321. *Stereochemistry of Plato-tetrammines.*

By H. D. K. Drew, F. S. H. Head, and H. J. Tress.

It has been claimed that the plato-tetrammine, $[Pt\ ib_2]Cl_2$, is resolvable into optical enantiomorphs, which would imply a non-planar distribution of four valencies about the platinum atom. In a previous paper, however, we described the isolation of *cis*- and *trans*-forms of this tetrammine, implying a planar distribution of valencies. The present paper describes attempts to resolve these *cis*- and *trans*-forms through the bromocamphorsulphonates: there was no resolution in either case, which supports our former conclusion. On the other hand, attempts to resolve a new plato-tetrammine, $[Pt\ ib\ mt]Cl_2$, which should be resolvable on a planar or on a tetragonal bisphenoidal but not on a regular tetrahedral basis of valency distribution about platinum, all failed, although a number of resolving agents were tried.

Reihlen and also Rosenheim and their collaborators (see, *e.g.*, *Annalen*, 1931, **489**, 42; 1935, **519**, 80; 1935, **520**, 256; *Z. anorg. Chem.*, 1933, **210**, 289) have claimed evidence for

the optical resolution of plato-tetrammines. In particular, so far as the present work is concerned, Reihlen and Hühn (first reference, above) claimed the resolution of [Pt ib_2]Cl_2* as α-bromo-*d*-camphor-π-sulphonate. Although we showed later (J., 1934, 221) that this chloride existed in well-defined *cis*- and *trans*-planar forms, and that Reihlen and Hühn probably examined a mixture of both, yet it was recognised that a tetragonal bisphenoidal arrangement of the platinum valencies, which is a conceivable, but rather improbable, alternative to the planar arrangement adopted by us, would demand that both forms of [Pt ib_2]Cl_2 should be resolvable (since the chelate groups must necessarily span the skew and not the perpendicular edges of the bisphenoid, otherwise only one form could occur).

We have now attempted to resolve both forms of [Pt ib_2]Cl_2, but in each case the bromocamphorsulphonate appeared to be optically homogeneous. The two *salts* were well-crystallised substances, distinct from one another in appearance and in degree of hydration; both before and after fractionation, they gave rise, respectively, to the characteristic α- and β-forms of [Pt ib_2]$PtCl_4$ described by us (*loc. cit.*). The result confirms our former conclusion and throws some doubt on the claim of Reihlen and Hühn as regards this particular case. The not very great differences in the rotatory powers of the various fractions observed by the above authors may possibly have been due to the heterogeneity of the bromocamphorsulphonic acid used, since theoretically this acid could be a mixture of four stereoisomeric forms.

A plato-tetrammine of the form [Pt (a—b) (a—Cde—a)]X_2 should be resolvable if of planar or of bisphenoidal but not if of regular tetrahedral configuration. We prepared *isobutylenediamino-β-methyltrimethylenediaminoplatinous chloride*, [Pt ib mt]Cl_2, but failed to resolve it through the highly crystalline *α-bromocamphor-π-sulphonate* and *α-nitrocamphorate*; the *d*-tartrate, examined in less detail, also gave a negative result. At this stage in the work, Mills and Quibell (J., 1935, 839) described the resolution of a somewhat similar plato-tetrammine, [Pt ib sn]Cl_2 (sn = *meso*-NH_2·CHPh·CHPh·NH_2) by using diacetyl-*d*-tartaric anhydride. We accordingly tried this reagent and also dibenzoyl-*d*-tartaric anhydride with our plato-tetrammine, but without success. It was intended to repeat the work on a larger scale, but, being unable to continue, we record the new substances prepared.

Experimental.

β-Methyltrimethylenediamine (mt) was prepared by condensing potassium phthalimide with β-methyltrimethylene dibromide (Faworsky and Sokownin, *Annalen*, 1907, **354**, 358) in nitrobenzene at 185° (2 hours), and hydrolysing the purified bisphthalimido-compound with fuming hydrochloric acid (see Mann, J., 1927, 2904). The hydrochloride of the diamine formed prismatic needles, m. p. 192°. *iso*Butylenediamine (ib) was prepared as previously described (Drew and Head, J., 1934, 49); its dibenzoyl derivative melted at 181—182° (cf. Mills and Quibell, *loc. cit.*).

β-Methyltrimethylenediaminoplatinous chloride, Pt mt Cl_2, separated when a concentrated solution of potassium chloroplatinite containing a slight excess of mt was left for some hours at 0°; it contained a small proportion of the pink plato-salt of the tetrammine, from which it was separated by means of tetramminoplatinous chloride or by treatment with silver nitrate and then hydrochloric acid. It formed yellow rectangular needles from boiling water (Found: C, 13·2; H, 3·3; Pt, 55·3. $C_4H_{12}N_2Cl_2Pt$ requires C, 13·6; H. 3·4; Pt, 55·1%).

iso*Butylenediamino-β-methyltrimethylenediaminoplatinous chloride*, [Pt ib mt]Cl_2, was prepared by shaking together at 40—50° the powdered plato-diammine, Pt mt Cl_2 or Pt ib Cl_2, and a slight excess of the aqueous diamine, ib *or* mt; a colourless solution of the tetrammine resulted. The tetrammine was a hygroscopic white powder (Found: Pt, 43·9, 44·2. $C_8H_{24}N_4Cl_2Pt$ requires Pt, 44·1%), giving a pale red *chloroplatinite*, [Pt ib mt]$PtCl_4$, which separated from dilute hydrochloric acid as hexagonal and octagonal plates (Found: Pt, 54·9. $C_8H_{24}N_4Cl_4Pt_2$ requires Pt, 55·1%).

Ammonium α-bromo-*d*-camphor-π-sulphonate was prepared as colourless anhydrous prisms, having $[\alpha]_D$ + 85°; $[M]_D$ + 279° (*c* = 3·985, in water) (Reihlen and Hühn, *loc. cit.*, give $[\alpha]_D$ + 83°; $[M]_D$ + 273°).

*α-Bis*iso*butylenediaminoplatinous α-bromo*-d-*camphor-π-sulphonate*. A solution of 0·65 g. of α-[Pt ib_2]Cl_2,$2H_2O$ and 0·89 g. of ammonium bromocamphorsulphonate in 12 c.c. of warm

* ib = NH_2·CMe_2·CH_2·NH_2; mt = NH_2·CH_2·CHMe·CH_2·NH_2.

water gave 0·62 g. of the *salt*; recrystallisation from 7 c.c. of hot water gave 0·32 g. (Found : Pt, 19·8. $C_{28}H_{50}O_8N_4Br_2S_2Pt$ requires Pt, 19·7%). From the original mother-liquor a further crop of the salt was obtained, and this, after crystallisation from water, weighed 0·38 g. All crops consisted of colourless, anhydrous, slender needles, sometimes with domed ends; they gave the same buff α-plato-salt with potassium chloroplatinite, and had practically the same rotatory power : $[\alpha]_D^{20°}$ + 56°; $[\alpha]_{5780}^{20°}$ + 58°; $[\alpha]_{5461}^{20°}$ + 69° (*c* = 2·5, in water).

β-*Bis*iso*butylenediaminoplatinous* α-*bromo*-d-*camphor*-π-*sulphonate* was obtained similarly, as flat colourless hexagonal needles, which, however, consisted of a *monohydrate* (Found : Pt, 19·6; H_2O, 1·7. $C_{28}H_{52}O_9N_4Br_2S_2Pt$ requires Pt, 19·4; H_2O, 1·8%); it was homogeneous to crystallisation, the rotatory power being $[\alpha]_{5780}^{20°}$ + 55°, $[\alpha]_{5461}^{20°}$ + 68° (*c* = 1·371, in water); all crops gave with potassium chloroplatinite the pink β-plato-salt.

iso*Butylenediamino*-β-*methyltrimethylenediaminoplatinous* α-*bromo*-d-*camphor*-π-*sulphonate* was prepared by mixing warm concentrated solutions of [Pt ib mt]Cl_2 and ammonium bromocamphorsulphonate. It formed colourless tetrahedral crystals from water, and slender rectangular needles from aqueous alcohol (Found : Pt, 20·1. $C_{28}H_{50}O_8N_4Br_2S_2Pt$ requires Pt, 19·7%). Optical separation failed from water or alcohol, or by preparing the salt in presence of excess of [Pt ib mt]Cl_2; the specific rotation of all crops in water was sensibly the same : $[\alpha]_D$ + 55° (*c* = 2·59); $[\alpha]_{5780}$ + 56° (*c* = 1·95); $[\alpha]_{5461}$ + 68° (*c* = 1·6). From a number of the fractions, [Pt ib mt]Cl_2 was recovered through formation of the chloroplatinite and double decomposition with the equivalent of tetramminoplatinous chloride, Magnus's salt being filtered off; the filtrates were in all cases inactive.

Sodium α-nitro-*d*-camphorate (Lowry and Steele, J., 1915, **107**, 1040) was obtained, by mixing alcoholic solutions of nitrocamphor and sodium hydroxide, as slender needles having $[\alpha]_D$ + 295°; $[\alpha]_{5780}$ + 308°; $[\alpha]_{5461}$ + 368° (*c* = 1·08, in water).

iso*Butylenediamino*-β-*methyltrimethylenediaminoplatinous* α-*nitro*-d-*camphorate* was prepared in aqueous medium; it crystallised from aqueous alcohol as the *monohydrate* (Found : C, 43·5; H, 7·1; Pt, 25·7; H_2O, 2·8, 2·4. $C_{28}H_{54}O_7N_6Pt$ requires C, 43·0; H, 7·0; Pt, 25·0; H_2O, 2·3%), decomposing when rapidly heated to 295°; it formed rosettes of white needles from water, and had $[\alpha]_D$ + 165°; $[\alpha]_{5780}$ + 173°; $[\alpha]_{5461}$ + 206° (*c* = 1·644, in water). There was no decisive change of the rotatory power on recrystallisation from water or on preparing the salt in presence of 0·5 equiv. of the nitrocamphorate. In all cases inactive material was obtained on converting the nitrocamphorate into the chloride.

Tartrates.—The *d*-tartrate, diacetyl-*d*-tartrate, and dibenzoyl-*d*-tartrate corresponding with [Pt ib mt]Cl_2 were prepared and fractionated, but were not analysed, since all fractions examined gave rise to inactive chloride.

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QUEEN MARY COLLEGE (UNIVERSITY OF LONDON). [*Received, July* 31*st*, 1937.]