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# VII.—Complex Thio-oxalates.

By CHARLES STANLEY ROBINSON and HUMPHREY OWEN JONES.

IN a former paper (Jones and Tasker, Trans., 1909, **95**, 1904) it was shown that highly coloured complex compounds are formed when solutions of nickel or cobalt salts are added to a solution of potassium dithio-oxalate. These colours persist through a long range of dilution, being appreciable at a dilution of one part of nickel or cobalt in 40,000,000 of water. A complex salt containing nickel was isolated and shown to have the composition of a potassium salt of nickelodithio-oxalic acid,  $H_2(COS)_4Ni$ . The intense colour of solutions of this salt is so remarkable that it was considered of interest to prepare other salts, and also to isolate the compound formed by the interaction of solutions of a cobalt salt and of potassium dithio-oxalate.

We have prepared several metallic and some organic salts of nickelodithio-oxalic acid; a similar series of salts of palladiodithiooxalic acid has been obtained, and it has also been shown that salts of the complex ferrodithio-oxalic acid are formed, but these are extremely unstable.

The complex salts derived from cobaltidithio-oxalic and rhodiidithio-oxalic acids have been isolated.

The molecular weights and electrical conductivities in aqueous solution of some of these salts have been determined. The results of these experiments indicate that nickelodithio-oxalic acid and cobaltidithio-oxalic acids are dibasic and tribasic respectively. The thermal decomposition of certain salts of these acids was studied with a view to obtain some insight into their constitutions. The experimental evidence at present available is in agreement with the formula  $M'(COS)_2$ ·Ni·(COS)<sub>2</sub>M' for salts of nickelodithio-oxalic acid, which is shown to be an acid of about the same strength as sulphuric acid. The salts of palladio- and ferro-dithio-oxalic acids are derived from dibasic acids of similar constitution.

The cobalti- and rhodii-dithio-oxalates are, however, derived from tribasic acids, and the formula of the cobalt compound can best be represented as:

$$Co \leftarrow (COS)_2 M' (COS)_2 M' (COS)_2 M' .$$

When potassium cyanide is added to solutions of potassium

nickelodithio-oxalate, potassium palladiodithio-oxalate, or potassium ferrodithio-oxalate, the colour of these solutions is discharged.

It was found that approximately four molecules of potassium cyanide were needed to decolorise one molecule of potassium nickelodithio-oxalate.

Potassium cyanide, however, decomposes cobalti- or rhodii-dithiooxalates only when concentrated.

Experiments are in progress with the object of preparing the free acids and the esters of the above-mentioned complex acids, and also for preparing similar complex salts derived from thiomalonates, thiosuccinates, and thiocarbonates, with the view of tracing a relationship between the constitution, colour, and stability of these complex compounds.

As large quantities of potassium dithio-oxalate were needed for this investigation, experiments were made with the object of determining the best conditions for the preparation of this salt. As ethyl and phenyl mercaptans are objectionable on account of their odours, amyl dithio-oxalate was prepared by the action of amyl mercaptan on oxalyl chloride. It is a pale yellow oil, boiling at  $205^{\circ}/20$  mm. From this ester the potassium salt is produced by saponification with alcoholic potassium hydrosulphide, the best yield being obtained when the calculated quantities of a normal solution of potassium hydrosulphide and amyl ester are gently warmed together for a short time.

Sodium dithio-oxalate,  $(COSNa)_2$ , which had not been previously obtained, was prepared by the action of alcoholic sodium hydrosulphide on amyl dithio-oxalate.

When amyl dithio-oxalate is warmed with a slight excess of N-alcoholic sodium hydrosulphide solution, saponification takes place, and the sodium salt separates on keeping. It was recrystallised from hot alcohol, and separated as colourless plates. A solution of this salt gives the same characteristic colour as the potassium salt when mixed with a solution of a nickel salt:

0.1570 gave 0.1340 Na<sub>2</sub>SO<sub>4</sub>. Na = 26.60.

 $(COSNa)_2$  requires Na = 26.72 per cent.

With the view of obtaining barium dithio-oxalate, cold concentrated solutions of barium chloride and potassium dithio-oxalate were mixed. A white precipitate separated, but, contrary to expectation, this precipitate was found to be a mixture of barium sulphide and barium oxalate.

Aniline dithio-oxalate,  $(COS \cdot NH_3 \cdot C_6H_5)_2$ , separates in orangecoloured plates when cold aqueous solutions of aniline hydrochloride and potassium dithio-oxalate are mixed. Its solutions in

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warm water, cold alcohol, or acetone undergo rapid decomposition with evolution of hydrogen sulphide and separation of oxanilide.

Owing to the extreme ease with which this salt decomposes, it could not be prepared pure. Freshly prepared aqueous solutions of salt give the characteristic nickelodithio-oxalate colour on admixture with a solution of a nickel salt, but no colour is developed if the solution of the aniline salt is allowed to remain for some time before adding the nickel salt.

Potassium nickelodithio-oxalate,  $K_2(COS)_4Ni$ , separates as a black, crystalline precipitate when equal weights of nickel chloride and potassium dithio-oxalate in concentrated aqueous solutions are mixed. This salt crystallises from hot water in dark red octahedra.

As the composition of this salt is of fundamental importance, it was analysed several times.

The results obtained for carbon, hydrogen, and sulphur agree so closely with those given in the former paper (*loc. cit.*, p. 1908) that the determination of the percentage of nickel only need be given here to supplement the results already published:

0.4200 gave 0.0870 NiO. Ni=16.2.

 $K_2(COS)_4$ Ni requires Ni=15.8 per cent.

Sometimes it was found that potassium nickelodithio-oxalate separated as needles, whilst at other times it separated as octahedra from aqueous solutions. Both forms had the same composition, and on investigation this was found to be a case of dimorphism. On cooling a solution of potassium nickelodithio-oxalate to  $22^{\circ}$ , octahedra only separate, but if the solution is cooled rapidly to  $10^{\circ}$ , needles separate. Above  $20^{\circ}$ , needles in contact with water

> change slowly into octahedra, whilst if the octahedra are kept under water in an ice chamber for several hours, they change slowly into needles.

> The transition temperature is approximately  $20^{\circ}$ .

Mr. A. Hutchinson has kindly provided the following report on the octahedral form based on measurements made by Mr. A. F. Hallimond.

"Crystal system: Oblique. a:b:c =

1.7637:1:2.8664.  $\beta = 70^{\circ}56'.$ 

Forms observed:  $p\{111\}$  and  $s\{\overline{1}11\}$  large,  $A\{100\}$  small. The small black crystals are about 3 mm. in length, and belong to the holohedral sub-class of the oblique system. The habit is pyramidal, p and s being equally developed. This is shown in the figure, which is a plan on the plane of symmetry.



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## The following angles were observed:

Angle	No. of		Mean	
measured.	measurements.	Limits	observed.	Calculated.
$ps = (111) : (\overline{1}11)$	16	58°26′58°52′	58°35′	*
$ps' = (111) : (11\overline{1})$	14	34 30 - 34 50	34 44	*
$ss' = (\bar{1}11) : (11\bar{1})$	7	61 1661 23	61 195	*
$pp' = (111) : (\bar{1}1\bar{1})$	8	76 30 77 42	77 11률	77°21′
Ap = (100) : (111)	4	$55 \ 36 \56 \ 5$	55 52	55 46½
$As' = (100) : (11\overline{1})$	4	65 33 65 40	65 36 <del>1</del>	65 381

Cleavage:  $A \{100\}$  perfect,  $B \{010\}$  imperfect.

The specific gravity is 2.132 at 18.4° (compared with water at 4°). In very thin flakes the crystals are transparent and transmit brownish-red light. The extinction of a cleavage flake parallel to A was found to be parallel to B, and a flake parallel to B appeared to extinguish parallel to the edge AB. The crystals are very strongly pleochroic, vibrations parallel to the edge AB being totally absorbed. If the light is vibrating perpendicular to  $A\{100\}$ , only deep red is transmitted; pale brown is transmitted if the vibrations are perpendicular to B. An approximate value of 1.54 was obtained by the immersion method for the index of refraction of light vibrating perpendicular to A."

The potassium salt is too sparingly soluble in cold water to allow of trustworthy determinations of its molecular weight in solution to be made. The electrical conductivity, however, shows that it ionises into three ions.

# Electrical Conductivity of Potassium Nickelodithio-oxalate in Aqueous Solution.

Concentration	<b>M</b> /32	M/64	M/1024	M/2048
Molecular conductivity	217.3	227.4	265.1	276.0

If  $E_{32}$  and  $E_{1024}$  be the equivalent conductivities at dilutions M/32 and M/1024 per litre, then

$$\frac{E_{1024} - E_{32}}{10} = \frac{265 \cdot 1/2 - 217 \cdot 3/2}{10} = 2.39.$$

The salt is therefore derived from a dibasic acid, for which

$$\frac{E_{1024} - E_{32}}{10} = 2.$$

With increasing dilution a constant value for the conductivity cannot be obtained.

Barium nickelodithio-oxalate, Ba(COS), Ni,4H2O, is sparingly soluble in cold water, and is precipitated on mixing solutions of VOL. CI. F

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barium chloride and potassium nickelodithio-oxalate. It separates on cooling hot aqueous solutions in black, iridescent needles:

 $0.7780 \text{ gave } 0.3485 \text{ BaSO}_4$ . Ba = 26.33.

Total  $BaSO_4 = 1.395$ . S = 24.8.

0.4225 gave 0.0640 NiO. Ni=11.9.

0.5060, dried in a desiccator for two days, gave 0.1680 CO<sub>2</sub> and 0.0760 H<sub>2</sub>O. C=9.05; H<sub>2</sub>O=15.0.

(This result indicates that the salt still retained some water.)

 $Ba(COS)_4Ni,4H_2O$  requires Ba=26.9; S=25.2; Ni=11.6; C=9.44;  $H_2O=14.10$  per cent.

Lead Nickelodithio-oxalate,  $Pb(COS)_4Ni_2H_2O$ . — This salt separates in lustrous needles when solutions of lead acetate and potassium nickelodithio-oxalate are mixed. It is almost insoluble in cold water, and decomposes on boiling with separation of lead sulphide:

0.6092 gave 0.1935 CO<sub>2</sub> and 0.0435  $H_2O$ . C=8.63;  $H_2O$ =7.1.

0.5220 ,, 0.2860 PbSO<sub>4</sub> and 0.6780 BaSO<sub>4</sub>. Pb=37.4; S=23.3.

 $Pb(COS)_4Ni_2H_2O$  requires C=8.8;  $H_2O=6.6$ ; Pb=38.2; S=23.6 per cent.

Ammonium nickelodithio-oxalate,  $(NH_4)_2(COS)_4Ni, 4H_2O$ , was prepared by mixing hot concentrated solutions containing equivalent quantities of ammonium sulphate and barium nickelodithio-oxalate. After filtering off the barium sulphate, the remaining solution on evaporation yields the ammonium nickelodithio-oxalate in beautiful, lustrous, almost black needles.

On boiling with potassium hydroxide solution, 1.15 gave off ammonia which neutralised 5.57 c.c. of N-sulphuric acid.  $NH_4 = 8.71$ .

0.5955 gave 0.2505 CO<sub>2</sub> and 0.202 H<sub>2</sub>O. C=11.5; H=3.77.

The residue from the combustion was reduced, ignited, and gave 0.1090 NiO. Ni = 14.4.

 $(NH_4)_2(COS)_4Ni, 4H_2O$  requires  $NH_4 = 8.84$ ; C=11.79; H=3.9; Ni=14.5 per cent.

Molecular Weight of Ammonium Nickelodithio-oxalate.

0.192, in 25 c.c. of water, gave  $\Delta t - 0.1^{\circ}$ . M.W. = 138.2, but  $(NH_4)_2(COS)_4Ni_4H_2O$  requires 407.

Hence it appears that the salt has dissociated into three ions.

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Conductivity of Ammonium Nickelodithio-oxalate in Aqueous Solution.

Concentration Molecular conductivity	$\dots \qquad M/32 \ \dots \qquad 227$	M/1024 276
$\frac{E_{1024} - E_{32}}{10} =$	$\frac{276/2 - 227/2}{10}$	 2.4.

The salt is therefore derived from a dibasic acid.

At greater dilutions the conductivity increases still more, and within the limits of practical determination a constant value cannot be reached.

Sodium nickelodithio-oxalate,  $Na_2(COS)_4Ni, 2\frac{1}{2}H_2O$ , was prepared by mixing concentrated solutions of sodium dithio-oxalate and nickel chloride. The sparingly soluble sodium nickelodithio-oxalate separates in black prisms, which do not exhibit such a high lustre as the other salts:

0.2750 gave 0.1255 CO<sub>2</sub> and 0.0310 H<sub>2</sub>O. C=12.44; H<sub>2</sub>O=11.3. Na<sub>2</sub>(COS)<sub>4</sub>Ni,2<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O requires C=12.3; H<sub>2</sub>O=11.5 per cent.

When mercuric chloride in excess is added to a solution of potassium nickelodithio-oxalate, the mercury salt is not obtained, but the solution is decolorised, and a yellow precipitate is formed, which was found to be a mixture of mercury sulphide with mercury oxalate.

When excess of mercuric chloride is avoided, a coloured precipitate, probably of mercury nickelodithio-oxalate, is formed, and gradually decomposes, giving the yellow solid and carbon monoxide.

The nickel, cobalt, and silver salts of nickelodithio-oxalic acid decompose on keeping, with formation of a sulphide of the heavy metal. In fact, with the exception of lead, few salts of a metal which yields an insoluble sulphide are sufficiently stable to be prepared in the ordinary way.

Aniline nickelodithio-oxalate,  $(C_6H_5 \cdot NH_3)_2(COS)_4Ni$ , separates as a reddish-brown, microcrystalline powder when a solution of aniline hydrochloride is added to one of potassium nickelodithio-oxalate:

0.3200 gave 0.4576 CO<sub>2</sub>, 0.0930 H<sub>2</sub>O, and 0.0505 NiO. C = 39.0;

H = 3.24; Ni = 12.4.

0.2950 gave 0.5590 BaSO<sub>4</sub>. S = 26.0.

0.2500 , 11.4 c.c. N<sub>2</sub> at 0° and 760 mm. N = 5.72.

 $(C_6H_5\cdot NH_3)_2(COS)_4Ni$  requires C=39.4; H=3.3; Ni=12.1;

 $S\!=\!26^{\cdot}28\,;~N\!=\!5^{\cdot}75$  per cent.

This salt is so insoluble in water containing an excess of aniline hydrochloride that the supernatant liquid is colourless; it was thought therefore that its formation might be utilised in the

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estimation of aniline. Fairly accurate results were obtained with concentrated solutions, but at greater dilutions the method was not a success, probably owing to hydrolysis of the salt.

# Thermal Decomposition of Aniline Nickelodithio-oxalate.

When aniline nickelodithio-oxalate is heated, decomposition begins at 180°, and is completed slowly at 210°. Among the products of this decomposition, oxanilide, aniline, hydrogen sulphide, and carbon monoxide were identified, whilst the residue contained only nickel and sulphur.

An attempt was made to estimate these decomposition products with the object of ascertaining the mode of decomposition, and, if possible, of obtaining some insight into the constitution of the salt. A weighed quantity of the salt was heated to 210° in a hard glass tube fitted to an air condenser.

The carbon monoxide and hydrogen sulphide escaped, and the contents of the tube and condenser were extracted with hot benzene, which dissolved both the aniline and the oxanilide. This benzene solution was shaken with a solution of hydrochloric acid. The aqueous layer containing aniline hydrochloride was separated from the benzene layer containing the oxanilide. Both solutions were evaporated to dryness, and the residues weighed.

It was only possible to get approximate values for the amounts of aniline and oxanilide, partly on account of the loss of aniline due to hydrolysis, and partly on account of the slight solubility of oxanilide in benzene.

Experiment I.—0.813 gave 0.241 aniline hydrochloride and 0.134 oxanilide. Hence aniline per gram-molecule = 103 grams; oxanilide = 80 grams.

Experiment II.—0.860 gave 0.250 aniline hydrochloride and 0.160 oxanilide. Hence aniline per gram-molecule=99 grams; oxanilide=89 grams.

Experiment III.—1.34 gave 0.334 aniline hydrochloride and 0.278 oxanilide. Hence aniline per gram-molecule=93 grams; oxanilide=109 grams.

The gases evolved when a weighed quantity of the salt was heated in a vacuum were collected by means of a Topler pump, and the volume of gas was measured before and after treatment with concentrated aqueous potassium hydroxide solution.

The residual gas was carbon monoxide, whilst the gas absorbed by the alkali was hydrogen sulphide, with possibly carbonyl sulphide.

Experiment I.-0.198 gave 44.5 c.c. at 18° and 756 mm., of which 18.7 c.c. were carbon monoxide.

Total gas		108.5	litres	per	gram-molecule	of	salt.
Carbon monoxide	-	44·3	,,		"		,,
$\mathbf{Residue} = 0.043$	==	110.5	grams	3	**		,,

Experiment II.—

Total gas	=	106.2	litres	per	gram-molecule	of	salt
Carbon monoxide	==	<b>4</b> 3·0	,,		""		,,
Residue	=	106.0	grams	3	,,		,,

Experiment III.---

Total gas	== (	110 <b>∙0</b>	litres	$\mathbf{per}$	gram-molecule	of	salt.
Carbon monoxide	.=	43·5	"		**		,,
Residue	<del>~</del> ]	106.0	grams	8	"		,,

From these results, which are fairly consistent with each other, it appears that each molecule of aniline nickelodithio-oxalate gives two molecules of carbon monoxide and five molecules of hydrogen sulphide or of a mixture of this gas with carbonyl sulphide. It was found impossible to decide whether both these gases were present by liquefaction and fractional distillation, but the behaviour of the gas towards an aqueous solution of lead acetate indicated that some carbonyl sulphide was present.

In order to ascertain if carbonyl sulphide was present, and to determine its amount, phenyltrimethylammonium nickelodithiooxalate,  $[C_6H_5 \cdot N(CH_3)_3]_2(COS)_4Ni$ , was prepared by mixing solutions of the iodide of the organic base with the potassium salt of the acid, when it separated in diamond-shaped, red plates, showing a high lustre, which melted and decomposed at remarkably 215-216°:

0.2030 gave 0.3430 CO<sub>2</sub> and 0.0884  $H_2O$ . C=46.1; H=4.84.

 $[C_6H_5 \cdot N(CH_3)_3]_2(COS)_4$ Ni requires C=46.2; H=4.91 per cent.

A weighed quantity of this salt was heated to about 250° in a stream of dry nitrogen, the evolved gases were passed through a U-tube cooled by ice, in order to condense dimethyl sulphide, and then into a receiver cooled in liquid air.

In this way the carbonyl sulphide was solidified, whilst the nitrogen and most of the carbon monoxide escaped; a small amount of carbon monoxide, however, appears to be retained by the solid oxysulphide. The cooled receiver was then connected to a gas burette, and by allowing the temperature to rise slowly the solidified gas vaporised, and was swept into the burette by a stream of nitrogen.

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The volume of gas was measured before and after treatment with aqueous potassium hydroxide; the contraction represents the volume of carbonyl sulphide evolved from the phenyltrimethylammonium salt. From this the number of litres of carbonyl sulphide evolved from a gram-molecule of phenyltrimethylammonium nickelodithiooxalate is calculated.

It seems reasonable to assume that the gram-molecule of the aniline salt gives the same amount of carbonyl sulphide.

Experiment I.—0.412 gave 16.3 c.c. COS, corrected to  $0^{\circ}$  and 760 mm. Hence one gram-molecule of the salt gives 22.6 litres COS.

*Experiment II.*—0.405 gave 15.6 c.c. COS, corrected to  $0^{\circ}$  and 760 mm. Hence one gram-molecule of the salt gives 22.0 litres COS.

Therefore one gram-molecule of the salt yields one gram-molecule of carbonyl sulphide.

The results obtained in the above experiments indicate that the decomposition of aniline nickelodithio-oxalate is best represented by the equation:

 $2Ni(COS)_4(C_6H_5\cdot NH_3)_2 =$ 

 $\mathbf{Ni}_2\mathbf{S}_3 + \mathbf{4CO} + \mathbf{2COS} + \mathbf{3H}_2\mathbf{S} + \mathbf{2C_6H_5} \cdot \mathbf{NH}_2 + (\mathbf{CO} \cdot \mathbf{NH} \cdot \mathbf{C_6H_5})_2.$ 

Products of Decomposition per Gram-molecule of Salt.

	Found.	Calculated.
Carbon monoxide	43.8 litres	44.4 litres
Carbonyl sulphide	22.3 ,,	22.2 ,,
Hydrogen sulphide	42.0 ,,	33.3 ,,
Aniline	97.0 grams	93.0 grams
Oxanilide	109.0 ,,	120.0 ,,
Nickel sulphide	110.5 ,,	103.0 ,,

The only discrepancy is observed in the amount of hydrogen sulphide found, and as this value is obtained by differences, this may be due to the decomposition of some of the carbonyl sulphide into hydrogen sulphide and carbon dioxide by moisture.

A very large number of organic bases, such as aromatic amines, quinoline derivatives, and alkaloids, give crystalline nickelodithiooxalates which are very sparingly soluble in water. Of these, the *guanidine* salt is the most striking, as it is very sparingly soluble in cold water, and separates from hot water in long, black, lustrous needles.

# Nickelodithio-oxalic Acid.

It seemed reasonable to suppose that by mixing sulphuric acid and barium nickelodithio-oxalate in equivalent quantities, free nickelodithio-oxalic acid would be obtained in solution.

However, on evaporation of the resulting solution, after removal

of the barium sulphate, decomposition with evolution of hydrogen sulphide and separation of nickel oxalate took place.

The behaviour of this acid in solution can, however, be followed by measuring the electrical conductivity.

A solution of barium nickelodithio-oxalic was made, and its electrical conductivity measured; 10 c.c. of this solution were mixed with 10 c.c. of an equivalent sulphuric acid solution. The resulting solution, neglecting the barium sulphate which is precipitated, should be a solution of nickelodithio-oxalic acid.

Its conductivity was measured, and was found to be nearly four times that of an equivalent solution of the barium salt. Moreover, the conductivity of this acid increased with dilution, but decreased steadily on keeping, which would be expected if the acid decomposed into insoluble substances, such as nickel oxalate, sulphur, and carbon monoxide, or into such a feeble electrolyte as hydrogen sulphide.

Strength of solution of barium salt	M/361	<b>M</b> /722
Molecular conductivity	181	196
Strength of solution of nickelodithio- oxalic acid Molecular conductivity	<i>M</i> /722 736	<i>M</i> /1444 767

A comparison of the conductivity of this acid with that of equivalent solutions of hydrochloric and sulphuric acids shows that it is a comparatively strong acid, with a conductivity approximately equal to that of sulphuric acid. (The molecular conductivity of sulphuric acid at a dilution of 722 litres is 742.)

# Palladio dithio-oxalates.

Potassium palladiodithio-oxalate,  $K_2(COS)_4Pd$ .—When a solution of palladium chloride is added to a concentrated solution of potassium dithio-oxalate, a yellow, crystalline precipitate separates. This salt is deposited from a hot aqueous solution as yellow, fluorescent prisms:

Barium palladiodithio-oxalate,  $Ba(COS)_4Pd, 3H_2O$ , was prepared by adding barium chloride solution to a solution of the potassium salt. It separates in orange-coloured needles:

0.2915 gave 0.0960 CO<sub>2</sub> and 0.0295  $H_2O$ . C=8.3;  $H_2O=10.1$ . Ba(COS)<sub>4</sub>Pd,3H<sub>2</sub>O requires C=8.95;  $H_2O=10.0$  per cent.

Aniline palladiodithio-oxalate,  $(C_6H_5\cdot NH_8)_2(COS)_4Pd$ , separates from a solution of potassium palladiodithio-oxalate on addition of a solution of aniline hydrochloride as a yellow, microcrystalline precipitate :

0.3435 gave 0.4540 CO<sub>2</sub> and 0.0935 H<sub>2</sub>O. C=36.1; H=3.0. 0.4710 " 0.0880 Pd. Pd = 18.7. 0.4280 BaSO4. 0.2400S = 24.5. ,,  $(C_6H_5 \cdot NH_3)_2(COS)_4Pd$  requires C=36.7; H=3.06; S=24.4; Pd = 18.2 per cent.

Solutions of palladiodithio-oxalates have an intense yellow colour, which persists at high dilutions, and is probably due to the formation of a complex anion containing palladium. In agreement with this we find that the ordinary tests for palladium when applied to these solutions fail; thus potassium iodide does not precipitate insoluble palladium iodide, whilst hydrogen sulphide does not cause separation of palladium sulphide.

This complex acid radicle is fairly stable, as the colour is not destroyed by dilute mineral acid, but potassium cvanide decolorises solutions of palladiodithio-oxalates. The following reactions were examined:

Silver nitrate gives a yellow precipitate, which immediately decomposes with evolution of carbon monoxide and formation of silver sulphide.

Mercuric chloride gives a yellow precipitate which blackens on keeping.

Lead acetate gives an orange-red precipitate which darkens after keeping.

Nickel chloride causes formation of a moderately soluble brick-red nickel salt.

Cobalt chloride causes formation of a fairly soluble cobalt salt.

When a solution of palladium chloride in excess is added to one of potassium palladiodithio-oxalate rapid decomposition takes place with separation of palladium sulphide, so that when preparing potassium palladiodithio-oxalate it is important to use an excess of thio-oxalate.

# Ferrodithio-oxalates.

When a solution of ferrous ammonium sulphate is added to one of potassium dithio-oxalate, a brownish-purple colour is developed. This colour is due to formation of a complex ferrodithio-oxalate, but owing to the instability of this substance, ferrous sulphide separates when solutions of ferrous ammonium sulphate and potassium dithio-oxalate are mixed, and the isolation of a pure salt proved to be difficult. If, however, dilute solutions were used, it was possible to isolate the sparingly soluble aniline salt by the addition of aniline hydrochloride to the filtered solution.

Aniline ferrodithio-oxalate separated in black needles, which were collected rapidly and dried in a vacuum over sulphuric acid. Even when dry, this salt decomposed slowly, with evolution of hydrogen sulphide and formation of oxanilide, so that no consistent analytical results were obtained, but the following serve to establish the composition of the salt:

0.1525 gave 0.2085 CO<sub>2</sub> and 0.0485 H<sub>2</sub>O. C=37.35; H=3.53.

0.2600 ,, 13 c.c.  $N_2$  at 23° and 763 mm. N = 5.67.

0.1880 , 0.3780 BaSO<sub>4</sub>. S=27.6.

 $(C_6H_5 \cdot NH_3)_2(COS)_4Fe,H_2O$  requires C=38.2; H=3.58; S=25.5; N=5.77 per cent.

# Cobaltidithio-oxalates.

When solutions of cobalt salts and potassium dithio-oxalate are mixed, an intense reddish-brown colour results, and this colour is recognisable at dilutions as great as one part of cobalt in 40,000,000 parts of water.

This colour, unlike the corresponding colour for nickel, is not discharged by potassium cyanide or by boiling with moderately strong hydrochloric acid. The colour is therefore due to the formation of a stable complex cobaltidithio-oxalate.

When concentrated solutions of equal weights of cobalt chloride and potassium dithio-oxalate are mixed, an intense reddish-brown colour is developed, and much cobalt sulphide separates. The solution was filtered, and to the filtrate barium chloride solution was added. A reddish-brown, microcrystalline precipitate separated. This was dissolved in hot water, and on cooling very minute, reddish-brown needles separated.

Analysis showed this salt to be *potassium barium cobaltidithio*oxalate,  $BaK(COS)_6Co, 4H_2O$ .

The potassium was estimated by decomposing the salt by nitric acid; the barium was then removed as barium sulphate, the solution was made alkaline by ammonia, and the cobalt removed as cobalt sulphide. The liquid was then evaporated to dryness, ignited, and the potassium in the residue estimated as platinichloride, but the results obtained were always low:

2.1860 gave 0.7735 BaSO<sub>4</sub> and 0.1890 Co. Ba=20.8; Co=8.64. 0.3545 , 0.7385 BaSO<sub>4</sub>. S=28.6.

0.6515 ,, 0.2655  $CO_2$  and 0.0715  $H_2O$ . C=11.1;  $H_2O$ =11.0. 0.7485 barium salt gave 0.231  $K_2PtCl_6$ . K=4.95.

 $BaK(COS)_6Co, 4H_2O$  requires C=10.8;  $H_2O=10.8$ ; S=28.78; Ba=20.53; Co=8.7; K=5.83 per cent.

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Potassium cobaltidithio-oxalate, K<sub>8</sub>(COS)<sub>6</sub>Co,2H<sub>2</sub>O, was prepared by mixing solutions of equivalent quantities of potassium sulphate and barium potassium cobaltidithio-oxalate, removing the barium sulphate, and evaporating the filtrate until the tripotassium salt separated in very dark brown, stumpy prisms. This was recrystallised from hot water:

0.5015 gave 0.2270 CO<sub>2</sub> and 0.0330 H<sub>2</sub>O. C=12.35; H<sub>2</sub>O=6.58. 0.9370  $K_2$ PtCl<sub>6</sub> and 0.0712 Co. K = 21.4; Co = 10.34. 0.6890,,  $1.2120 \text{ BaSO}_4$ . S=33.3. 0.5000,,

 $K_3(COS)_6Co, 2H_2O$  requires K = 20.45; C = 12.58; S = 33.54;  $C_0 = 10.31$ ;  $H_0O = 6.29$  per cent.

The behaviour of cobaltidithio-oxalates in solution was studied by means of the freezing point and conductivity of solutions in the case of the corresponding nickel compounds:

0.4140 potassium salt in 20 c.c. water gave  $\Delta t - 0.22^{\circ}$ . M.W. = 167. 1.0300 in 40 c.c. water gave  $\Delta t = 0.27^{\circ}$ . M.W. = 172.

 $K_8(COS)_6Co, 2H_2O$  requires M.W. = 572.

Hence the salt appears to ionise, giving four ions-3K' and  $Co(COS)_{6}^{\prime\prime\prime}$ .

Conductivity Experiments.

Dilution	$M/32 \\ 306$	M/64	M/128	M/1024
Molecular conductivity		330 <b>·6</b>	360	400

Hence:

$$\frac{E_{1024} - E_{82}}{10} = \frac{400/3 - 306/3}{10} = 3.12.$$

Cobaltidithio-oxalic acid is therefore tribasic.

Aniline cobaltidithio-oxalute, (C6H5·NH3)2(COS)6,2H2O, separates as a dark reddish-brown, crystalline precipitate on mixing concentrated solutions of aniline hydrochloride and potassium cobaltidithio-oxalate. The sparingly soluble salt separates from hot water in small, dark brown octahedra:

0.3765 gave 0.5425 CO<sub>2</sub>, 0.1190 H<sub>2</sub>O, and 0.0300 Co. C=39.3; H = 3.51; Co = 7.59.

0.3235 gave 15.4 c.c. N<sub>2</sub> at 15° and 779 mm. N=5.75.

0.5800 BaSO<sub>4</sub>. S = 26.28.0.3030 ,,

 $(C_6H_5 \cdot NH_3)_3(COS)_6Co_2H_2O$  requires C = 39.08; H = 3.80; Co = 8.00; N = 5.70; S = 26.0 per cent.

If to a solution of potassium cobaltidithio-oxalate a solution of quinine sulphate is added, quinine cobaltidithio-oxalate separates as a brownish-yellow, microcrystalline precipitate. This salt is apparently quite insoluble in water, so that its formation might be used to estimate quinine.

Lead, silver, nickel, and cobalt salts of cobaltidithio-oxalic acid were not isolated, as they decompose immediately after formation with deposition of sulphides and evolution of carbon monoxide, and, as in the case of nickelodithio-oxalic acid, only those metals which do not form insoluble sulphides give stable salts.

The thermal decomposition of aniline cobaltidithio-oxalate was examined in the manner already described in the case of aniline nickelodithio-oxalate.

This salt decomposes at about 200°, giving oxanilide, aniline, hydrogen sulphide, carbon monoxide, presumably carbonyl sulphide, and a sulphide of cobalt.

I. 0.1620 gave 38.6 c.c. gas at  $17^{\circ}$  and 754 mm.

After KOH absorption, 13.3 c.c. gas at 17° and 754 mm.

# Hence :

164 litres gas per gram-molecule of salt.

55.6 litres carbon monoxide per gram-molecule of salt.

- II. 0.5330 gave 0.079 residue = 109 grams per gram-molecule of salt.
- III. 162 litres total gas per gram-molecule. 55.7 litres carbon monoxide per gram-molecule.
- IV. 161'8 litres total gas per gram-molecule. 54'4 litres carbon monoxide per gram-molecule.
- V. 0.6380 gave 0.1430 oxanilide and 0.1320 aniline hydrochloride.

# Hence :

150 grams aniline per gram-molecule.

165 " oxanilide per gram-molecule.

It was not found possible to estimate carbonyl sulphide in this case as the phenyltrimethylammonium salt is very soluble, and was not obtained pure.

The equation which represents the decomposition of the aniline salt most nearly is:

 $\begin{aligned} &2\mathrm{Co}(\mathrm{COS})_6(\mathrm{C}_6\mathrm{H}_5\cdot\mathrm{NH}_3)_3, &2\mathrm{H}_2\mathrm{O} = \\ &2\mathrm{H}_2\mathrm{O} + (\mathrm{CO}\cdot\mathrm{NH}\cdot\mathrm{C}_6\mathrm{H}_5)_2 + 4\mathrm{C}_6\mathrm{H}_5\cdot\mathrm{NH}_2 + 4\mathrm{H}_2\mathrm{S} + 5\mathrm{COS} + 5\mathrm{CO} + \mathrm{Co}_9\mathrm{S}_3. \end{aligned}$ 

Products of Decomposition per Gram-molecule of Salt.

	Found.	Calculated.
Carbon monoxide	55.6 litres	55.5 litres
Hydrogen sulphide and carbonyl		
sulphide	107.4 ,.	99·9 ,,
Aniline	150.0 grams	186.0 grams
Oxanilide	165.0 ,,	120°0,
Cobalt sulphide	109.0 ,,	107.0 ,,

#### Rhodiidithio-oxalates.

On adding a solution of sodium rhodiichloride to a concentrated solution of potassium dithio-oxalate no apparent change takes place; the addition of barium chloride to the mixed solutions does not cause separation of barium rhodiidithio-oxalate. On warming the solution becomes orange-coloured, and barium chloride now causes separation of a brilliant yellow microcrystalline precipitate. This is soluble in hot water, and separates on cooling as orangeyellow needles of *potassium barium rhodiidithio-oxalate*, KBa(COS)<sub>6</sub>Rh,4H<sub>2</sub>O:

Aniline Rhodiidithio-oxalate,  $(C_6H_5\cdot NH_3)_3(COS)_6Rh, H_2O$ , sepa rates in orange-red needles when a solution of barium rhodiidithio-oxalate is added to a solution of aniline hydrochloride:

0.2625 gave 0.3610 CO<sub>2</sub> and 0.0840 H<sub>2</sub>O. C=37.5; H=3.5. 0.2290 , 0.4270 BaSO<sub>4</sub>. S=25.6. (C<sub>6</sub>H<sub>5</sub>·NH<sub>3</sub>)<sub>3</sub>(COS)<sub>6</sub>Rh,H<sub>2</sub>O requires C=37.7; H=3.40; S=25.2 per cent.

Solutions of rhodiidithio-oxalates have an intense yellow colour, which persists at great dilutions.

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