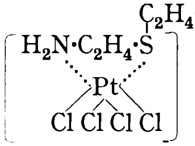
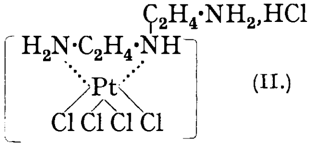
108. *The Constitution of Complex Metallic Salts. Part II. The Platinum Derivatives of ββ′-Diaminodiethylamine.*

By Frederick G. Mann.

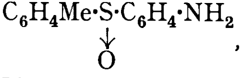
In Part I (Mann, J., 1930, 1745) stereochemical evidence was adduced to show that molecules of ammonia, water, organic sulphides, arsines, etc., are joined to the central metallic atom in complex salts by means of a co-ordinate link. For this purpose, tetrachloro-(ββ′-diaminodiethyl sulphide monohydrochloride)platinum (I) was synthesised and resolved into optically active forms. The sulphur atom in the original diaminodiethyl sulphide molecule had thus become asymmetric by the process of co-ordination, and was now stereochemically, and probably electronically, identical with the sulphur atom in the dissymmetric sulphoxides, such as *p*′-amino-*p*-methyldiphenyl sulphoxide,

(I.)



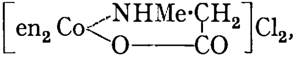


(II.)



$$\underset{\downarrow \atop O}{C_6H_4Me\cdot S}\cdot C_6H_4\cdot NH_2$$

, which had been resolved into optically active forms by Harrison, Kenyon, and Phillips (J., 1926, 2079). The evidence thus obtained for a co-ordinate link joining sulphur and platinum in the compound (I), although very strong, is not absolute, since it is possible that a singlet link might join these atoms and also enable optical activity to exist: parachor measurements of a number of similar salts are now being made to provide physical evidence on this point. Meanwhile, further stereochemical evidence for the co-ordinate link has been sought, utilising amine instead of sulphide molecules. If an asymmetric tertiary amine were co-ordinated to metal, giving a group such as $R_1R_2R_3N \rightarrow Pt$, the nitrogen atom would now become stereochemically identical with that in Meisenheimer's tertiary amine oxides, *e.g.*, $PhEtMeN \longrightarrow O$ (*Ber.*, 1908, **41**, 3966), and a complex salt containing such a nitrogen atom should therefore be similarly resolvable into optically active forms. Such a case is difficult to realise in practice, however, because tertiary amino-groups usually co-ordinate very feebly, if at all, with metallic atoms. Resort was therefore had to the much stronger co-ordinating properties of secondary amino-groups, and it was found that ββ′-diaminodiethylamine trihydrochloride, $(H_2N{\cdot}C_2H_4)_2NH,3HCl$ (see preceding paper), co-ordinated readily with chloroplatinic acid, giving *tetrachloro-*(ββ′*-diaminodiethylamine monohydrochloride*)*platinum* (II). The nitrogen atom in the central secondary amine group now resembles the sulphur atom in (I), inasmuch as, although it was symmetric in the trihydrochloride, it has become asymmetric in the complex salt by the process of co-ordination, and the compound (II) should therefore be resolvable into optically active forms.

It was recognised that, although the utilisation of a secondary in place of a tertiary amine group would give considerably increased chemical stability, it would also give considerably decreased optical stability, and that the presence of the hydrogen atom directly joined to the asymmetric nitrogen atom might cause very rapid racemisation. The results which Meisenheimer (*Annalen*, 1924, **438**, 261) had obtained with bis(ethylenediamine)-sarcosinecobaltic dichloride,  $\left[\mathrm{en_2Co}\begin{array}{l}\mathrm{\diagup NHMe{\cdot}CH_2}\\ \mathrm{\diagdown O{-\!-\!-}CO}\end{array}\right]\mathrm{Cl_2}$, gave promise, however, that the racemisation of the platinum compound (II) would not prove too rapid for experimental observation. A consideration of Meisenheimer's compound shows that, irrespective of the asymmetric nitrogen atom, the complex ion is itself dissymmetric, since it consists essentially of three chelate groups arranged around the central cobalt atom : the nitrogen atom may theoretically act in addition as a secondary source of optical activity, so that for stereochemical purposes the racemic complex may be conveniently written as $[\mathrm{Co^{\pm}N^{\pm}}]$. Meisenheimer converted the dichloride into the dibromocamphorsulphonate, which was then separated into a less soluble fraction (A), having $[M]_D = -920°$, and a more soluble fraction (B), having $[M]_D = +2020°$. These fractions were considered to contain the active cobalt complex but the racemic nitrogen : allowing a value of $+273°$ for each sulphonate ion, (A) has thus the $[\mathrm{Co^{-}N^{\pm}}]$ ion of $[M] = -1466°$, and (B) has the $[\mathrm{Co^{+}N^{\pm}}]$ ion of $[M] = +1474°$. The fraction (B) was then further recrystallised and gave a less soluble fraction (B_1), having $[M] = +2290°$, which, however, on standing in aqueous solution for several hours, fell to the original value of $+2020°$: a more soluble fraction (B_2) had $[M]_D = +1775°$, which increased in solution to $+1825°$ instead of to the original value. The fractions (B_1) and (B_2) were therefore considered to possess the $[\mathrm{Co^{+}N^{+}}]$ and the $[\mathrm{Co^{+}N^{-}}]$ complexes respectively, the change in rotation being due in each case to the racemisation of the nitrogen atom, the final activity of the complex ion being due to the cobalt alone.

These results, involving a partial racemisation of a complex ion which already possessed considerable activity due to its own molecular dissymmetry, are clearly unsatisfactory as evidence for the linkage of the asymmetric nitrogen atom. They are further weakened by the fact that the fractions (B_1) and (B_2), when converted even under the most favourable conditions into the corresponding di-iodides, showed an optical activity due to the cobalt alone : no evidence for the activity of the nitrogen atom could thus be obtained when once the camphorsulphonate radical had been removed.

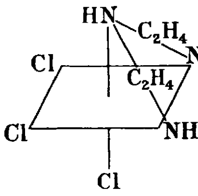
The stereochemical properties of tetrachloro(diaminodiethylamine monohydrochloride)-platinum are simpler than those of Meisenheimer's compound, since in the platinum derivative the nitrogen atom is the only possible source of optical activity : if, therefore, the monohydrochloride had given a camphor- or bromocamphor-sulphonate which in turn had shown partial racemisation, this variation in activity must have been due to the asymmetric nitrogen atom alone.

Treatment of the monohydrochloride with ammonium camphorsulphonate, the method employed in the resolution of the sulphide-platinum compound (I), did not, however, give *tetrachloro*(*diaminodiethylamine camphorsulphonate*)*platinum* (III), and both this compound and the *bromocamphorsulphonate* had to be prepared by double decomposition with the corresponding silver sulphonates. This method, although successful, gave a low yield, since a simultaneous side reaction occurred precisely similar to that shown by compound (I), *viz.*, the silver sulphonate abstracted hydrogen chloride from the platinum derivative, and the amino-group thus liberated co-ordinated at once with the metal, giving the univalent trichlorodiaminodiethylamineplatinic complex, which in turn formed a camphorsulphonate. The result was therefore that silver camphorsulphonate gave a mixture of the required sulphonate (III) and *trichloro(diaminodiethylamine)platinic camphorsulphonate* (IV), some

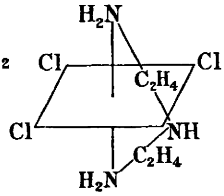
$$[Cl_4Pt(H_2N\cdot C_2H_4)_2NH,HCl] \begin{array}{l} \nearrow [Cl_4Pt(H_2N\cdot C_2H_4)_2NH,C_{10}H_{15}O\cdot SO_3H] \quad (III.) \\ \searrow [Cl_3Pt(H_2N\cdot C_2H_4)_2NH]C_{10}H_{15}O\cdot SO_3 \quad (IV.) \end{array}$$

unchanged monohydrochloride necessarily remaining in solution. Fractional recrystallisation of the camphor- and the bromocamphor-sulphonates, although attempted under various conditions, gave no indication of activity due to the nitrogen, the rotation of the compounds being always constant and equal to that due to the camphorsulphonate ion alone. It appeared, therefore, that even if recrystallisation of the sulphonate derivatives was producing optical separation, the latter was being completely masked by a subsequent very rapid racemisation, and further attempts to resolve this platinic compound were therefore abandoned.

The complex ion present in the compound (IV) is stereochemically parallel to the corresponding diaminodiethyl sulphide compound (Mann, *loc. cit.*) and should also exist in two isomeric forms, in one of which (IV*a*) the triamine occupies the three apices of a triangular face of the 6-co-ordination octahedron, whilst in the second (IV*b*) it occupies the three apices of a square cross-section. The *monochloride* of this complex crystallises in magnificent pale yellow prisms which are not apparently a mixture: an *X*-ray examination of these crystals is now being made.



(IV*a*.)



(IV*b*).

When tetrachloro(diaminodiethylamine monohydrochloride)platinum was treated with chloroplatinic acid, the corresponding slightly soluble *platinichloride*,

$$[Cl_4Pt(H_2N\cdot C_2H_4)_2NH,HCl]_2PtCl_4,H_2O,$$

was immediately precipitated. Hofmann (*Proc. Roy. Soc.*, 1862, **11**, 417) probably prepared both these compounds when studying the properties of diaminodiethylamine platinichloride, $2(H_2N\cdot C_2H_4)_2NH,3H_2PtCl_6$, described in the previous paper (p. 465), for he says " The platinum salt of this (amine), as well as of several other triammonias I have examined, cannot be recrystallised without at least partial decomposition. New platinum compounds are thus produced, in some of which the chloride is united with a smaller number of molecules of platinum tetrachloride,* whilst others, almost insoluble in water, to judge from the enormous amount of platinum which they contain, appeared to be produced by platinic substitution."

In view of the failure to resolve the tetrachloro-platinum compound (II), attempts were made to prepare the dichloro(diaminodiethylamine monohydrochloride)platinum, $[Cl_2Pt(H_2N\cdot C_2H_4)_2NH,HCl]$, (V), in case this platinous salt should possess greater optical stability; they were, however, unsuccessful. In one experiment, a small quantity of the corresponding *platinochloride*, $[Cl_2Pt(H_2N\cdot C_2H_4)_2NH,HCl]_2PtCl_2,H_2O$, was isolated, but in most experiments a mixture of very soluble salts was obtained. The chief component of this mixture was probably *monochlorodiaminodiethylamineplatinous monochloride*, $[ClPt(H_2N\cdot C_2H_4)NH]Cl$, since concentrated sodium bromide solution precipitated the *bromide*, $[BrPt(H_2N\cdot C_2H_4)_2NH]Br$. The co-ordinated halogen atom is extraordinarily labile in these compounds, since an aqueous solution of this bromide when treated with cold potassium iodide solution rapidly precipitated in turn the *di-iodo*-compound,

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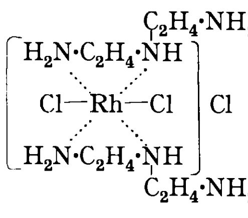
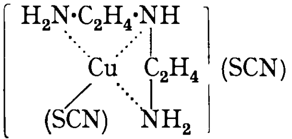
* Termed *dichloride* by Hofmann, although he changed the name shortly afterwards.

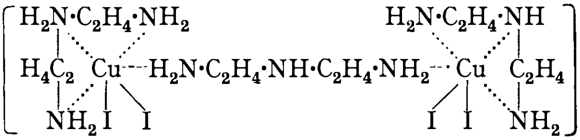
$[IPt(H_2N{\cdot}C_2H_4)_2NH]I$. In this series of compounds the triamine is co-ordinated to the platinum by all three amino-groups, and the apparent absence of the platinous compound (V), in which co-ordination occurs through only two amino-groups, represents the chief and most striking difference between the co-ordination chemistry of diaminodiethylamine and that of diaminodiethyl sulphide and triaminopropane.


(V*a*.)

Efforts were now made to synthesise a rhodium compound in which the diamino co-ordination would also occur and which should therefore be resolvable by virtue of the asymmetric secondary amine group. These efforts were only partially successful, however. The trihydrochloride of the base reacted with sodium rhodiochloride to give *dichlorobis(diaminodiethylamine monohydrochloride)rhodium monochloride* (V*a*) : this compound in solution furnishes three chlorine ions, and thus combined with unchanged sodium rhodiochloride to give the corresponding *rhodiochloride*, $\{[Cl_2Rh\{(H_2N{\cdot}C_2H_4)_2NH,HCl\}_2]Cl\}RhCl_3$. No efforts were made to convert this very stable substance into the simpler compound (V*a*), since not only does the latter possess two similar asymmetric nitrogen atoms, and should therefore theoretically be capable of existence in racemic and *meso*-forms, but in addition, if the two co-ordinated chlorine atoms are in the *cis*-position, the complex itself, irrespective of the nitrogen atoms, possesses molecular dissymmetry : it would therefore be an unsuitable compound for the required purpose. Potassium thiocyanate was added to the mother-liquor from the preparation of the above rhodiochloride in the hope of precipitating the thiocyanate of some more soluble rhodium complex. After long standing, fine yellow crystals separated : these were rhodium-free, however, and proved to be *oxythiocyanic acid*, $(HCNSO)_n$, a compound which is apparently related to the perthiocyanic acid, $[(HCNS)_2S]_n$, described by Chattaway and Stevens (J., 1897, **71**, 607, 833).

Triaminopropane co-ordinates readily with copper sulphate, and treatment with a feebly acidic solution of potassium thiocyanate gives the deep blue bis(triaminopropane monothiocyanate)cupric dithiocyanate, $[Cu(H_2N{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN)_2](SCN)_2$ (Mann, J., 1926, 2681; 1927, 1224). Diaminodiethylamine also co-ordinates readily with cupric salts, but even in the presence of a large excess of the amine, weakly acidic potassium thiocyanate precipitated only the intense blue *monothiocyanatodiaminodiethylaminecupric monothiocyanate* (VI). Here again, as in the platinous series, the latter base seems unable to co-ordinate through two amino-groups alone with a 4-co-ordination metallic atom. When the solution of copper sulphate in excess of diaminodiethylamine was treated with concentrated potassium iodide solution, large deep blue crystals of *tris(diaminodiethylamine)biscupric iodide dihydrate*, $3(H_2N{\cdot}C_2H_4)_2NH,2CuI_2,2H_2O$, slowly formed. The constitution of this compound is difficult to decide. The water molecules were easily lost in a vacuum and represent therefore true water of crystallisation : an aqueous solution of the compound gave no immediate precipitate with silver nitrate and thus did not apparently contain iodine ions. It is possible, therefore, that each copper atom is showing a co-ordination number of 6, and by uniting with four amino-groups and two iodine atoms forms a neutral non-ionic complex : the third triamine molecule bridges the copper atoms, uniting to each by a primary amine group, the central secondary amine group remaining un-co-ordinated (VII). When solutions containing this substance were made weakly acid with a stream of carbon dioxide, this third amine molecule was split off : the co-ordination number of the copper dropped to 4, and *monoiododiaminodiethylaminecupric monoiodide*, $[ICu(H_2N{\cdot}C_2H_4)_2NH]I$ (VIII), crystallised.


(VI.)


(VII.)

Tervalent cobalt combined with the triamine to give salts such as *bis(diaminodiethyl-*

amine)cobaltic tri-iodide, $[Co\{(H_2N{\cdot}C_2H_4)_2NH\}_2]I_3$, in which all three amino-groups of each triamine molecule are co-ordinated to the cobalt. A description of a number of such salts with the 6-co-ordination metals, and a discussion of their stereochemistry, will be published later.

Since the primary purpose of this investigation, namely, to obtain stereochemical evidence for the co-ordinate link between nitrogen and the central metallic atom, has thus not been achieved, compounds of platinum with other polyamines, such as ββ'-diaminodiethylmethylamine, $(H_2N{\cdot}C_2H_4)_2NMe$, and β-aminodiethylmethylamine, $H_2N{\cdot}C_2H_4{\cdot}NMeEt$, are now being studied. In these compounds the asymmetric nitrogen is now part of a tertiary amine group and should therefore possess much greater optical stability than the secondary amine compounds described in the present paper: at the same time the co-ordination of the tertiary amine group should be greatly strengthened by the chelated ring of which this group forms part.

EXPERIMENTAL.

All the rotations given in this paper were measured at 15° in a 4-dcm. polarimeter tube, with the mercury green line (λ = 5461).

Tetrachloro-(ββ'-diaminodiethylamine monohydrochloride)platinum Monohydrate (II).—An aqueous solution of chloroplatinic acid (67 c.c., containing 10% of platinum) was added to a solution of ββ'-diaminodiethylamine trihydrochloride (15·0 g.; 2 mols.) in hot water (240 c.c.), and the mixture boiled under reflux for 6 hours, the colour becoming pale orange. If the pure recrystallised trihydrochloride had been used, the solution was now clear, but if the crude trihydrochloride mentioned in the previous paper was used, a small quantity of a precipitate had separated. In the latter case, the precipitate was filtered off, washed with hot water, alcohol and ether, and dried, and so obtained as a fine amorphous olive-coloured powder, which darkened at 265° but otherwise remained unchanged below 290°. This compound is a derivative of the piperazine present in the crude trihydrochloride as a by-product: its identity is uncertain, as it may be *tetrachloropiperazineplatinum*, $[Cl_4Pt(HNC_4H_8NH)]$, or the isomeric *dichlorodipiperazineplatinic platinichloride*, $[Cl_2Pt(HNC_4H_8NH)_2]PtCl_6$ (Found: C, 11·5; H, 2·5; N, 6·65; Pt, 45·4. $C_4H_{10}N_2Cl_4Pt$ requires C, 11·3; H, 2·4; N, 6·6; Pt, 46·1%. The platinum content was always slightly low). After removal of this precipitate, the filtrate was evaporated on the water-bath until crystals appeared on the surface; cooling then caused copious crystallisation of the crude yellow monohydrochloride. The latter, twice recrystallised from water, gave the pure *tetrachloro(diaminodiethylamine monohydrochloride)platinum monohydrate* as lemon-yellow crystals, which began to shrink at 215°, melted to a red plastic mass at 221°, and decomposed with effervescence at 228—230° (Found: C, 9·8; H, 3·5; N, 8·35; Pt, 39·25. $C_4H_{16}ON_3Cl_5Pt$ requires C, 9·7; H, 3·3; N, 8·5; Pt, 39·45%). The monohydrochloride is moderately soluble in cold water and freely in hot water: the dry material is stable unless exposed to the light for several weeks; it then develops a red colour on the surface.

In earlier experiments, attempts were made to prepare this compound by boiling an aqueous solution containing equimolecular quantities of diaminodiethylamine trihydrochloride and sodium platinichloride. The solution, however, rapidly deposited the platinichloride of the above monohydrochloride, its identity being confirmed by a direct preparation from the monohydrochloride and chloroplatinic acid. *Tetrachloro(diaminodiethylamine monohydrochloride)-platinum platinichloride dihydrate*, $[Cl_4Pt(NH_2{\cdot}C_2H_4)_2NH,HCl]_2PtCl_4,2H_2O$, was thus obtained as fine yellow-orange crystals, which could be recrystallised from much boiling water (Found: C, 7·3; H, 2·4; N, 6·25; Pt, 44·2. $C_8H_{32}O_2N_6Cl_{14}Pt_3$ requires C, 7·2; H, 2·4; N, 6·3; Pt, 44·2%).

When a cold saturated aqueous solution of tetrachloro(diaminodiethylamine monohydrochloride)platinum was diluted with twice its volume of concentrated sodium bromide solution, deep orange crystals of the *dichlorodibromo-monohydrochloride*,

$$[Cl_2Br_2Pt(H_2N{\cdot}C_2H_4)_2NH,HCl],H_2O,$$

separated after several minutes: since attempted recrystallisation from hot water caused rapid decomposition, they were separated, washed with ice-cold water, alcohol, and ether, and dried (Found: C, 8·4; H, 2·85; N, 7·4; Pt, 33·1. $C_4H_{14}N_3Cl_3Br_2Pt,H_2O$ requires C, 8·2; H, 2·8; N, 7·2; Pt, 33·4%).

Aqueous solutions of tetrachloro(diaminodiethylamine monohydrochloride)platinum were treated with ammonia and with ethylenediamine in the expectation that the amino-group thus liberated from the monohydrochloride would co-ordinate with the metal, evicting an atom of chlorine, and giving trichlorodiaminodiethylamineplatinic monochloride,

$[Cl_3Pt(H_2N{\cdot}C_2H_4)_2NH]Cl$,

a reaction which would have been parallel to that shown by the corresponding derivatives of triaminopropane and diaminodiethyl sulphide (Mann, *loc. cit.*). Actually, this compound was never obtained by this method : instead, the monohydrochloride behaved abnormally, for the addition of ammonia or of ethylenediamine produced first an orange-red colour, which rapidly faded to a very pale yellow : a fine deposit of heavy orange crystals then separated in small amount, the major portion of the platinum remaining in solution in the form of some very soluble deliquescent derivative. The orange crystals were separated, washed with a little ice-cold water, and dried. Their identity remains obscure : it is possible that reduction had occurred, giving dichloro(diaminodiethylamine hydrochloride)platinum (V), or that a neutral non-ionic compound, trichlorodiaminodiethylamineplatinum, $[Cl_3Pt(H_2N{\cdot}C_2H_4)_2NH]$ (C), has been formed. The production of neither of these compounds is probable : the compound (V) would be moderately soluble in cold water and certainly much paler in colour than the parent tetrachloro-compound, whilst the actual product was almost insoluble in cold water and darker in colour; the compound (C) entails a tervalent platinum atom of co-ordination number 6, a very rare phenomenon [Found : C, 11·8; H, 3·5, 3·45; N, 10·5; Pt, 48·1; Cl, 25·1. (V) requires C, 11·8; H, 3·45; N, 10·35; Pt, 48·1; Cl, 26·2%. (C) requires C, 11·9; H, 3·2; N, 10·4; Pt, 48·2; Cl, 26·3%].

*Tetrachloro(diaminodiethylamine mono-*d*-camphor-β-sulphonate)platinum* (III).—A solution of silver *d*-camphor-β-sulphonate (16·0 g.; 1 mol.) in water (60 c.c.) was rapidly added with stirring to a solution of the platinum-monohydrochloride (23·0 g.) in hot water (120 c.c.). The mixture was boiled for 2 minutes, filtered, and the filtrate evaporated on the water-bath to small bulk. On cooling, clumps of pale yellow crystals slowly appeared : these were separated and recrystallised from a little hot water, giving the above pure *mono-*d*-camphor-β-sulphonate* (Found : C, 24·8; H, 4·5; Pt, 29·0. $C_{14}H_{29}O_4N_3Cl_4SPt$ requires C, 25·0; H, 4·35; Pt, 29·0%). A 1·3183% aqueous solution had $\alpha + 0{\cdot}48°$, $[\alpha] + 9{\cdot}1°$, $[M] + 61°$. The sulphonate was recrystallised thrice from small quantities of hot water, the final crop having $[M] + 63°$. Since the camphorsulphonate ion has $[M] + 65{\cdot}8°$ (Graham, J., 1912, **101**, 746), it was clear that no resolution was occurring, a fact which was confirmed by treating the final camphorsulphonate in cold saturated solution with concentrated calcium chloride solution. The crystalline monohydrochloride thus regenerated, when separated, washed repeatedly with alcohol and dried, was chemically pure (Found : Pt, 39·1%) but optically inactive. Further evaporation of the original filtrate gave a series of crops whose increasingly high platinum content showed clearly the presence of a by-product. To check the formation of this compound, the above preparation was repeated, using, however, suitably diluted cold aqueous solutions, the camphorsulphonate being added drop by drop with mechanical stirring over a period of ½ hour. The liquid was filtered and then evaporated to small bulk at room temperature in a vacuum. The yellow crystals which separated were recrystallised from hot water, and proved to be *trichlorodiaminodiethylamineplatinum* d*-camphor-β-sulphonate* (IV) (Found: C, 26·1; H, 4·4; Pt, 30·8. $C_{14}H_{28}O_4N_3Cl_3SPt$ requires C, 26·4; H, 4·4; Pt, 30·7%). A 0·9817% aqueous solution had $\alpha + 0{\cdot}38°$, $[\alpha] + 9{\cdot}7°$, $[M] + 62°$. The identity of this compound was confirmed by treating it in cold saturated solution as before with calcium chloride : the yellow precipitate which rapidly separated was recrystallised from hot water, and gave *trichlorodiaminodiethylamineplatinic chloride monohydrate*, $[Cl_3Pt(H_2N{\cdot}C_2H_4)_2NH]Cl,H_2O$, as magnificent, heavy, pale yellow prisms (Found : C, 10·7; H, 3·25; Pt, 42·5. $C_4H_{15}ON_3Cl_4Pt$ requires C, 10·5; H, 3·3; Pt, 42·6%). Working in cold solution had thus markedly increased the proportion of trichloro-platinum complex ion, and it would appear that the tetrachloro-platinum sulphonate can be successfully prepared only in hot solution.

*Tetrachloro(diaminodiethylamine mono-*d*-α-bromocamphor-π-sulphonate)platinum Dihydrate*, $[Cl_4Pt(H_2N{\cdot}C_2H_4)_2NH,C_{10}H_{14}BrO{\cdot}SO_3H],2H_2O$.—The preparation of this compound was first attempted by adding a solution of silver bromocamphorsulphonate (19·2 g.; 1 mol.) in hot water (100 c.c.) rapidly with stirring to one of the platinum monohydrochloride (20·0 g.) also in hot water (80 c.c.). The mixed solutions were boiled for 5 minutes, filtered, evaporated on the water-bath to about half-bulk, cooled, and finally concentrated in a vacuum at room temperature. The heavy yellow crystals which slowly formed in the almost syrupy solution were separated, washed with a little water, and dried : they proved to be an inactive sample of the almost pure, unchanged platinum hydrochloride (Found : Pt, 38·7%). The filtrate slowly deposited a further crop of crystals, paler in colour than the first crop : after several days they were separated and recrystallised twice from water, and proved to be *trichlorodiaminodiethylamineplatinum* d-*bromocamphorsulphonate*, $[Cl_3Pt(H_2N{\cdot}C_2H_4)_2NH]C_{10}H_{14}BrOSO_3$, very pale lemon-coloured crystals, m. p. 263—264° (decomp.) (Found : C, 23·7; H, 3·9; Pt, 27·0. $C_{14}H_{27}O_4N_3Cl_3BrSPt$ requires C, 23·5; H, 3·8; Pt, 27·3%). A 0·6690% aqueous solution had $\alpha + 1{\cdot}27°$, $[\alpha] + 47{\cdot}6°$, $[M] + 340°$. The identity of this compound was also confirmed by treating it in cold saturated aqueous solution with calcium chloride, and thus precipitating again the monohydrated chloride of the complex (Found : Pt, 42·5%).

The preparation was now repeated at room temperature, a solution of silver bromocamphorsulphonate (11·5 g.) in cold water (150 c.c.) being slowly added during 30 minutes to a solution of the platinum monohydrochloride (12 g.) also in cold water (150 c.c.). When the filtered solution was evaporated in a vacuum desiccator to small bulk, a small crop of the inactive unchanged hydrochloride was again deposited. After removal of this, the filtrate slowly deposited heavy crystalline orange spherical nodules, interspersed with a fine yellow powder. The latter was easily removed by dissolution in a little hot water, and the nodules were then powdered and investigated before recrystallisation lest the latter process should change either the rotation or the composition. They proved to be the required *tetrachloro(diaminodiethylamine-*d-*bromocamphorsulphonate)platinum dihydrate* (Found : C, 21·1; H, 4·3; Pt, 24·75. $C_{14}H_{32}O_6N_3Cl_4BrSPt$ requires C, 21·3; H, 4·1; Pt, 24·8%). A 0·8910% aqueous solution had $\alpha + 1{\cdot}54°$, $[\alpha] + 43{\cdot}2°$, $[M] + 340°$. The substance was now rapidly recrystallised twice from a little hot water, and thus obtained as yellow crystals, which softened slightly at *ca.* 120° as water of crystallisation escaped and finally melted at 205—208° (decomp.) : the composition and rotatory power were unchanged, and since, moreover, the bromocamphorsulphonate ion itself has $[M]$ 347° (Pope and Read, J., 1910, **97**, 2201), it is clear no resolution was occurring (Found : Pt, 25·0%. A 1·156% aqueous solution had $\alpha + 2{\cdot}03°$, $[\alpha] + 43{\cdot}9°$, $[M] + 346°$). Whereas the required tetrachloro-camphorsulphonate could thus be successfully obtained only by working in hot solution, the corresponding bromocamphorsulphonate could be obtained only in cold solution.

Attempts were made to convert the tetrachloro(diaminodiethylamine hydrochloride)platinum into the corresponding tartrate by shaking a lukewarm aqueous solution of the former with the required quantity of silver tartrate. The filtered solution on evaporation at room temperature deposited, however, large crystals of the trichlorodiaminodiethylamineplatinic monochloride (Found : C, 10·6; H, 3·5%), the silver tartrate having merely removed hydrogen chloride from the hydrochloride.

Action of Diaminodiethylamine Trihydrochloride on Potassium Platinochloride.—The trihydrochloride (15·4 g.; 2 mols.) was added to a solution of potassium platinochloride (15 g.) in hot water (300 c.c.) and the mixture boiled under reflux for 8 hours, the colour becoming pale orange-red. Evaporation to small bulk, followed by cooling, caused the separation of much potassium chloride : this was removed and the filtrate after 48 hours gave a considerable further deposit of colourless crystals. These were obviously a mixture and were difficult to purify by recrystallisation : the chief component was therefore isolated as the less soluble bromide by treatment in aqueous solution with saturated sodium bromide solution. The product which separated was then recrystallised from hot water, and *monobromo(diaminodiethylamine)platinous monobromide*, $[BrPt(H_2N{\cdot}C_2H_4)_2NH]Br$, thus obtained as heavy cream-coloured crystals, which darkened to a grey colour at *ca.* 200° but underwent no further change below 300° (Found : C, 10·5; H, 3·0; N, 9·0; Pt, 42·6. $C_4H_{13}N_3Br_2Pt$ requires C, 10·5; H, 2·9; N, 9·2; Pt, 42·6%). When a cold saturated solution of this compound was treated with potassium iodide solution, long cream-coloured needles of *monoiodo(diaminodiethylamine)platinous monoiodide* rapidly separated : these, when recrystallised from a little hot water and dried, darkened at 270° and melted at 280—281° (decomp.) (Found : C, 8·9; H, 2·55; N, 7·6; Pt, 35·5. $C_4H_{13}N_3I_2Pt$ requires C, 8·7; H, 2·4; N, 7·6; Pt, 35·35%).

This experiment was now repeated, but to the original mixed solution was added *N*-hydrochloric acid (72 c.c.; 2 mols.) in the expectation that the increased concentration of acid would prevent the co-ordination of the third amino-group. Evaporation to small bulk again gave a deposit of potassium chloride, which now contained some reddish crystals. The mixture was filtered off, and the potassium chloride eliminated by shaking with a minimum of ice-cold water. The small undissolved residue was twice recrystallised from hot water, and *dichloro(diaminodiethylamine monohydrochloride)platinum platinochloride monohydrate* obtained as fine reddish-brown crystals (Found : C, 9·05; H, 2·8; N, 7·7; Pt, 53·3. $C_8H_{30}ON_6Cl_8Pt$ requires C, 8·8; H, 2·8; N, 7·7; Pt, 53·4%). The original filtrate in this preparation again contained a mixture of very soluble compounds.

In order to check the formation of this platinochloride and to obtain the parent monohydrochloride, the experiment was repeated with 4 mols. of the amine trihydrochloride : the product, however, was again a mixture difficult to purify, and the chief product isolated by means of sodium bromide was the above monobromide. Attempts to prepare the required dichloromonohydrochloride were therefore abandoned.

Dichlorobis(diaminodiethylamine monohydrochloride)rhodium Rhodiochloride.—A solution of sodium rhodiochloride dihydrate (6·0 g.) in water (20 c.c.) was diluted with *N*-hydrochloric acid (43 c.c. ; 3 mols.), added to a solution of the amine trihydrochloride (6·1 g. ; 2 mols.) in water (150 c.c.), and boiled under reflux for 9 hours. The pale yellowish-red solution, on cooling, gave no deposit, and was therefore evaporated to small bulk : directly crystals appeared on the surface, the solution was filtered and allowed to cool. A considerable quantity of an apparently amorphous reddish-brown substance separated : this compound, when filtered from the original solution, was found to redissolve very sparingly in hot water, but, when once dissolved, it did not readily separate again on cooling. It was therefore purified by repeated washing with hot water, then with alcohol and ether, and dried. The *dichlorobis(diaminodiethylamine monohydrochloride)rhodium rhodiochloride* obtained always gave low chlorine results on analysis, but the percentage of the other elements indicated that the substance was pure (Found : C, 14·0; H, 4·2; N, 12·25; Cl, 38·3; Rh, 29·3. $C_8H_{28}N_6Cl_8Rh_2$ requires C, 13·8; H, 4·0; N, 12·05; Cl, 40·7; Rh, 29·5%). To obtain the monochloride (V*a*) and to prevent the formation of the rhodiochloride, the experiment was now repeated with 4 mols. of the amine trihydrochloride. The experiment proceeded precisely as before, however, and the same compound was isolated (Found : N, 12·1; Cl, 38·5; Rh, 29·4%).

A saturated solution of potassium thiocyanate was added to the filtrate from the above rhodiochloride in the hope of precipitating a simpler rhodium compound as a thiocyanate. After 1 month, small clusters of fine yellow crystals had separated in very small amount. These were filtered off, washed with cold water, in which they appeared to be insoluble, and recrystallised from much boiling water, from which, on cooling and standing for several hours, the characteristic clusters of minute, dark yellow crystals reappeared. A second recrystallisation did not change the composition of the *oxythiocyanic acid* thus obtained (Found : C, 16·1; H, 1·5; N, 18·8; S, 43·1. CHONS requires C, 16·0; H, 1·3; N, 18·7; S, 42·7%). The acid melted to a plastic mass at 200—202° (decomp.).

The Cupric Derivatives of ββ'-Diaminodiethylamine.—A solution of hydrated copper sulphate (10 g.) in water (30 c.c.) was added to a solution of the free amine prepared by dissolving diaminodiethylamine trihydrochloride (9·3 g. ; 2·2 mols.) in 15% sodium hydroxide solution (35·2 c.c.), a transient precipitate, followed by the production of a clear, intensely deep blue solution, being thus obtained. A portion of this solution, when diluted with almost saturated potassium thiocyanate solution, gave no precipitate even after 2 weeks : when, however, the potassium thiocyanate solution contained a few drops of acetic acid, a deep blue precipitate rapidly formed. This was twice recrystallised from a little hot water, and *thiocyanato(diaminodiethylamine)cupric monothiocyanate* (VI) obtained as compact, deep blue crystals, m. p. 165—167° (decomp.) (Found : C, 25·7; H, 4·6; N, 24·6; Cu, 22·8; total SCN liberated by acids, 41·2. $C_6H_{13}N_5S_2Cu$ requires C, 25·45; H, 4·6; N, 24·75; Cu, 22·5; 2SCN, 41·1%). This compound is moderately soluble in cold and freely in hot water : it is at once decomposed by strong acids, the intense blue colour being replaced by the much paler colour of the cupric ion.

When another portion of the original solution was diluted with a saturated potassium iodide solution and kept for 2 days, large, deep blue prisms slowly appeared. These dissolved rapidly in hot water, but did not separate again readily on cooling : they were therefore filtered off, washed twice with ice-cold water, and dried over calcium chloride. The *tris(diaminodiethylamine)dicupric tetraiodide dihydrate* (VII) was thus obtained pure (Found : C, 14·9; H, 4·5; N, 12·9; I, 52·1; Cu, 13·1. $C_{12}H_{39}N_9I_4Cu_2,2H_2O$ requires C, 14·7; H, 4·4; N, 12·85; I, 51·8; Cu, 13·0%). Confinement in a vacuum over sulphuric acid for 3 days gave the pure anhydrous material (Found : N, 13·3; I, 53·6. $C_{12}H_{39}N_9I_4Cu_2$ requires N, 13·35; I, 53·8%). When a cold aqueous solution of the iodide was treated with silver nitrate solution, a fine opalescence was alone produced, and became steadily heavier on standing : boiling hastened considerably the precipitation of silver iodide. When pure carbon dioxide was bubbled through the filtrate from which the above tetraiodide had separated, small dark green crystals slowly appeared : these also proved to be too soluble in cold water to allow useful recrystallisation, and were therefore filtered off, washed twice with chilled water, and dried in a vacuum. *Monoiodo(diaminodiethylamine)cupric monoiodide* (VIII) was thus obtained in small, characteristically bottle-green leaflets : an aqueous solution when treated with silver nitrate gave an immediate precipitate of silver iodide (Found : C, 11·7; H, 2·9; N, 9·85; I, 60·3. $C_4H_{13}N_3I_2Cu$ requires C, 11·4; H, 3·1; N, 10·0; I, 60·4%).

Bis(diaminodiethylamine)cobaltic Tri-iodide.—Diaminodiethylamine trihydrochloride (8·9 g.; 2·25 mols.) and aquopentamminocobaltic trichloride (5·0 g.) were added in turn to *N*-sodium hydroxide (125 c.c.), and the mixture heated on the water-bath for 2 hours, ammonia being freely evolved. The solution was then evaporated to about one-third of its original volume, filtered, and allowed to cool. The addition of saturated potassium iodide solution rapidly gave a crystalline precipitate, which was separated and twice recrystallised from hot water, *bis(diaminodiethylamine)cobaltic tri-iodide* being obtained in heavy, dark brown crystals which were unchanged on heating to 280° and were macroscopically indistinguishable from the corresponding triaminopropane compound (Found : C, 15·0; H, 4·1; N, 12·9; I, 58·8. $C_8H_{26}N_6I_3Co$ requires C, 14·9; H, 4·05; N, 13·0; I, 58·95%).

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