904; Robinson and Jones, this vol., p. 62) that when certain metallic salts are added to solutions of dithio-oxalates, intense colours are produced, and that the production of these colours is due to the formation of complex acid ions. It seemed of interest to prepare thiomalonates and thiosuccinates, and to compare their properties with those of the thio-oxalates and the properties and colours of complex thiomalonates, thiosuccinates, and thiocarbonates, if formed, with those of the complex thio-oxalates previously described. This paper contains an account of the study of the derivatives of dithiomalonic acid, $\text{CH}_2(\text{CO}\cdot\text{SH})_2$.

It was found that when the theoretical quantity of amyl mercaptan was added to malonyl chloride, interaction took place with the formation of a pale yellow oil, and hydrogen chloride was evolved. In order to purify this oil it was distilled in a vacuum, but decomposition took place with the formation of a large quantity of a red solid, which appeared to have the composition and properties of polymerised carbon suboxide, $(\text{C}_3\text{O}_2)_x$ (Diels and Wolf, *Ber.*, 1906, **39**, 689). The same kind of decomposition was observed to a less

extent in the case of ethyl dithiomalonate (Purvis, Jones, and Tasker, *Trans.*, 1910, **97**, 2289). Consequently, the oil could not be obtained pure, and as distillation involved considerable loss, for the purposes of this investigation it was sufficient to remove the dissolved hydrogen chloride by allowing the oil to remain over lime in a vacuum.

Potassium Dithiomalonate, $\text{CH}_2(\text{CO}\cdot\text{SK})_2$.—The amyl dithiomalonate was saponified by heating on the water-bath with the theoretical quantity of alcoholic *N*-potassium hydrosulphide for about an hour, and then allowing to remain in the cold. After a few days potassium dithiomalonate separated in long, colourless needles:

0.2145 gave 0.1330 CO_2 and 0.020 H_2O . $\text{C}=16.90$; $\text{H}=1.04$.

0.2280 „ 0.5065 BaSO_4 . $\text{S}=30.5$.

$\text{C}_3\text{H}_2\text{O}_2\text{S}_2\text{K}_2$ requires $\text{C}=16.93$; $\text{H}=0.95$; $\text{S}=30.2$ per cent.

The behaviour of aqueous solutions of this salt towards various metallic salts was next examined.

Lead Acetate.—Yellow precipitate which blackens on keeping.

Mercuric Chloride.—Yellow precipitate soluble in excess of thiomalonate, which does not change much in appearance on boiling.

Mercurous Nitrate.—Black precipitate.

Silver Nitrate.—Yellow precipitate which blackens on keeping.

Copper Sulphate.—Yellow precipitate which blackens on heating.

Nickel Chloride.—Claret coloration.

Cobalt Chloride.—Green coloration with separation of sulphide.

Calcium Chloride.—Yellow precipitate.

Palladium Chloride.—Intense yellow coloration. If excess of palladium chloride is added, carbon monoxide is evolved, and palladium disulphide separates.

Ferrous Sulphate.—Reddish-purple coloration.

Bismuth, antimony, and tin give precipitates of the sulphides on boiling.

Aqueous solutions of potassium dithiomalonate thus behave in a similar manner to solutions of potassium dithio-oxalate. Colours are developed with solution of nickel, cobalt, palladium, and iron salts, and these colours, as will be shown later in two cases, are due to the formation of complex acid ions containing metal.

Reaction with Aniline Hydrochloride.—On mixing concentrated solutions of potassium dithiomalonate and aniline hydrochloride in the cold, a brisk effervescence due to evolution of hydrogen sulphide sets in immediately, and lustrous plates separate from the solution. These crystallised from alcoholic solution in needles melting at $222-223^\circ$, and proved to be malonanilide.

This reaction is similar to the decomposition of aniline dithio-oxalate (*loc. cit.*, p. 64).

Nickelodithiomalonates.

Potassium Nickelodithiomalonate, $\text{Ni}[(\text{COS})_2\text{CH}_2]_2\text{K}_2$.—When solutions of nickel chloride and potassium dithiomalonate are mixed, a claret coloration is developed. This colour persists at great dilution, being appreciable at a dilution of 1 part of nickel in 4,000,000 of water. The colour of the corresponding nickelothio-oxalate is perceptible at a dilution of 1 part of nickel in 40,000,000 of water. On mixing concentrated solutions of nickel chloride and potassium dithiomalonate, a red, crystalline precipitate separates. This salt dissolves in hot water, from which it crystallises on cooling in small, brick-red, flat-sided prisms:

0.3132 gave 0.1995 CO_2 and 0.0307 H_2O . $\text{C}=17.3$; $\text{H}=1.08$.

0.2560 „ 0.5940 BaSO_4 . $\text{S}=31.84$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{K}_2\text{Ni}$ requires $\text{C}=17.7$; $\text{H}=0.99$; $\text{S}=31.62$ per cent.

Barium Nickelodithiomalonate.—This salt separates in long needles when barium chloride is added to a concentrated solution of potassium nickelodithiomalonate. When exposed to air the crystals lose weight, and when dried in a desiccator over calcium chloride they lose water and become green. If these green crystals are moistened with water and allowed to dry in the open air, they become red once more. The change in colour is therefore due to dehydration.

The red salt was analysed with the following results:

0.4320 gave 0.1950 CO_2 and 0.1070 H_2O . $\text{C}=12.3$; $\text{H}=2.7$.

0.4806 „ 0.1922 BaSO_4 . $\text{Ba}=23.5$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{BaNi}, 6\text{H}_2\text{O}$ requires $\text{C}=12.6$; $\text{H}=2.8$; $\text{Ba}=23.9$ per cent.

The green salt obtained after allowing the red salt to remain in a desiccator over calcium chloride for several days gave the following results on analysis:

0.5040 gave 0.2680 CO_2 and 0.0465 H_2O . $\text{C}=14.5$; $\text{H}=1.02$.

0.5342 „ 0.2855 CO_2 „ 0.0535 H_2O . $\text{C}=14.5$; $\text{H}=1.1$.

0.4973 „ 0.2445 BaSO_4 . $\text{Ba}=28.9$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{BaNi}, 2\text{H}_2\text{O}$ requires $\text{C}=14.4$; $\text{H}=1.6$; $\text{Ba}=27.6$ per cent.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{BaNi}, 1\text{H}_2\text{O}$ „ $\text{C}=15.0$; $\text{H}=1.25$; $\text{Ba}=28.7$ „ „

The salt is therefore most probably the monohydrate. The same monohydrate is obtained by treatment of the red salt with alcohol and removal of the alcohol in a desiccator.

Aniline Nickelodithiomalonate.—This salt separates in chocolate-brown needles when a solution of aniline hydrochloride is added to one potassium nickelodithiomalonate:

0.2542 gave 0.3790 CO_2 and 0.0870 H_2O . $\text{C}=40.69$; $\text{H}=3.8$.

0.3002 „ 0.5314 BaSO_4 . $\text{S}=24.30$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{Ni}(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$ requires $\text{C}=40.53$; $\text{H}=3.8$;
 $\text{S}=24.0$ per cent.

Palladiodithiomalones.

Potassium Palladiodithiomalonate, $\text{Pd}[(\text{COS})_2\text{CH}_2]_2\text{K}_2$.—When a concentrated solution of palladium chloride is added slowly with stirring to a strong solution of potassium dithiomalonate, a yellow, crystalline salt separates. The addition of palladium chloride is continued until the liquid darkens in colour. Beyond this point further addition of palladium chloride causes decomposition, with separation of palladium disulphide.

The crystalline precipitate, after being collected and recrystallised from hot water, separates in pale yellow plates:

0.4145 gave 0.2315 CO_2 and 0.0370 H_2O . $\text{C}=15.25$; $\text{H}=0.90$.

0.2445 „ 0.5105 BaSO_4 . $\text{S}=28.65$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{K}_2\text{Pd}$ requires $\text{C}=15.7$; $\text{H}=0.89$; $\text{S}=28.3$ per cent.

Barium palladiodithiomalonate separates in long, yellow prisms when a solution of barium chloride is added to one of potassium palladiodithiomalonate.

Aniline Palladiodithiomalonate.—This salt separates in long needles or lustrous, hexagonal plates on adding a solution of aniline hydrochloride to a solution of potassium palladiodithiomalonate:

0.2445 gave 0.3400 CO_2 , 0.0835 H_2O , and 0.0465 Pd . $\text{C}=37.90$;
 $\text{H}=3.79$; $\text{Pd}=19.0$.

$\text{C}_6\text{H}_4\text{O}_4\text{S}_4\text{Pd}(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2$ requires $\text{C}=38.4$; $\text{H}=3.56$;
 $\text{Pd}=18.6$ per cent.

The free nickel- and palladio-thiomalonic acids are less stable than the corresponding thio-oxalic acids, and have hitherto not been obtained in a pure state.

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