287. *Plato- and Plati-diammines containing Methylamine.*

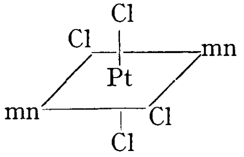
By H. D. K. Drew and H. J. Tress.

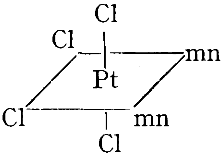
Jörgensen (*J. pr. Chem.*, 1886, **33**, 530) found that an analogue of Peyrone's chloride, β-$Pt(NH_3)_2Cl_2$, could not be obtained from methylamine (mn) and potassium chloroplatinite (the general method for preparing the *cis*-forms of platinous diammine dichlorides), although *n*-propylamine (pn) gave pure β-Pt pn_2Cl_2, and ethylamine (etn) gave a mixture of β-Pt etn_2Cl_2 and the pink plato-salt [Pt etn_4]$PtCl_4$; he remarks: "With methylamine unfortunately the reaction does not take place because it seems that [*cis*-Pt mn_2Cl_2] cannot be prepared." Instead, he obtained only the green plato-salt, [Pt mn_4]$PtCl_4$. This apparent anomaly has now been re-examined: the explanation appears to lie in the greater solubility in water of β-Pt mn_2Cl_2 over the corresponding compounds with ammonia, with ethylamine, and with propylamine, which facilitates its conversion into the tetrammine and then into the plato-salt. The required diammine can be produced by this method but only in minute yield. However, it is found that when potassium bromoplatinite is used, the less soluble β-*di*(*methylamino*)*platinous bromide*, β-Pt mn_2Br_2, is readily obtained, although the green plato-salt, [Pt mn_4]$PtBr_4$, accompanies it. These two substances can be separated, and the bromide is readily converted into the required β-*chloride* by the action of silver nitrate and then hydrochloric acid.

The same method can be employed with ethylamine, the yield of β-*di*(*ethylamino*)-*chloride* obtained through the *bromide* being much better than that through the direct method.

The α-series of *diamino-chlorides* was also prepared for comparison, by heating the tetrammines with halogen acid (the standard method for the preparation of *trans*-platinous diammine dichlorides). Although in the ammonia series the β-dichloride is deeper yellow than the α-, this relationship is reversed in the ethylamine series; in the methylamine series, the shades of the α- and the β-isomeride are almost the same.

(I; α-.)

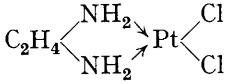




(II; β-.)

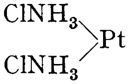
The α- and β-dichlorides of the methylamine series were oxidised respectively to the very crystalline bright yellow α- and β-*tetrachlorides*, Pt mn_2Cl_4, (I) and (II). These substances are of interest, since the only pairs of plati-diammines hitherto described are the compounds from ammonia (Gerhardt; Cleve) and from pyridine. Another similar pair of tetrachlorides was obtained from the ethylamine dichlorides. The α- and β-*tetrathiocyanates* (orange-yellow and orange-red, respectively), Pt $mn_2(NCS)_4$, were also prepared. These substances may be compared with the following plato-compounds, which were analysed: α-Pt $mn_2(NCS)_2$, cream-yellow; α-Pt $etn_2(NCS)_2$, yellow.

We have already drawn attention (J., 1933, 1338; J., 1934, 1790) to the differences between β-$Pt(NH_3)_2Cl_2$ and the chelated compounds, β-Pt $enCl_2$ and β-Pt $trCl_2$, in their behaviour towards such reagents as phenoxtellurine dibisulphate, concentrated sulphuric acid, and hydrochloric acid (see also Drew and Wyatt, J., 1934, 59). These differences pointed to a structural difference among the *cis*-diammines, as shown in the formulæ (III)—(VI).



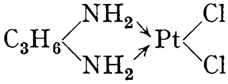
$$C_2H_4\left\langle\begin{matrix}NH_2\searrow\\NH_2\nearrow\end{matrix}\right.Pt\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$$

(III.)



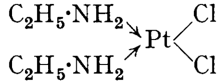
$$\left.\begin{matrix}ClNH_3\\ClNH_3\end{matrix}\right\rangle Pt$$

(IV.)



$$C_3H_6\left\langle\begin{matrix}NH_2\searrow\\NH_2\nearrow\end{matrix}\right.Pt\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$$

(V.)



$$\begin{matrix}C_2H_5\cdot NH_2\searrow\\C_2H_5\cdot NH_2\nearrow\end{matrix}Pt\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$$

(VI.)

It is now found that β-Pt etn_2Cl_2 and β-Pt etn_2Br_2 both resemble Pt $enCl_2$ in giving no salt of Cossa's type with hydrochloric acid, and no colour reaction with sulphuric acid or with phenoxtellurine dibisulphate. These β-diammines are therefore of the structural type of Pt enCl_2, as shown in (VI). The methylamine analogues appear to be similar, as judged from their lack of reaction towards phenoxtellurine dibisulphate. It is possible that the small proportion of Cossa's ethylamine salt obtainable from the amine and potassium chloroplatinite may arise from an initially produced unstable form of the monoammine, Pt Cl(etnCl), analogous in structure to the diammine (IV).

EXPERIMENTAL.

β-*Di(methylamino)platinous bromide* was prepared as follows. An aqueous solution of potassium bromoplatinite (1 mol.) was made by heating concentrated aqueous solutions of the chloroplatinite (1 mol.) and the bromide (6 mols.); it was cooled to 0°, and aqueous methylamine (33%; 3—4 mols.) stirred in; separation of the *bromide* (yellow needles) continued for 1 hr., but the precipitate contained also some [Pt mn_4]$PtBr_4$ (slender green needles), which mainly separated in the second half-hour. The latter salt was best removed by adding $[Pt(NH_3)_4]Cl_2$ to the hot aqueous solution of the mixture, filtering from insoluble $[Pt(NH_3)_4]PtBr_4$ and cooling the filtrate; the diammine separated, leaving the tetrammines in solution. The required salt formed yellow rectangular needles from dilute hydrobromic acid (Found: C, 5·9; H, 2·5; Pt, 46·3. $C_2H_{10}N_2Br_2Pt$ requires C, 5·8; H, 2·4; Pt, 46·8%). The β-*di(ethylamino)-bromide* was similarly obtained as yellow plates (Found: C, 10·8; H, 3·2; Pt, 43·4. $C_4H_{14}N_2Br_2Pt$ requires C, 10·8; H, 3·2; Pt, 43·8%).

β-*Di(methylamino)platinous chloride* was obtained only in minute yield from aqueous potassium chloroplatinite and methylamine (best in the presence of its hydrochloride) at 0°, the main product being green needles of [Pt mn_4]$PtCl_4$. It was prepared from the bromide (above) by grinding with hot aqueous silver nitrate, filtering the solution from silver bromide, adding hydrochloric acid to the filtrate, and extracting the resulting precipitate with boiling water, silver chloride remaining undissolved. The chloride separated from dilute hydrochloric acid as pale yellow needles with oblique ends; 1 g. dissolved in about 15 c.c. of boiling water, giving a yellow solution. This diammine was not coloured by concentrated sulphuric acid or by phenoxtellurine dibisulphate (Found: C, 7·5; H, 3·1; Pt, 59·1. $C_2H_{10}N_2Cl_2Pt$ requires C, 7·3; H, 3·1; Pt, 59·5%).

The corresponding α-*chloride* was prepared as above from the α-bromide, obtained by heating with concentrated hydrobromic acid the mother-liquors (containing [Pt mn_4]Br_2) from the preparation of β-Pt mn_2Br_2. The chloride, which was less soluble than the β-isomeride, formed pale yellow square plates (Found: C, 7·4; H, 2·9; Pt, 59·7. $C_2H_{10}N_2Cl_2Pt$ requires C, 7·3; H, 3·1; Pt, 59·5%).

β-Di(ethylamino)platinous chloride was prepared, together with the pink chloroplatinite, from ethylamine and aqueous potassium chloroplatinite, and was purified as above; it was also obtained through the corresponding β-dibromide. It formed pale yellow, square plates (Found: C, 13·3; H, 3·7. Calc. for $C_4H_{14}N_2Cl_2$: C, 13·5; H, 4·0%).

The α-chloride, prepared in the same way as its methylamino-analogue, formed light yellow rectangular plates (Found: C, 13·5; H, 4·1. Calc. for $C_4H_{14}N_2Cl_2$: C, 13·5; H, 4·0%).

The α-*nitrite* was prepared from the α-nitrate by means of aqueous sodium nitrite, as colourless rhombic tables (Found: C, 6·9; H, 2·7. $C_2H_{10}O_4N_4Pt$ requires C, 6·9; H, 2·9%). The β-nitrite forms voluminous colourless needles. The α-*thiocyanate*, prepared from the nitrate by means of aqueous potassium thiocyanate, formed cream-yellow needles, m. p. 137° (decomp.), unstable to boiling water (Found: C, 13·1; H, 2·6. $C_4H_{10}N_4S_2Pt$ requires C, 12·8; H, 2·7%). The β-salt formed small orange-yellow needles.

α-*Di(ethylamino)platinous thiocyanate*, obtained as above, formed yellow rectangular needles (Found: C, 17·8; H, 4·1; Pt, 48·2. $C_6H_{14}N_4S_2Pt$ requires C, 17·9; H, 3·5; Pt, 48·6%).

Platinic Diammines.—Prepared by oxidising the corresponding platinous compounds with hydrogen peroxide and hydrochloric acid, these beautifully crystalline substances dissolved in hot water to deep yellow solutions which oxidised tetramminoplatinous chloride as follows: Pt mn_2Cl_4 + $[Pt(NH_3)_4]Cl_2$ = Pt mn_2Cl_2 + $[Pt(NH_3)_4Cl_2]Cl_2$.

The β-*di(methylamino)platinic chloride* formed bright-yellow rhombic plates (Found: C, 6·0; H, 2·6. $C_2H_{10}N_2Cl_4Pt$ requires C, 6·0; H, 2·5%); and the *thiocyanate*, small orange-red needles (Found: C, 14·2; H, 2·2. $C_6H_{10}N_6S_4Pt$ requires C, 14·7; H, 2·1%). The α-*chloride* formed bright yellow needles (Found: C, 6·1; H, 2·7. $C_2H_{10}N_2Cl_4Pt$ requires C, 6·0; H, 2·5%); and the *thiocyanate*, bright orange needles with oblique ends (Found: C, 15·1; H, 2·2; Pt, 40·4. $C_6H_{10}N_6S_4Pt$ requires C, 14·7; H, 2·1; Pt, 39·9%). The α- and β-tetra(ethylamino)-chlorides were also obtained, each in the form of yellow, sparingly soluble, rhombic plates.

The Action of the Halogen Acids on the cis-*Diammines of Ethylamine.*—β-$[Pt(NH_3)_2Cl_2]$ is chiefly converted into Cossa's ammonium salt, $NH_4[Pt(NH_3)Cl_3],H_2O$, when heated in *N*-hydrochloric acid for 30 hrs. in the boiling-water bath, but its ethylamine analogue was much more stable, separating unchanged after treatment as above with 2*N*-acid in a closed vessel, or for 15 hrs. under reflux. The mother-liquors gave only slight precipitates of Magnus's green salt (on one occasion, the pink form of this salt) on treatment with $[Pt(NH_3)_4]Cl_2$, and on evaporation left only small residues composed chiefly of chloroplatinite and unchanged β-dichloride.

Similarly, the β-bromide separated unchanged, mixed with a little platinum, after being heated under reflux for 8 hrs. with *N*/4-hydrobromic acid. Insoluble green needles of Magnus's salt were precipitated from the orange mother-liquor by a slight excess of $[Pt(NH_3)_4]Cl_2$, and the filtrate on evaporation left only a small residue composed chiefly of the original β-dibromide.

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