301. *Plato- and Pallado-sulphines.*

By H. D. K. Drew, G. H. Preston, W. Wardlaw, and G. H. Wyatt.

We have recently shown that the palladodiammines exist in only one form, whereas the platodiammines occur in α- and β-forms unless a chelate diamine is present, in which case only the β-form is found. The plato- and pallado-disulphines follow the same rule as their respective diammines with regard to numbers of isomerides, but they differ remarkably from the diammines in many chemical properties, *e.g.*, they are interconvertible and the derived tetrasulphines decompose to give β-disulphines, whereas the platodiammines cannot be interconverted and their tetrammines decompose to give α-diammines. In an earlier paper (J., 1930, **349**) we showed that, unless intramolecular migrations of the sulphur atoms occur during certain simple reactions, all of the platodisulphines have their pairs of sulphur atoms in neighbouring positions with respect to platinum. The stereochemical and structural relationships between the diammines and disulphines of the two metals present a complex problem which is still very obscure; in order to throw light upon it we have repeated and extended the work of Tschugaeff and others on certain disulphines.

The principal result of the present work is to show that the yellow plato- and palladodisulphines are without doubt monomeric substances, $\mathrm{Pt(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)Cl_2}$ in boiling acetone, and $\mathrm{Pd(SEt_2)_2Cl_2}$ in boiling chloroform or in freezing benzene, being unimolecular. In some instances the platodisulphines occur, in addition to these yellow forms, in dimeric pink " forms " which are merely the plato-salts of the unstable tetrasulphines, and, like the dimeric pink " forms " of the palladodiammines, are easily convertible into the monomeric yellow forms. In the palladodisulphine series the dimeric " forms " are too rapidly changed to be isolable, and in some instances (*e.g.* $\mathrm{[Pt(SEt_2)_4]PtCl_4}$) this is also true of the plato-analogues. The tetrasulphines are known only in solution :

$$\begin{array}{lclclcl}
\text{(yellow)} & \xrightarrow[\text{es, etc.)}]{\text{(excess of}} & \begin{array}{l}\text{(tetrammine or}\\ \text{tetrasulphine)}\end{array} & \xrightarrow[\text{etc.)}]{(\mathrm{K_2PdCl_4},} & \text{(pink)} & \xrightarrow[\mathrm{H_2O)}]{\text{(boiling}} & \text{(yellow)} \\
\mathrm{Pd\ es\ Cl_2} & \longrightarrow & \mathrm{([Pd\ es_2]Cl_2)} & \longrightarrow & \mathrm{([Pd\ es_2]PdCl_4)} & \longrightarrow & \mathrm{Pd\ es\ Cl_2} \\
\mathrm{Pd(NH_3)_2Cl_2} & \longrightarrow & \mathrm{[Pd(NH_3)_4]Cl_2} & \longrightarrow & \mathrm{[Pd(NH_3)_4]PdCl_4} & \longrightarrow & \mathrm{Pd(NH_3)_2Cl_2} \\
\mathrm{Pt\ es\ Cl_2} & \longrightarrow & \mathrm{([Pt\ es_2]Cl_2)} & \longrightarrow & \mathrm{[Pt\ es_2]PtCl_4} & \longrightarrow & \mathrm{Pt\ es\ Cl_2} \\
\mathrm{Pt(SMe_2)_2Cl_2} & \longrightarrow & \mathrm{([Pt(SMe_2)_4]Cl_2)} & \longrightarrow & \mathrm{[Pt(SMe_2)_4]PtCl_4} & \longrightarrow & \mathrm{Pt(SMe_2)_2Cl_2}
\end{array}$$

$$(\mathrm{es} = \mathrm{EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt})$$

Direct determinations of molecular weight have already shown that the yellow palladodiammines are monomeric, a conclusion supported by many reactions (J., 1932, **1895**); the analogy with the monomeric yellow palladodisulphines supplies further confirmation. The assertion of Krauss and Mählmann (*Siebert Festschr.*, 1931, 215; see also *Ann. Reports*, 1932, **29**, 92) that the pink and the yellow palladodiammines are all bimolecular substances was made prior to the publication of our paper and can no longer be regarded as valid.

Ardell has shown (*Z. anorg. Chem.*, 1896, **14**, 143; Diss., Lund, 1896) that $\mathrm{Pd(SEt_2)_2Cl_2}$ is isomorphous with the α-form of $\mathrm{Pt(SEt_2)_2Cl_2}$, which would appear to indicate that the palladodisulphine is both structurally and stereochemically similar to the platodisulphine. On the other hand, Pd es $\mathrm{Cl_2}$ and Pt es $\mathrm{Cl_2}$ are very closely similar to one another and are both *cis*-compounds as regards the disposition of the sulphur atoms, since a chelate group is present. This indicates either that all the pallado- and plato-disulphines are stereochemically *cis*-compounds, or else that two stereochemical arrangements of the pairs of sulphur atoms are possible in the palladodisulphines although only one form has been observed in any case among either the pallado-disulphines or -diammines. We find that Pt es $\mathrm{Cl_2}$ has pronounced conductivity in aqueous solution and that with silver oxide it gives a base which yields the original compound when neutralised with hydrochloric acid. Pd es $\mathrm{Cl_2}$ gives a similar base with silver oxide. The evidence seems to show, therefore, that both of these disulphines are stereochemically and structurally similar to β-$\mathrm{Pt(SEt_2)_2Cl_2}$.

Diethyl disulphide and acetonebisethylthioacetal did not appear capable of acting as chelate groups, suggesting that three- and four-membered rings are not possible in the plato- and pallado-disulphine series.

EXPERIMENTAL.

Ethylene Diethyl Disulphide and Potassium Chloroplatinite.—At low temperatures and especially in dilute solution the pink plato-salt, $\mathrm{[Pt\ es_2]PtCl_4}$, is the chief product; at 100° and in more concentrated solutions the yellow disulphine, $\mathrm{Pt\ es\ Cl_2}$, is largely produced, but mixtures are always obtained. These products may be separated by extraction with acetone, in which the pink salt is insoluble. $\mathrm{Pt\ es\ Cl_2}$ crystallises from water in clusters of lemon-yellow triboelectric plates or needles, m. p. 185° [Found : C, 16·85; H, 3·5; Pt, 46·8, 46·7; *M* (in boiling acetone; *c*, 0·61; *e*, 0·03°), 455. Calc. : C, 17·3; H, 3·35; Pt, 46·95%; *M*, 416]. It gives no colour with phenoxtellurine dibisulphate. It is almost insoluble in benzene but slightly soluble in chloroform. With cold aqueous silver oxide it gives a base, in the form of a yellow glass; the alkaline solution of this gives with hydrochloric acid the original disulphine. $\mathrm{[Pt\ es_2]PtCl_4}$ melts at about 180° but transformation into $\mathrm{Pt\ es\ Cl_2}$ has already occurred. It dissolves in boiling water to a solution which is momentarily red, then changes to yellow, and deposits $\mathrm{Pt\ es\ Cl_2}$ on cooling; the presence of hydrochloric acid makes the change slower. The plato-salt gives Magnus's salt with hot aqueous $\mathrm{[Pt(NH_3)_4]Cl_2}$; with phenoxtellurine dibisulphate it gives a deep brick-red coloration. In presence of an excess of aqueous ethylene diethyl disulphide both the pink and the yellow substance give solutions of the unstable $\mathrm{[Pt\ es_2]Cl_2}$, as recorded by Tschugaeff and Subbotin (*Ber.*, 1910, **43**, 1203); potassium chloroplatinite precipitates the pink salt from these solutions.

Ethylene Diethyl Disulphide and Potassium Chloropalladite.—At room temperature reaction is rapid, giving rise apparently to one substance only (cf. Tschugaeff and Iwanoff, *Z. anorg. Chem.*, 1924, **135**, 157, who suggest that two closely similar substances may be produced), *viz.*, $\mathrm{Pd\ es\ Cl_2}$, soluble in hot chloroform. From hot water it separates first in dendritic crystals, redissolves, and reappears as rosettes of square prisms (change complete in 15 mins.); both forms are yellow and have m. p. 182°; admixture causes no depression (Found : Pd, 32·15; 32·35. Calc. : Pd, 32·55%). With alcohol as solvent the change is more rapid.

$\mathrm{Pd(SEt_2)_2Cl_2}$, prepared as described by Ardell (*loc. cit.*), who gives m. p. 78°, was obtained in theoretical yield as bright yellow rectangular or hexagonal needles, m. p. 83°, from light petroleum; it is soluble in benzene or carbon tetrachloride. In hot water it dissolves but some diethyl sulphide is set free [Found : Pd, 30·1, 29·8; *M*, 362, 359 (in freezing benzene; *c*, 1·029, 0·758; *d*, 0·1675°, 0·1225°), 349, 349 (in boiling chloroform; *c*, 1·006, 0·938; *e*, 0·075°, 0·070°). Calc. : Pd, 29·8%; *M*, 358]. It is soluble in aqueous ethyl sulphide, giving a solution of the unstable $\mathrm{[Pd(SEt_2)_4]Cl_2}$ which loses ethyl sulphide in air, regenerating the original pallado-disulphine (Found : Pd, 29·9%), as shown by a mixed m. p. determination and other properties. With aqueous silver oxide a yellow solution of a base, alkaline to litmus is produced, and this again gives the above disulphine when neutralised with hydrochloric acid.

$\mathrm{Pd(SMe_2)_2Cl_2}$ was similarly prepared from potassium chloropalladite and methyl sulphide or from the unstable aqueous solution of $\mathrm{[Pd(SMe_2)_4]Cl_2}$; it had m. p. 128° (Found : Pd, 35·0. Calc. : Pd, 35·4%).

Conductivity of $\mathrm{Pt\ es\ Cl_2}$.—The aqueous solution of the compound is decomposed by direct current into hydrochloric acid, platinous oxide, and ethylene diethyl disulphide, but is stable to alternating current and to the platinum black on the electrodes. The water used retained a constant conductivity of $2{\cdot}6 \times 10^{-6}$ mho at 25°. The solubility of the disulphine was found to be 0·130 g. per 100 c.c. of solution at this temperature. At this dilution (319 l. per g.-mol.) the value $\mu = 28$ was found. Thus, if we take $\mu_\infty = 100$, the ionisation is about 30% at $v = 319$. This value is greater than that found by Tschugaeff and Kobljanski (*Z. anorg. Chem.*, 1913, **83**, 8) even if allowance is made for the fact that they used methyl alcohol as solvent.

Acetonebisethylthioacetal and Potassium Chloroplatinite.—Between 0° and 100° the product was yellow to orange, microcrystalline, and insoluble in water, acetone, benzene, or chloroform. It was not a plato-salt since it gave no Magnus's salt with aqueous $\mathrm{[Pt(NH_3)_4]Cl_2}$ nor any coloration with phenoxtellurine dibisulphate. It had no definite m. p. and gave various analyses in different samples [Found : Pt, 53·4, 53·9, 57·7, 58·1. Calc. for $\mathrm{(Pt\ Cl_2)_2(EtS{\cdot}CMe_2{\cdot}SEt)}$: Pt, 56·05%. Calc. for the chelate disulphine formula : Pt, 45·35%].

Diethyl disulphide gave with potassium chloropalladite an insoluble orange precipitate, and with the chloroplatinite a mixture of orange and yellow substances, which yielded irregular results on analysis and were not further examined.

We thank H.M. Department of Scientific and Industrial Research for grants, and the Chemical Society and Messrs. The Mond Nickel Co. for the loan of precious metals.

EAST LONDON COLLEGE, UNIVERSITY OF LONDON.
UNIVERSITY OF BIRMINGHAM, EDGBASTON.

[*Received, July* 12*th*, 1933.]