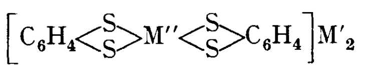
35. *Stereochemistry of Some New Complex Thio-salts of Mercury, Cadmium, and Zinc.*

By WILLIAM H. MILLS and ROBERT E. D. CLARK.

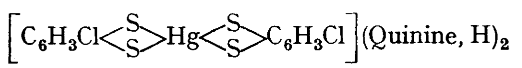
THE general stability of the sulphur compounds of the heavy metals, and the power shown by mercury and allied elements of forming 4-co-ordination sulphur compounds like the mercuri- and zinci-thiocyanates, $K_2M''(SCN)_4$ (M'' = Hg or Zn), gave reason to suppose that benzene-1 : 2-dithiols might yield stable co-ordination derivatives of mercury and similar metals of the general formula (I) (M' = alkali metal). Spirocyclic metallic compounds of this type would, if suitably substituted, provide a means of investigating the stereochemistry of the metals (in the 4-covalent state) from which they were derived.

With the object, therefore, of obtaining molecularly dissymmetric metallic derivatives of this kind, we undertook the preparation of *o*-dithiolbenzenes containing an additional substituent group. The preparation of *o*-dithiolbenzene itself has been described by Pollak (*Monatsh.*, **1913**, **34**, 1673) and by Hartley and Smiles (J., 1926, 1821), and we prepared the substitution derivatives of the type required by analogous methods. We obtained *toluene*-3 : 4-*dithiol* (II; R = Me) and 1-*chlorobenzene*-3 : 4-*dithiol* (II; R = Cl) by reducing the chlorides of the corresponding *o*-disulphonic acids, and found that these substituted *o*-dithiols did, in fact, give rise to complex salts of mercury, cadmium, and zinc of the type contemplated. For instance, when an alcoholic solution of the mono-potassium salt of (I; R = Me) was heated with mercuric oxide, the crystalline *potassium* salt (III) was produced, and salts of the analogous zinc and cadmium complex acids could be prepared in the corresponding manner.



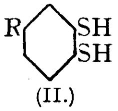
$$\left[\mathrm{C_6H_4}<^{\mathrm{S}}_{\mathrm{S}}>\mathrm{M''}<^{\mathrm{S}}_{\mathrm{S}}>\mathrm{C_6H_4}\right]\mathrm{M'_2}$$

(I.)

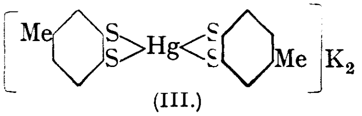


$$\left[\mathrm{C_6H_3Cl}<^{\mathrm{S}}_{\mathrm{S}}>\mathrm{Hg}<^{\mathrm{S}}_{\mathrm{S}}>\mathrm{C_6H_3Cl}\right](\mathrm{Quinine, H})_2$$

(IV.)



(II.)



(III.)

Various crystalline alkaloid salts of these acids were investigated, but in no case could direct evidence of their optical resolution be obtained. However, the *quinine* salt (IV) of the spirocyclic mercuric complex acid derived from the chloro-dithiol (II; R = Cl) was found to show a highly characteristic behaviour. It exists in two forms, interconvertible in a remarkable way. When prepared by heating equimolecular quantities of the dithiol and quinine in chloroform solution with mercuric oxide, the α-modification is formed. This is sparingly soluble in chloroform but it dissolves very easily in acetone, and the resulting solution within a few seconds begins to deposit the salt in a new form, the β-form, which is sparingly soluble in acetone and shows great crystallising power. This β-form shows the converse behaviour. It dissolves rapidly in cold chloroform, and the solution then sets to a jelly, which on keeping at 40—60° for some time crystallises, yielding the α-form. The interconversion of the two forms in this way can be repeated indefinitely.

$$\begin{tikzcd}
 & \text{acetone solution} \arrow[dr] & \\
\alpha\text{-form} \arrow[ur] & & \beta\text{-form} \arrow[dl] \\
 & \text{chloroform solution} \arrow[ul] &
\end{tikzcd}$$

The corresponding *zinc* and *cadmium* compounds behave in an exactly similar manner. Their quinine salts each exist in two forms, which are intertransformable by means of acetone and chloroform, and the process is even more rapid than with the mercury compound.

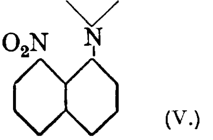
Both the α- and the β-forms of these salts crystallise with solvent of crystallisation, but the solvent is very loosely bound, and the crystals effloresce on exposure to air, yielding cream-coloured powders.

In the desolvated powders, the crystal-lattices of the solvated salts must have been destroyed, but the α- and β-modifications still retain their individuality, since the desolvated α-powders, like the α-crystals, dissolve easily in acetone but not in chloroform, and the β-powders show the converse behaviour. Also, the β- differ from the α-powders in being conspicuously triboelectric: a similar distinction was observed by Angel, Drew, and Wardlaw (J., 1930, 357) between α- and β-modifications of the halides of bis(diethyl-sulphide)platinum.

There must, therefore, be a real molecular difference between the two forms. They cannot be merely crystalline modifications produced by the crystallisation of the same molecular species in different lattices.

Acetone and chloroform are not the only solvents by which the transformation can be effected. The α-forms dissolve in methyl ethyl ketone and, in the cases of the cadmium and the zinc complexes, the β-forms separate on standing (the mercuric compound is too soluble). The β-forms are soluble in methylene chloride, giving solutions which, like the chloroform solutions, set to jellies passing over into the crystalline α-forms when kept warm.

The convertibility of these salts into different modifications by treatment with solvents recalls a similar phenomenon encountered by Mills and Elliott (J., 1928, 1291) with the brucine salt of benzenesulphonyl-8-nitro-1-naphthylglycine (V). The salt of the *l*-form of this acid dissolved easily in cold methyl alcohol, and from the solution, after a short interval, the salt of the *d*-acid crystallised (as a dihydrate). The latter salt was easily soluble in cold acetone, and this solution rapidly deposited the brucine salt of the *l*-acid. In this case it could be proved that the behaviour was due to the presence in the salt of a molecularly dissymmetric anion which underwent rapid autoracemisation. It is probable that the analogous behaviour of the quinine salts of these spirocyclic metallic complexes is to be referred to a similar cause.



(V.)

If the four sulphur atoms in the complex anion are arranged tetrahedrally round the central metallic atom, the anion is dissymmetric and will exist in enantiomorphous *d*- and *l*-forms. It will then give two quinine salts, *viz.*, *l*B,*d*A and *l*B,*l*A. If, of these two diastereoisomeric salts, one is considerably the more soluble in chloroform and the other in acetone, and if, further, the anion undergoes rapid autoracemisation in solution, then an intertransformation corresponding with that observed will result.[*]

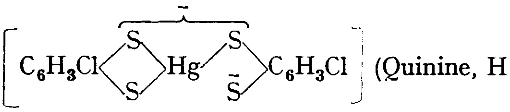
The rapidity with which interconversion of the α- and β-forms takes place would indicate that, if this view of the inter-relationship of the two forms is correct, the rate of racemisation of the optically active complexes must be very high. It was therefore unlikely that their optical activity would be sufficiently persistent to be observable after removal of the quinine, and solutions of the sodium salts, prepared by the addition of sodium hydroxide to either form and extraction of the alkaloid with chloroform, were in fact inactive.

It seemed, however, that it might not prove impossible to observe the oppositely directed mutarotations of the two forms that should be caused by the passage of the optically active anions into the *dl*-equilibrium mixture when the crystalline salts passed into solution.

No mutarotation could be detected at 0°. A silica apparatus (see fig.) was therefore constructed which enabled solutions to be examined at temperatures down to — 35° and polarimetric readings to be taken, sometimes within 20 seconds of bringing the solid salt into contact with the solvent. Solutions of the α-forms of the quinine salts in acetone and also in methyl ethyl ketone, and of the β-forms in chloroform and in methylene chloride, were examined, but even under the lowest practicable temperatures and with the greatest rapidity of working which we could attain, no mutarotation could be observed. It cannot be concluded from this, however, that mutarotation does not occur. A time of the order of ½ minute is enormously long in comparison with the periods of molecular vibrations, and mutarotation may well have occurred and proceeded to completion before our polarimetric observations on the solutions could begin.

It is difficult to find a satisfactory alternative to the view that the isomerism is diastereoisomerism due to the dissymmetry of the complex acids. If the valencies of the central metallic atom had a uniplanar distribution, geometrical isomerism dependent on the *cis*- or *trans*-arrangement of the unsymmetrically substituted phenylene groups would be possible, but a valency arrangement of this kind is improbable, since *X*-ray examination of the complex cyanides of potassium with zinc, cadmium, and mercury of the type $K_2[X(CN)_4]$—in which an analogous configuration of the anion is to be expected—has indicated a tetrahedral arrangement of the co-ordinated cyanogen groups round the central metallic atom (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774). Moreover, the isomerism would then be independent of the dissymmetry of the base and should be shown also by metallic salts of the complexes.

It also seems improbable that the isomerism is structural, dependent on an internal dissociation of the spirocyclic salt, analogous to the dissociation of the mercuritetrathiocyanate ion into the mercuritrithiocyanate and the thiocyanate ion: $Hg(SCN)''_4 \rightleftharpoons Hg(SCN)'_3 + SCN'$. On this view, one form would possess the normal spirocyclic structure (IV) and the other would have a formula (VI) with 3-co-ordinated mercury and an ionised thiol group. It is to be observed, however, that the dissociation of the mercuritetrathiocyanate ion occurs to an appreciable extent only at high dilutions (Grossmann, *Z. anorg. Chem.*, 1905, **43**, 369), whilst in a compound of formula (VI) the mercury and sulphur would be held in relative positions corresponding with the very highest concentrations.



(VI.)

This view of the isomerism would require that the salts of the complex anion should exist in solution as equilibrium mixtures of the spirocyclic and internally dissociated forms, so that one or the other could crystallise according to the solvent employed. Alcoholic or chloroform solutions of the mercuric compound can, however, contain no appreciable amount of an internally dissociated modification, since these solutions do not react with mercuric oxide, as they should if the ionised thiol group Ar-$\bar{S}$ was present, to form a mercaptide linking Ar-S-Hg- (Ar representing the aromatic group contained in these compounds). This is shown by the fact that when alcoholic solutions of the potassium salts, or chloroform solutions of the alkaloidal salts, of the dithiols are brought into contact with mercuric oxide, the oxide dissolves until the amount required to form the 4-co-ordination derivative has been taken up, and then the action ceases.

The corresponding test cannot be made with acetone solutions, as acetone itself reacts with mercuric oxide. It is conceivable that solvation by acetone of the 3-co-ordinated mercury atom or of the ionised thiol group might make the proportion of the internally dissociated form higher in this than in other solvents, but the acetone is loosely bound in the crystalline β-forms, and on its removal these forms show no tendency to pass into the isomeric α-modifications.

Hence, although in the absence of evidence of optical activity, the interpretation of the isomerism of these quinine salts as diastereoisomerism due to the dissymmetry of the spirocyclic complex acids from which they are derived has not been proved, it is the most probable of the explanations which we are able to suggest, and it is strongly supported by the analogous behaviour of the brucine salt of benzenesulphonylnitronaphthylglycine.

EXPERIMENTAL.

Toluene-3 : 4-*disulphonyl Chloride*.—Powdered sodium toluene-3 : 4-disulphonate (14·8 g.) was refluxed for 4 hours with phosphorus pentachloride (21 g.) and oxychloride (10 c.c.). The mixture was poured on ice, and the oil solidified (9·9 g.); recrystallised from light petroleum (b. p. 80—100°), it had m. p. 109° (Found : Cl, 24·3; S, 22·2. Calc. for $C_7H_6S_2O_4Cl_2$: Cl,24·6; S, 22·15%) (compare Klason, *Ber.*, 1887, **20**, 356; Wynne and Bruce, J., 1898, **73**, 751).

Toluene-3 : 4-*dithiol*.—The above sulphonyl chloride (45 g.) was reduced by boiling with tin (350 g.) and hydrochloric acid (1000 c.c.). After 20 minutes, the flask was rapidly cooled, and benzene (150 c.c.) added, the mixture being immediately filtered (temperature about 40°). The aqueous layer was again extracted with benzene after separation, and the combined benzene extracts dried with sodium sulphate. The benzene was removed, and the residual oil distilled in a vacuum; b. p. 185—187°/84 mm., 174°/41 mm. The colourless oil crystallised readily; m. p. 35°, yield 37·4 g. (79%) (Found : C, 53·8; H, 5·1; S, 40·4. $C_7H_8S_2$ requires C, 53·9; H, 5·1; S, 41·0%).

p-*Chloroanilinesulphonic Acid*.—The following method, based on Fries's (*Annalen*, 1895, **286**, 377) preparation of the bromo-derivative, was employed. *p*-Chloroacetanilide (52 g.) and concentrated sulphuric acid (30 g.) were heated in a dish and stirred with a thermometer. Acetic acid boiled off at 140—190°, at which temperature the mass suddenly became solid. It was kept at 180° for 1—2 hours and recrystallised from water (charcoal); yield 43—45 g. (Found, by titration : equiv., 206·5. Calc. : 207·5).

1-*Chlorobenzene*-3 : 4-*disulphonyl Chloride*.—*p*-Chloroanilinesulphonic acid in lots of 83 g. was dissolved in sodium hydroxide (400 c.c. of *N*, with 500 c.c. of water), and the solution added to ice (1 kg.) and hydrochloric acid (200 c.c.). The finely divided acid thus precipitated readily dissolved when sodium nitrite (30 g.) was sifted in. After being stirred for ½ hour, the mixture was neutralised by addition of sodium bicarbonate (159 g.), and 100 g. of potassium xanthate in 100 c.c. of water were run in. The liquid was warmed to decompose the diazonium xanthate, evaporated to dryness, and the residue extracted with alcohol. After removal of alcohol, the residue was oxidised with nitric acid (*d* 1·4; 240 c.c. for the product from each lot of 83 g. of chloroanilinesulphonic acid). The oxidation can be carried out on the combined products of several operations. After removal of nitric acid on the water-bath, barium chloride (200 g. per 83 g. of original acid) was added, and the crude *barium* salt thus precipitated (Found : Ba, 33·8. $C_6H_3O_6ClS_2Ba$ requires Ba, 33·7%) was then treated with sodium sulphate, the resulting sodium salt being obtained by evaporation. This was treated with phosphorus pentachloride (250 g. per 170 g. of sodium salt), and the reaction mixture poured on to ice after being heated for 3 hours at 140°. The crude *sulphonyl chloride* was crystallised from benzene as rapidly as possible, the product washed with petrol, and dried; yield 800 g. from 1594 g. of sodium salt. Recrystallised from a large volume of light petroleum (b. p. 100—120°), it gave colourless crystals, m. p. 82—83° (Found : C, 23·4; H, 1·1; Cl, 34·6; S, 20·7. $C_6H_3O_4Cl_3S_2$ requires C, 23·3; H, 1·0; Cl, 34·4; S, 20·7%).

1-*Chlorobenzene*-3 : 4-*dithiol*.—The above sulphonyl chloride (150 g.) was reduced with tin (500 g.) and hydrochloric acid (1·2 l.) by boiling until nearly all the tin had dissolved. The flask was plunged in ice-water with vigorous shaking until the temperature was reduced to 70°; benzene (200 c.c.) was then added, and the strongly vesicant liquid filtered rapidly. The mother-liquor was extracted once with benzene (50 c.c.) after separation. The benzene was distilled off after drying with sodium sulphate and reserved for subsequent preparations. The residual oil distilled at 165°/32·5 mm., giving a colourless liquid which crystallised on standing;

m. p. 31° (Found : C, 40·8; H, 2·9; Cl, 19·9; S, 36·8. $C_6H_5ClS_2$ requires C, 40·8; H, 2·8; Cl, 20·1; S, 36·3%). The yield varied from 40 to 65 g., since no method of avoiding the formation of the red tin compound could be relied upon. The red compound, obtained as a by-product when the yield was low, was decomposed by boiling with hydrochloric acid and then worked up as above.

*Dipotassium Bis(toluene-*3 : 4*-dithiol)mercury* (III).—Potassium (3·22 g.) was dissolved in absolute alcohol (80 c.c.), and toluene-3 : 4-dithiol (13·1 g.) added. Yellow mercuric oxide (9·0 g.) was then added, and the mixture refluxed for 20 minutes. The oxide dissolved, and, on cooling, the colourless highly crystalline *potassium* salt separated (13·0 g.); it was washed with a little absolute alcohol and air-dried. The mother-liquor deposited another 5·3 g. on addition of anhydrous ether. Total yield, 17·8 g. (72%) (Found : C, 30·4; H, 3·6; K, 12·5; Hg, 32·0; EtOH, 7·4. $C_{14}H_{12}S_4K_2Hg,C_2H_6O$ requires C, 30·3; H, 2·8; K, 12·3; Hg, 31·6; EtOH, 7·3%). On heating to 100—110° for 1—2 hours, or on prolonged standing in a desiccator, the alcohol-free substance was obtained as a faint yellow powder, easily soluble in water and alcohol (Found : C, 28·6; H, 2·6; S, 21·9; K, 13·5. $C_{14}H_{12}S_4K_2Hg$ requires C, 28·7; H, 2·05; S, 21·8; K, 13·3%). The aqueous solution slowly decomposed, depositing the mercury mercaptide, but the solution was stable to carbon dioxide. The potassium salt was very soluble in alcohol containing a small quantity of water, and filtrations had to be performed out of contact with moist air.

When cadmium hydroxide was used in the above preparation, addition of ether afforded a gum, which passed on standing into large, highly hygroscopic crystals having the expected properties of the quinine–cadmium salt. Zinc oxide gave a high yield of a quinine–zinc salt which readily crystallised from alcohol.

Alkaloidal Salts.—Alkaloidal salts were prepared (1) by interaction of dipotassium salts with the hydrochloride or sulphate of the base dissolved in alcohol, and (2) directly from mercuric oxide (1 mol.) with a chloroform solution of the base (2 mols.) and the thiol (2 mols.). The products appeared to be identical. Brucine, strychnine, quinine, cinchonine, morphine, nor-*d*-ψ-ephedrine, methylstrychnidinium, methylbrucidinium, and bromostrychnine salts of the mercury complex were prepared, but none crystallised except the last-named. Beautifully crystalline quinine salts of the zinc and cadmium complexes were prepared, but no evidence of resolution could be obtained.

*Diquinine Dihydrogen Bis-(*1*-chlorobenzene-*3 : 4*-dithiol)mercury.*—Quinine (13·0 g.) and 1-chlorobenzene-3 : 4-dithiol (7·1 g.) were dissolved in chloroform (80 c.c., free from carbonyl chloride), and mercuric oxide (4·4 g.) added. The latter dissolved, generating sufficient heat to boil the liquid. The mixture was refluxed until, after 5—10 minutes, it set to a jelly. The flask was then placed in a water-bath at 55—65° for 2 hours, the jelly then crystallising. The crude product (25·0 g.) was removed by filtration and washed with chloroform. It was then dried in a steam-oven until most of the chloroform was removed (*ca.* 15 mins.), but on no account longer.

β-*Form.* Small portions (1—2 g.) of the above crude α-form were placed in a flask, and acetone (not less than 15 c.c.) added. The flask was immediately plunged into boiling water for 4 seconds, and the liquid then instantly filtered at the pump. The acetone solution deposited the β-*form* (15·5 g. from 25 g. crude), which was removed by filtration in ½—¾ hour, and washed with acetone. The colourless crystals were dried at 100° and gave a cream-coloured powder, m. p. 138° (Found : Cl, 5·6; S, 11·3; Hg, 16·7; Quinine, 53·6. $C_{12}H_8Cl_2S_4Hg,2C_{20}H_{24}O_2N_2$ requires Cl, 5·9; S, 10·7; Hg, 16·7; Quinine, 54·0%).

α-*Form.* 23·5 G. of the β-form (above) were treated in quantities of 4·0 g. with 25 c.c. of chloroform, plunged into boiling water (3 secs.), and filtered rapidly.* The filtrate set to a jelly. This was kept at 60° for 2 hours, and the crystalline product filtered off hot and washed with chloroform; yield, 16·5 g. after drying at 100°. The filtrate on evaporation gave a gum which in acetone deposited the β-form (3·2 g.). The α-*form* had m. p. 142° to a viscous yellow liquid. It dissolved immediately in cold acetone, depositing the β-form in 90% yield (Found : Cl, 5·8; S, 11·1; Hg, 17·2; Quinine, 53·2%). Specific rotations : α-form (in acetone; $c = 0{\cdot}93$; $l = 2$), $\alpha_{5461}^{15^\circ} = -3{\cdot}38^\circ$; whence $[\alpha]_{5461}^{15^\circ} = -182^\circ$; β-form (in chloroform; $c = 0{\cdot}502$; $l = 2$), $\alpha_{5461}^{17^\circ} = -2{\cdot}41^\circ$; whence $[\alpha]_{5461}^{17^\circ} = -240^\circ$. In order to compare the rotations of the two

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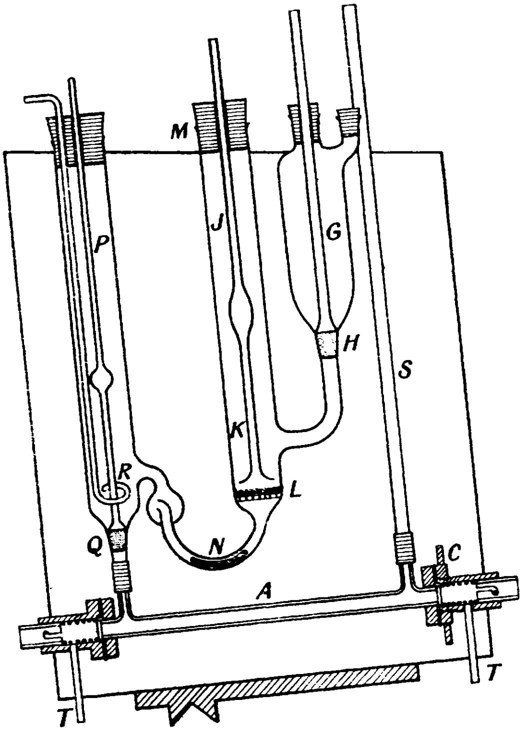
* The β-form dissolves in chloroform at once at the ordinary temperature, but at 0° a small quantity persists in the form of a fine suspension for a few seconds. At still lower temperatures the suspension may remain undissolved for a considerable time. The same phenomenon is to be observed with the zinc and cadmium complexes.

forms in the same solvent, the α-form was dissolved in acetone and an equal volume of chloroform added, and the β-form was dissolved in chloroform and an equal volume of acetone added. For $c = 1$ the values found were: α-form, $[\alpha]_{5461}^{20^\circ}$ − 191°; β-form, $[\alpha]_{5461}^{20^\circ}$ − 188°. These may be taken as identical within the limits of experimental error, for it was more difficult to obtain rapid solution of the β-form.

Diquinine Dihydrogen Bis-(1-*chlorobenzene-*3 : 4-*dithiol*)*cadmium.*—β-*Form.* The chlorothiol (7·1 g.), quinine (13·0 g.), and cadmium hydroxide (3·2 g.; calc., 3·0 g.) were boiled with chloroform (80 c.c.). The hydroxide dissolved with little heat evolution. When the mixture set to a solid mass, it was removed to a bath at 60° and kept there for 2 hours to crystallise; crude yield, 22 g. This substance (15 g.) was converted into the β-form (9·6 g.) by treating it in quantities of 4 g. with acetone (22 c.c.) as described in the case of the mercury compound. The pure β-*form* (obtained by converting this product into the α-form and back again) had m. p. 157° (Found: N, 4·8; Cl, 6·5; Cd, 9·8; Quinine, 57·2. $C_{12}H_8Cl_2S_4Cd,2C_{20}H_{24}O_2N_2$ requires N, 5·0; Cl, 6·4; Cd, 10·1; Quinine, 58·3%).



α-*Form.* The β-form (4·0 g.) was treated with chloroform (30 c.c.), plunged into boiling water (4 secs.), and filtered at the pump. The liquid set to a jelly far more rapidly than in the case of the mercury analogue. It became crystalline on keeping at 60° for 2 hours. It was filtered off hot and washed with chloroform; yield, 7·5—8·0 g., from 9·5 g. of β-form. Unlike the mercury compound, the air-dried material contained chloroform of crystallisation which had partly effloresced. When dried, the product always gave high values for chlorine, but it was finally obtained pure (Found: Cl, 6·5; Cd, 9·8%) by employing methylene chloride instead of chloroform in the above preparation.

Diquinine Dihydrogen Bis(*toluene-*3 : 4-*dithiol*)*zinc.* — α-*Form.* Quinine (13·0 g.) and toluene-3 : 4-dithiol (7·1 g.) in chloroform (70 c.c.) were treated with zinc oxide (1·9 g.; calc., 1·7 g.) which dissolved without appreciable heat evolution. On boiling, the liquid rapidly set to a solid (3—5 mins.). It was kept at 60° for an hour, and the crystals which formed were filtered off (after addition of 20 c.c. more chloroform) and dried (21 g.). The crude compound dissolved immediately in cold acetone, but the β-form separated so rapidly that filtration was impossible. Purification was effected as follows. Portions of the above crude product (4·0 g.) were dissolved by boiling with 60 c.c. of acetone–chloroform (1 : 1 by vol.), and filtered quickly. On cooling, the original α-*form* (13·0 g., from 21 g. crude) separated; m. p. 155°. It was free from chloroform of crystallisation (Found, in air-dried substance: Cl, 6·8; S, 11·7; Zn, 6·1; Quinine, 60·3. $C_{12}H_8Cl_2S_4Zn,2C_{20}H_{24}O_2N_2$ requires Cl, 6·8; S, 12·3; Zn, 6·3; Quinine, 60·1%).

β-*Form.* The above α-form, in lots of 2 g., was treated with acetone (15 c.c.), which quickly dissolved it, giving a completely clear solution. The β-*form* separated rapidly (1·7 g. per 2·0 g. of α-form). This was filtered off and washed with acetone; m. p. 145° (sintering at 128°) (Found: Cl, 6·7; Zn, 5·9; Quinine, 60·9%).

Apparatus for Rapid Low-temperature Polarimetry.

The apparatus (see fig.) consists of three vertical containers, *G*, *J*, and *P*, held in a metal tank for the cooling liquid and connected with the 2-dcm. observation tube *A*. The tank is fixed on the stand of the polarimeter so that *A* is correctly placed between the polariser and analyser of the polarimeter, which is tilted so that the top of the tank is horizontal.

The solvent is stored in *G* and allowed to attain the temperature of the bath.* By temporarily raising the stopper *H* it is then admitted to *J*, which is fitted at the bottom with a filter *L* on which the substance to be examined is placed. Solution of the substance is promoted by means of the stirrer *K* which has a tubular stem. The upper end of *K* is connected, through a rubber tube closed with a clip, to a reservoir of air under pressure.

When the substance has dissolved, the stirrer *K* is raised until the bulb on its stem closes the boring in the rubber stopper *M*. The clip is then opened and the solution, which till now has been prevented from passing the filter by the back pressure of the mercury column *N*, is driven through into *P*. Here it is rendered homogeneous by a few strokes of the stirrer *R*, which is then raised till it lifts the stopper *Q* by engaging with the bulb on its stem, and the solution flows into the slightly inclined observation tube *A*, the displaced air escaping through *S*.

The observation tube is held in the tank by pressure applied by the screw *C* to rubber washers bearing on brass flanges cemented on to the ends of the tube. The end-plates are held in position by spiral springs secured externally by tubes kept in position by bayonet-catches. The condensation of moisture on the end-plates is prevented by a current of dry air admitted by the tubes *TT*.

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