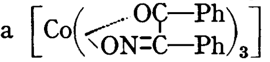
108. *The Complex Metallic Salts of Sulphamide: an Optically Active Inorganic Salt.*

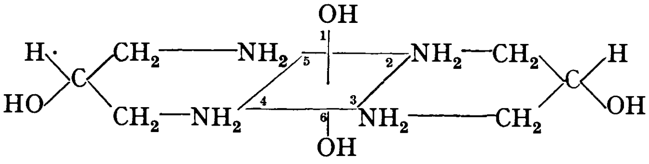
By Frederick G. Mann.

A consideration of those chelate molecules and radicals which, when co-ordinated to a metallic atom, each occupy two co-ordinate positions with consequent ring formation, shows that such groups can be divided into two definite classes. (1) The first class consists of those groups which can fully saturate metallic atoms whether these have the co-ordination number 4 or 6; *e.g.*, ethylenediamine, aminoacetic acid, and the oxalate radical, the former giving salts such as [Ni en_2]Cl_2 and also [Co en_3]Cl_3. Other less familiar examples of chelate molecules capable of complete saturation of 6-co-ordination metallic atoms are αα′-dipyridyl (Werner, *Ber.*, 1912, **45**, 433; Morgan and Burstall, J., 1931, 2213), α-nitroso-β-naphthol (Morgan and Smith, J., 1921, **119**, 704), and *N*-nitrosophenylhydroxylamine (Bamberger and Baudisch, *Ber.*, 1909, **42**, 3576; Baudisch, *Chem. Z.*, 1909, **33**, 1298). (2) The second class consists of those groups which, although saturating metallic atoms of co-ordination number 4, apparently never fully saturate those of co-ordination number 6. A particularly good example in this class is dimethylglyoxime, whose complex salts were examined in detail by Tschugaeff and his co-workers (*Z. anorg. Chem.*, 1905, **46**, 144; 1913, **83**, 1; *Ber.*, 1906, **39**, 2692; 1907, **40**, 3498; 1908, **41**, 2226): whereas it readily co-ordinates with the bivalent nickel, palladous, and platinous atoms, giving, *e.g.*, the non-ionic $[Ni(C_4H_7N_2O_2)_2]$, yet 3 molecules of the dioxime never combine similarly with the 6-co-ordination cobaltic atom; instead, only 2 molecules combine, the remaining two co-ordination positions being occupied by non-chelate molecules and radicals, as in $[Co(C_4H_7N_2O_2)_2(NH_3)_2]Cl$, $[Co(C_4H_7N_2O_2)_2(NH_3)Br]$, and $[Co(C_4H_7N_2O_2)_2(NO_2)_2]NH_4$. Rhodium gives similar compounds such as $[Rh(C_4H_7N_2O_2)_2(NH_3)_2]Cl$, the metal again never combining with 3 molecules of the dioxime: moreover, these compounds were each definite chemical individuals, since no trace of *cis-trans*-isomerism could be detected. Methylethylglyoxime and other homologues behave similarly. This behaviour is in striking contrast to that of α-benzilmonoxime, a chelate molecule falling definitely into the first class, since it unites readily with cobalt to give the stable non-ionic compound of formula  $\left[Co\left(\begin{matrix}OC-Ph\\ ON=C-Ph\end{matrix}\right)_3\right]$ (Tschugaeff, *J. pr. Chem.*, 1907, **76**, 91).

Another chelate molecule in the second class is αγ-diamino-β-hydroxypropane, for it has been shown by Mann (J., 1927, 2907) that, when cobalt is treated even with a large excess of this diamine, only 2 molecules of the latter co-ordinate, the product being dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic monochloride,

$$[(HO)_2Co\{(NH_2\cdot CH_2)_2CH\cdot OH\}_2]Cl.$$

No compound having 3 molecules of the diamine co-ordinated could be isolated. In a discussion of this and other similar examples of chelate groups falling into the second class, it was suggested (Mann, *loc. cit.*) that probably a *steric factor* alone prevented the co-ordination of the third chelate group. Thus, if in the formation of the above compound, the first two molecules of the diamine were to occupy the 2 : 3 and the 4 : 5 apices in the 6-co-ordination octahedron, *i.e.*, were to arrange themselves in one plane, then the remaining two apices, being in the 1 : 6 or *trans*-positions, would be too far apart for union with the third molecule of the diamine, and would necessarily be saturated by other non-chelate groups.



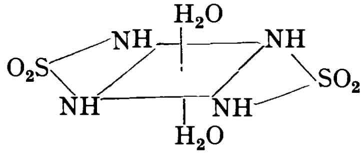
Although this assumption that the second chelate group, by arranging itself in the same plane as the first, prevents the co-ordination of the third group, did apparently explain the behaviour of the second class of chelate group, yet it threw no light on the factor which decides to which of these two classes a particular chelate group would belong. Moreover, an investigation on the complex metallic salts of sulphamide, $SO_2(NH_2)_2$, has now shown that this steric factor does not explain completely the behaviour of this class of chelate group, and that it is supplemented, and sometimes possibly even replaced, by a second factor, *viz.*, the *stability factor.*

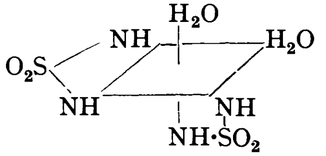
Sulphamide has long been known to act as a weak dibasic acid, and to give insoluble salts with the heavy metals, *e.g.*, $SO_2(NHAg)_2$. Salts with the alkali metals are freely soluble in water, and the sodium salt may be obtained in solution by adding sulphamide to a warm aqueous solution of sodium carbonate. If now sodium rhodiochloride is added to this solution, co-ordination occurs rapidly, but even if a considerable excess of sulphamide be used, the product is always *sodium diaquorhodiumdisulphamide*,

$$Na[(H_2O)_2Rh(N_2H_2SO_2)_2],$$

and no trisodium rhodiumtrisulphamide, $Na_3[Rh(N_2H_2SO_2)_3]$, can be detected. This monosodium salt should be capable of existence in the usual two isomeric forms, (A) and (B), in which the two molecules of water occupy respectively the 1 : 6 or *trans*- and the

(A.)





(B.)

1 : 2 or *cis*-apices. These isomerides differ essentially in that (A) is symmetric and non-resolvable into optically active forms, whilst (B) is dissymmetric and should therefore be resolvable.

Now, if the absence of the third sulphamide residue indicated that the steric factor alone determined the configuration of this monosodium salt, the latter would consist solely of the isomeride (A). Actually, however, the sodium diaquorhodiumdisulphamide has been resolved into optically active forms, having $[M]_{5780}$ + 31° and − 34°, and thus must consist wholly or in part of the isomeride (B). It is clear, therefore, that the absence of the third chelate group does not necessarily entail the *trans*-configuration, and that the stability factor must sometimes determine the composition of these salts. It is thus probable that when certain chelate groups are added in excess to the 6-co-ordinating metal, there is an immediate tendency for the metal to unite fully with three of these groups. The compound so formed, however, under the conditions of the preparation, is far less stable than that having only two chelate groups, and therefore has only a transient existence, one of the chelate groups breaking off and being replaced by other simpler non-chelate groups : the two groups replacing the third chelate group would thus necessarily enter the *cis*-positions, and their orientation could be confirmed by optical resolution. In the formation of any particular complex salt having two chelate groups, it is possible that either or both of the factors may come into play : when the *trans*-(A) and the *cis*-(B) compound are formed side by side, it is probable that the former owes its existence to the first or steric factor, and the latter to the second or stability factor.*

A point arises here which affects the constitution, but not the configuration, of these complex sulphamide salts. It has been shown by Traube (*Ber.*, 1893, **26**, 609) and confirmed by the author that, when sulphamide is boiled under reflux with sodium hydroxide solution, one molecule of ammonia is rapidly evolved with the formation of aminosulphonic acid, which then strongly resists further hydrolysis; when the sulphamide is similarly treated with dilute hydrochloric acid, aminosulphonic acid is again rapidly formed, but now does slowly undergo complete hydrolysis to ammonia and sulphuric acid. These

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* Hence in the preparation of trichelate metallic complexes, it is frequently advantageous to use as low a temperature as the general process of co-ordination allows. The steric factor would militate against the formation of such complexes probably at both low and high temperatures, the stability factor only at high temperatures. When, moreover, the *cis*- and the *trans*-dichelate compound are interconvertible in solution (as in the diaquochromiumdioxalates, Werner, *Annalen*, 1914, **406**, 270 *et seq.*), a maximum yield of the trichelate metallic complex is obtained at a temperature high enough for the equilibrium

$$\textit{trans}\text{-dichelate complex} \rightleftarrows \textit{cis}\text{-dichelate complex}$$

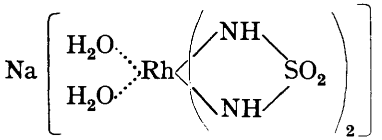
to be rapidly attained, and low enough to prevent the operation of the stability factor in forcing the equilibrium

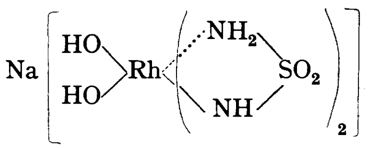
$$\textit{cis}\text{-dichelate complex} + \text{chelate group} \rightleftarrows \text{trichelate complex}$$

to the left. At this compromise temperature, and in the presence of an excess of the co-ordinating chelate groups, both equilibria will shift continuously to the right, with a steady production of the trichelate complex.

results would indicate that sulphamide, particularly in alkaline solution, tends to act chemically more as the monoamide of aminosulphonic acid than as the diamide of sulphuric acid. It therefore appeared probable that one amino-group in the sulphamide molecule

(C.)





(D.)

might co-ordinate as a basic amine group, and the other as an acidic amide group: the rhodium derivative would therefore be the dihydroxyrhodiumdisulphamide (D), and not the isomeric diaquorhodiumdisulphamide (C). Since each compound is of the " diamminotetracido " type, these considerations obviously do not affect the stereochemical properties.

This point, however, was settled by an investigation of the platinic derivatives of sulphamide. When an excess of sulphamide, again dissolved in hot sodium carbonate solution, was treated with sodium chloroplatinate, the only product isolated was *sodium monoamminomonohydroxyplatinicdisulphamide*, $Na[(NH_3)(HO)Pt(N_2H_2SO_2)_2]$, the molecule of ammonia arising from that which is always present in the solution owing to partial hydrolysis of the excess of sulphamide. This platinum compound must be of the type (C), in which each sulphamide residue is acting as a dibasic acid: no isomeric compound of the type (D), in which each sulphamide residue is acting as an amino-acid, is now possible. The nearest approach would be a compound of the type

$$Cl[(NH_3)(HO)Pt(H_2N{\cdot}SO_2{\cdot}NH)_2],$$

in which the univalent complex ion becomes electropositive, forming, *e.g.*, a monochloride, instead of electronegative. It follows by analogy that the rhodium compounds have also the constitution (C).

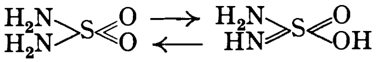
Sodium diaquorhodiumdisulphamide and sodium monoamminomonohydroxyplatinicdisulphamide are extraordinarily similar in their general properties. Both are stable, yellow, microcrystalline salts, freely soluble in cold water, but only slightly soluble in aqueous alcohol; they are thus easily isolated from aqueous solution by precipitation with a small quantity of alcohol. The corresponding *potassium* and *ammonium* salts are markedly less soluble, and are immediately precipitated from concentrated aqueous solutions of the sodium salts on addition of soluble potassium and ammonium salts. Both sodium derivatives are salts of insoluble weak complex acids, but it would appear that the free platinic *acid*, of formula $H[(NH_3)(HO)Pt(H_2N_2SO_2)_2]$, although definitely more stable than the free rhodium *acid*, $H[(H_2O)_2Rh(H_2N_2SO_2)_2]$, has even more weakly acidic properties. The feebly acidic nature of these free acids, combined with their almost complete insolubility in water, necessarily made attempts at optical resolution extremely difficult. For instance, if an aqueous solution of the sodium rhodium salt were treated with an equivalent quantity of the hydrochloride of a weak base such as brucine, considerable hydrolysis at once occurred, and the precipitated brucine rhodium salt, itself of very low solubility, was always contaminated with much insoluble free acid; even had it been possible to recrystallise this brucine salt, the process would merely have given increasing quantities of the free acid. To obtain evidence of optical resolution, it was therefore essential to use a strongly basic active amine, preferably of low molecular weight, in order to give a salt which would show minimum hydrolysis and maximum solubility, and to effect separation, not by recrystallisation, but by slow fractional precipitation at low temperatures. Ultimately the best results were obtained when an excess of *d*-α-phenylethylamine hydrochloride was slowly added to a solution of the sodium rhodium salt; the initial slight precipitate rapidly redissolved as the addition of the amine became complete, and the clear solution on standing for 24 hours gave a small precipitate of the chemically pure d-*base* d-*rhodiumsulphamide*; later precipitates were increasingly contaminated with the free acid. This initial crop was then decomposed by sodium hydroxide, and the *sodium* d-*rhodium* salt precipitated by alcohol: it had $[M] + 31°$. The corresponding *l*-sodium salt, having $[M] - 30°$, was obtained in the same way, by means of *l*-α-phenylethylamine. It was also obtained quite independently by using *d*-nor-ψ-ephedrine sulphate; the method was precisely as before, but the more weakly basic nature of the ephedrine caused separation of the free acid to occur more readily: a much smaller initial crop had to be taken to ensure that the d-*ephedrine* l-*rhodiumsulphamide* was chemically pure. The latter when treated with sodium hydroxide gave the *sodium* l-*rhodiumsulphamide* having [*M*] — 34°. These sodium salts possess considerable optical stability; the rotation in aqueous solution remains unchanged for several days at room temperature, but after 1 hour at 100° it falls by about 30%: this is probably due, however, not to racemisation, but to slow decomposition of the salt as the sulphamide residues are hydrolysed.

The free acid in the platinum series proved to be so weak that pure salts could not be obtained with amines. Fractional precipitation was attempted with the salts of various alkaloids, of *d*-α-phenylethylamine, of *d*-nor-ψ-ephedrine, and of *d*-*sec.*-butylamine, but in all cases even the smallest first crop of the salt was heavily contaminated with the free acid, and on treatment with sodium hydroxide gave inactive sodium salts. Attempts to resolve the platinum compound were therefore abandoned.

It is obviously very difficult to decide whether the two forms of sodium diaquorhodiumdisulphamide represent the optically pure enantiomorphs, although the closely similar rotatory powers of the sodium salts obtained from the phenylethylamine and the ephedrine salts suggest that these may represent the almost pure material. Since the proof of the configuration depended on the existence, and not upon the extent, of the optical activity, the isolation of the optically pure salts was not essential.

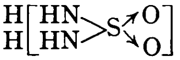
A salt which is structurally closely parallel to the above rhodiumsulphamide compound has been examined by Wahl [*Soc. Sci. Fennica Comm. Phys. Math.*, 1927, **4**, (14), 1], who, by treating copper sulphate with ethylenediamine has isolated the diaquobisethylenediaminocupric sulphate, $[(H_2O)_2Cu\,en_2]SO_4$. This compound also should exist in two isomeric forms, in which the two molecules of water are in the *cis*- and the *trans*-position. Wahl has shown that the compound can be resolved with the aid of tartaric acid, and has therefore the *cis*-configuration. The formation of this compound is evidently determined by the second (stability) factor, since Werner (*Z. anorg. Chem.*, 1899, **21**, 201) has shown that in cold concentrated solution copper will combine with 3 molecules of ethylenediamine, but that on dilution the third diamine molecule splits off: it would necessarily follow that the diaquo-compound must have the *cis*-configuration. These ethylenediaminocupric salts differ stereochemically from the rhodiumsulphamide compounds only in that with the former there is definite experimental evidence that union with the third chelate group is possible.

It has been suggested by Traube and Reubke (*Ber.*, 1923, **56**, 1656) that the properties of sulphamide—more particularly its acidic character—point to the existence of a tautomeric mixture of the normal form (E) with the *aci*-form (F). On modern formulation, the sulphur atom in (F) has now a decet of electrons (unless a co-ordinate link be assumed



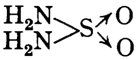
$\begin{matrix}H_2N\\H_2N\end{matrix}\!>\!S\!\ll\!\begin{matrix}O\\O\end{matrix} \rightleftarrows \begin{matrix}H_2N\\HN\end{matrix}\!\gg\!S\!<\!\begin{matrix}O\\OH\end{matrix}$

(E.) (F.)



$\begin{matrix}H\\H\end{matrix}\left[\begin{matrix}HN\\HN\end{matrix}\!>\!S\!\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right]$

(G.)



$\begin{matrix}H_2N\\H_2N\end{matrix}\!>\!S\!\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$

(H.)

between the HN═ group and the S atom, as well as between the O atom and the S atom), and formula (F) is therefore unlikely. It is more probable that sulphamide acts as an acid by direct ionisation of the hydrogen atoms, and should therefore be represented by (G). Further, since Hantzsch and Holl (*Ber.*, 1901, **34**, 3436) have shown that sulphamide is not itself an electrolyte, and that its aqueous solution gives a normal molecular weight and possesses only a feeble conductivity, it is clear that no appreciable ionisation occurs until alkali is added. Further direct evidence that the anhydrous material has the structure (H) has now been obtained by parachor measurements. The sulphamide used in these experiments was prepared by a modification of Ephraim and Gurewitsch's method (*Ber.*, 1910, **43**, 148), and recrystallisation of the crude material first from ethyl acetate and then from glycol monoethyl ether gave a very pure specimen, m. p. 93°. In spite of the recorded instability of molten sulphamide, this specimen, when fused and kept below 105°, remained unchanged long enough for an accurate parachor determination. This was kindly undertaken by Prof. S. Sugden, who obtained a value of 174 at 102°, the formula (H) requiring 178·3.

Attention should be drawn to the fact that sodium diaquorhodiumdisulphamide is the second inorganic (*i.e.*, carbon-free) compound to be isolated whose dissymmetry in solution has been definitely proved by optical resolution. The first such compound was dodeca-amminohexoltetracobaltic hexabromide, $[Co[(HO)_2Co(NH_3)_4]_3]Br_6$, which Werner (*Ber.*, 1914, **47**, 3087) prepared and resolved primarily to justify his theory of co-ordination and to remove any lingering doubts that the optical activity of other complex salts could possibly be due to the carbon atoms they contained.

The very rare occurrence of molecular dissymmetry in purely inorganic compounds is due primarily to the fact that such dissymmetry is almost invariably dependent on the presence of suitably co-ordinated cyclic systems : such systems are difficult to form with entirely inorganic elements, and are usually very unstable. Thus the demonstration of the dissymmetry which trihydrazinocobaltous sulphate, $[Co(N_2H_4)_3]SO_4$ (Curtius and Schrader, *J. pr. Chem.*, 1894, **50**, 311), should possess, would be difficult owing to the extreme instability of this compound. The sulphite radical is noteworthy in that it does give stable co-ordinated ring systems, but the molecular dissymmetry of its complex salts cannot be shown by the usual methods owing to their marked insolubility. Thus the alkali cobaltitrisulphites, such as $Na_3[Co(SO_3)_3]$, (Hahn, Meier, and Siegert, *Z. anorg. Chem.*, 1926, **150**, 127; Jantsch and Abresch, *ibid.*, 1929, **179**, 345), the corresponding rhodiotrisulphites (Dammer, " Handb. der Anorg. Chem.," 1893, **3**, 867) and the iridiotrisulphites (Birnbaum, *Annalen*, 1865, **136**, 183) are all insoluble salts.

Sodium rhodiochloride *dihydrate*, $Na_3RhCl_6,2H_2O$, has now been isolated; since the nonahydrate is efflorescent, its rhodium content cannot be assumed, but when kept over sulphuric acid in a vacuum, it rapidly gives the stable dihydrate, which is of great convenience in experiments requiring a known weight of rhodium in the form of the chloride.

EXPERIMENTAL.

All rotations were measured at 15° in a 4-dcm. tube with the Hg yellow line (λ 5780).

Sulphamide.—Various methods of prepn. were investigated, but that of Ephraim and Gurewitsch (*loc. cit.*) appeared best. SO_2Cl_2 was dropped into liquid NH_3; excess of the latter was allowed to evaporate, the solid residue dissolved in cold H_2O, and the solution acidified with dil. HCl and kept for 48 hr. whilst the imidosulphamide, $HN(SO_2NH_2)_2$, underwent hydrolysis. The long evaporation in a desiccator at room temp. was unnecessary, since if the solution was evaporated to dryness at 50° under reduced press., the yield of sulphamide was almost unaffected. The solid residue was extracted with boiling EtOAc, and on concn. crude sulphamide was deposited; two recrystns. from glycol monoethyl ether gave the pure material, m. p. 93°.

Prof. Sugden reports : " Sulphamide at 102° has $\gamma = 72{\cdot}35$ dynes/cm., and $D = 1{\cdot}611$ g./c.c., whence the parachor is 174·0. Formula (H) requires 178·3. Since compounds containing NH_2 groups are usually " associated liquids " and give low parachors, the agreement is as good as could be expected, and probably indicates that the fused sulphamide has essentially the normal structure."

Sodium Rhodiochloride Dihydrate, $Na_3RhCl_6,2H_2O$.—The chloride after recrystn. from hot H_2O was powdered and placed in a vac. over H_2SO_4 for 2 days. The *dihydrate* was obtained as a pale red powder, which even after a further 3 weeks in the desiccator, underwent no further dehydration (Found : Cl, 50·4; Rh, 24·6; H_2O, 8·4. $H_4O_2Cl_6Na_3Rh$ requires Cl, 50·6; Rh, 24·5; H_2O, 8·55%).

Sodium Diaquorhodiumdisulphamide.—The best results were obtained when 4 mols. of sulphamide were used for each mol. of the rhodiochloride, and it was essential to add the latter to the sulphamide solution; the reverse proceeding gave a final product which was often gelatinous and difficult to filter. Anhyd. Na_2CO_3 (18 g.) and sulphamide (16·8 g.) were dissolved in turn in H_2O (150 c.c.) at 30—40°; to this solution was added a solution of $Na_3RhCl_6,2H_2O$ (18 g.) in H_2O (80 c.c.) at 60—65°. The mixture was then heated on the water-bath for 20 min.; a small initial reddish ppt. rapidly redissolved, and the solution finally became clear reddish-yellow; CO_2 was evolved during the heating, and the final solution smelt of free NH_3.

The solution was then allowed to cool slowly, and a heavy, finely cryst. ppt. of the rhodium-disulphamide (8·0 g.) separated. This was filtered off, and a second crop (10 g.) then obtained by the cautious addition of EtOH to the cold filtrate (excess of EtOH caused contamination with NaCl, etc.); the above quantities represent the average yield over a number of similar prepns. The first crop consisted of an impure unstable dihydrate; the second crop was almost anhyd. Both crops were best purified by dissolution in cold H_2O, and repptn. with EtOH. The product so obtained, when dried in a vac., gave the anhyd. *sodium diaquorhodium disulphamide* as a yellow, microcryst. powder, which is apparently unchanged at 300° (Found: H, 2·1; N, 16·5; Rh, 29·1; S, 18·2. $H_8O_6N_4S_2NaRh$ requires H, 2·3; N, 16·00; Rh, 29·4; S, 18·3%). The values for N were always high, owing probably to the presence of a small amount of the corresponding monoaquomonoammino-compound.

Hydrogen Diaquorhodiumdisulphamide.—A cold aq. solution of the Na salt was treated cautiously with dil. HCl, preferably with ice-cooling, an immediate ppt. of the free *acid* being formed. This was filtered off, washed with H_2O, EtOH, and Et_2O, and dried in a vac.; it was thus obtained as a fine yellow powder, insol. in cold H_2O and unaffected by heating to 300°. It is slowly decomposed by strong acids, and their use in the initial preptn. afforded an impure product of high Rh content (Found: N, 17·0; Rh, 31·6; S, 19·3. $H_9O_6N_4S_2Rh$ requires N, 17·1; Rh, 31·35; S, 19·5%).

Ammonium salt. This *salt* was obtained as a yellow ppt. by the addition of NH_4Cl to a conc. aq. solution of the Na salt. It is only slightly sol. in cold H_2O, but attempts to wash it on the filter always caused slight hydrolysis, with consequent contamination with the free acid (Found: N, 20·3; Rh, 30·3; S, 18·5. $H_{12}O_6N_5S_2Rh$ requires N, 20·3; Rh, 29·8; S, 18·6%).

d-*α-Phenylethylamine* d-*Diaquorhodiumdisulphamide*, $C_8H_{11}N{\cdot}H[(H_2O)_2Rh(N_2H_2SO_2)_2]$.—A solution of *d*-phenylethylamine hydrochloride (5·4 g., 3 mols.) in H_2O (100 c.c.) was slowly added with stirring to a solution of the sodium rhodium salt (4 g.) in H_2O (60 c.c.). A faint ppt. was first formed but rapidly redissolved; as the addition approached completion, the clear solution again became faintly turbid, and the final portion of the hydrochloride solution was withheld if this turbidity appeared likely to develop immediately into a definite ppt. The solution was kept for 24 hr., and the fine yellow ppt. of the amine salt was then separated, further delay always causing an increasing contamination of the salt by the free complex acid. The ppt. of the *phenylethylamine* salt, which was only moderately sol. in cold H_2O, was then dried without washing, to prevent hydrolysis (Found: N, 15·5; Rh, 23·2; S, 14·5. $C_8H_{20}O_6N_5S_2Rh$ requires N, 15·6; Rh, 22·9; S, 14·3%).

Sodium d-*Diaquorhodiumdisulphamide.*—A paste of the finely powdered phenylethylamine salt and a little cold H_2O was treated with twice the theo. quantity of *N*-NaOH required to liberate the base, a clear solution being at once obtained. This was twice extracted with Et_2O, and the Na *salt* was then pptd. from the aq. solution by the addition of EtOH. It was washed repeatedly with EtOH and then Et_2O, and dried (Found: Rh, 29·5; S, 18·1%); α + 0·40°, $[\alpha]$ + 8·8°, $[M]$ + 31° (c = 1·1370). For solutions of this salt and of the sodium platinum salt, a concn. of about 1% was the highest permissible in a 4-dcm. tube, owing to the intense absorption of light..

In view of the comparatively low order of this rotation, it should be emphasised that the above method of isolating the Na salt ensured a complete absence of the active amine. The extraction with Et_2O, the pptn. with EtOH, and the final washing with organic solvents were each alone sufficient for this purpose, and the absence of the amine was confirmed by the analysis of the Na salt, and by the fact that the spec. rotation of the latter was approx. 3 times that of the active amine hydrochloride at the same dilution.

d-*Nor-ψ-ephedrine* l-*Diaquorhodiumdisulphamide*, $C_9H_{13}ON{\cdot}H[(H_2O)_2Rh(N_2H_2SO_2)_2]$.—To ensure the slow pptn. of the unhydrolysed amine salt, it was necessary to use a considerable excess of the amine (6 equiv.) and to work in dil. solution. The *d*-nor-*ψ*-ephedrine sulphate (10 g., 3 mols.) was dissolved in hot water (280 c.c.), the solution chilled, and then added to a solution of the Na salt (5 g.) in cold H_2O (60 c.c.), the mixture at first remaining clear. After 2 days, the yellow ppt. of the *ephedrine* salt which had slowly separated was removed and dried (Found: N, 14·5; Rh, 21·85; S, 12·9. $C_9H_{22}O_7N_5S_2Rh$ requires N, 14·6; Rh, 21·5; S, 13·4%).

Sodium l-*Diaquorhodiumdisulphamide.*—This was isolated from the slightly sol. ephedrine salt in precisely the same way as the sodium *d*-salt from the phenylethylamine salt; α − 0·42°, $[\alpha]$ − 9·6°, $[M]$ − 33·5° (c = 1·0980) (Found: Rh, 29·1; S, 18·2%). This *l*-Na salt was also obtained by repeating the former resolution using *l*-α-phenylethylamine hydrochloride; the amine salt was converted into the Na salt; α − 0·31°, $[\alpha]$ − 8·6°, $[M]$ − 30° (c = 0·8980).

Sodium Monoamminomonohydroxyplatinicdisulphamide.—Anhyd. Na_2CO_3 (30·4 g.) and sulphamide (27·2 g., 4 mols.) were dissolved in turn in warm H_2O (160 c.c.), and to this solution was added $Na_2PtCl_6,6H_2O$ (40 g.) also dissolved in H_2O (120 c.c.) at 50°. The mixture was heated on the water-bath for 1·5 hr., CO_2 being freely evolved; the solution, which smelt strongly of NH_3, was then allowed to cool slowly and kept over-night. The first crop (5·2 g.) of the Na salt, fine heavy orange-coloured crystals, was then filtered off, and the second crop (13·1 g.) was obtained by pptn. from the mother-liquor with EtOH. The first crop consisted of an unstable hydrate, and the anhyd. material was readily obtained from both crops by drying in a vac. over P_2O_5. The *sodium* salt was thus obtained as a fine yellow microcryst. powder, also apparently unchanged at 300° (Found: N, 15·4; Pt, 44·2; S, 14·45. $H_8O_5N_5S_2PtNa$ requires N, 15·9; Pt, 44·3; S, 14·55%). The values for N, unlike those of the Rh compound, were always low: the reason, however, is probably similar, *viz.*, that this Pt salt contained a small quantity of the corresponding monoaquomonohydroxy-compound.

Hydrogen Monoamminomonohydroxyplatinicdisulphamide.—This was obtained in precisely the same way as the complex Rh acid; it is, however, much more stable, and could be pptd. by comparatively strong acids without decomp. It is a fine yellow powder, insol. in cold H_2O, and unchanged by heating to 300° (Found: N, 16·2; Pt, 46·8; S, 15·45. $H_9O_5N_5S_2Pt$ requires N, 16·7; Pt, 46·65; S, 15·3%).

Potassium salt. This was at once pptd. when KCl was added to an aq. solution of the Na salt. It is a yellow microcryst. powder, feebly sol. in cold H_2O (Found: N, 14·7; Pt, 42·55; S, 14·0. $H_8O_5N_5S_2KPt$ requires N, 15·3; Pt, 42·75; S, 14·0%).

The ammonium salt is also only slightly soluble in water and could be similarly precipitated; it was always found, however, to be mixed with the free complex acid, and therefore to be low in its N content and high in Pt. The acidic character of the complex acid is so feeble that all salts, except those formed with strong bases, hydrolyse readily, the process being aided by the pptn. of the insol. complex acid. It was probably this factor, and not any question of configuration, that prevented optical resolution. In spite of careful investigation of the conditions, pure salts of the complex acid with *d*-α-phenylethylamine, *d*-nor-ψ-ephedrine, or *d*-*sec.*-butylamine were never obtained, the product always containing much free acid. Thus a typical preparation of the phenylethylamine salt had the composition: C, 13·1; H, 3·2; Pt, 40·1 (Calc. for $H_{20}C_8O_5N_6S_2Pt$: C, 17·8; H, 3·7; Pt, 36·2%). The impure phenylethylamine salt on treatment with NaOH sometimes gave a Na salt having a minute rotation: these results, however, could not be repeated and were probably without significance. Most preparations of the salt with this amine, and all those with nor-ψ-ephedrine and with *sec.*-butylamine gave completely inactive sodium salts.

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