The Stereochemistry of Tellurium.

By Prof. T. M. LOWRY, F.R.S.

NEARLY ten years ago the late Mr. R. H. Vernon made a remarkable series of observations on the occurrence of isomerism in the alkyl derivatives of tellurium.¹ The initial compound can be prepared by the direct action of metallic tellurium on methyl iodide, $\text{Te} + 2\text{CH}_3\text{I} \rightarrow \text{Te}(\text{CH}_3)_2\text{I}_2$. Silver oxide then liberates from the iodide a weak 'α' base, $\text{TeMe}_2(\text{OH})_2$, which when dehydrated undergoes a molecular rearrangement, and is converted into a rather stronger 'β' base. From this 'β' base a series of 'β' salts can be obtained, which have the same composition as the 'α' salts derived from the 'α' base. Measurements of boiling-points of solutions in acetone, and of freezing-points of solutions in benzene and in nitrobenzene, indicated that the two chlorides had the same normal molecular weight, but that, whilst the α-dibromide and the α-di-iodide were also normal, the β-compounds were partially polymerised thus:

MOLECULAR WEIGHTS.

	α (Obs.).	β (Obs.).			Calc.
Chlorides in acetone . .	229	226	230	223	228
Bromides in acetone . .	335	430	459	525	
Bromides in nitrobenzene . .	..	400	445	370	317
Iodide in benzene . .	401	..	..	..	
Iodide in acetone . .	..	509	707	..	411

In view of the equality of molecular weights of the chlorides, and of the methods by which the α and β salts were produced, Vernon supposed that they represented the *trans* and *cis* forms of molecules having a square configuration, like that which Werner assigned in 1893 to the isomeric platinumous compounds of the type $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, thus:

The thorough character of the work, the simplicity of the explanation, and the obvious analogy with platinum, won for this scheme an immediate and universal acceptance, and it was a source of pleasure to me, in view of my intimate association with Vernon's earlier activities, to be able to record in December last² the fulfilment of Vernon's prediction in reference to the diethyl base that "If this base does not decompose when its solution is evaporated to dryness, but gives diethyltelluronium oxide, the existence of two haloid series would be highly probable." A detailed physico-chemical study with Mr. Gilbert³ of Vernon's own compounds had also confirmed the equality of molecular weights of the α- and β-compounds, since measurements of the freezing-points of aqueous solutions gave almost identical values for van't Hoff's *i*-factor, namely, 1.1 for the α- and β-bases, and about 1.8 for the α- and β-hydroxychlorides $\text{TeMe}_2(\text{OH})\text{Cl}$.

Although, however, Vernon's experiments were impregnable, and the evidence for identity of molecular weight appeared to be ample, the writer concluded⁴ that "The striking difference in colour of the α- and β-dihalides shows that the isomerism

of the α- and β-compounds must include some factor which is not expressed completely by merely putting two halogen atoms and two alkyl radicals at adjacent or at opposite corners of a square." Serious reasons for doubting the validity of the whole scheme were found for the first time, however, when further experiments showed⁵ that a *cyclo*-telluropentane

and Burgess,⁶ and the bases and salts derived from it, behaved in five different points like the corresponding α-compounds of Vernon's series, to which he had assigned a *trans*-configuration. Examination of models showed that, whilst it was easy to form a strainless ring in the case of a *cis*-compound, the formation of a *trans*-ring involved as usual an intolerable strain, which produced a corresponding strain on the theory and made it desirable to look round for possible alternatives. An analysis of the facts which were then available, showed that a larger number of them could be covered by assigning to quadrivalent tellurium a tetrahedral instead of a planar configuration;⁷ but, in order to explain the formation of α- and β-isomerides, it was necessary to distort the regular tetrahedron, which is accepted universally in the case of sulphur, by making one valency different from the other three.

A new series of experiments, described by Dr. H. D. K. Drew before the Chemical Society on Jan. 17 (*Jour. Chem. Soc.*, p. 560, 1929), has removed the last obstacle to a complete analogy between sulphur and tellurium, by showing that the changes recorded by Vernon involve an alteration of structure which goes beyond the limits of stereoisomerism. This change of structure was actually observed by Vernon, who showed, while the α-di-iodide and potassium carbonate gave a basic salt,

the β-di-iodide and potassium carbonate gave trimethyltelluronium iodide, by the wandering of a methyl group,

Vernon supposed that this wandering took place under the influence of the alkali, but Drew's experiments show that it had already taken place in the preparation of the β-base, since the β-di-iodide is itself a complex salt, which can be synthesised readily from the *mono*- and *tri*-methyltelluronium iodides,

The structure of these compounds was confirmed by a corresponding synthesis of the "β-dibromide" TeMe_3Br , TeMeBr_3 , and of mixed halides of the composition TeMe_3Br , TeMeI_3 and TeMe_3I , TeMeBr_3 .

The simple salts from which the more complex β-compounds were synthesised are obviously derivatives of trimethyltelluronium hydroxide, TeMe_3OH , and of the monomethyl compound $\text{Me} \cdot \text{TeO} \cdot \text{OH}$, which Drew describes as telluracetic acid. He there-

¹ *J. Chem. Soc.*, **117**, 86, 889; 1920: **119**, 105, 687; 1921.

² F. L. Gilbert and T. M. Lowry, *J. Chem. Soc.*, pp. 3179-3189; 1928.

³ *J. Chem. Soc.*, 1997-2010; 1928.

⁴ *J. Chem. Soc.*, p. 308; 1928.

⁵ Gilbert and Lowry, *J. Chem. Soc.*, 2658-2667; 1928.

⁶ *J. Chem. Soc.*, 321-329; 1928.

⁷ *Chem. and Ind.*, **47**, 1246; Nov. 23, 1928.

fore assigned to the β -base the structure of an *anhydride*, $\text{TeMe}_3\text{O} \cdot \text{TeMeO}$. Since, however, the monomethyl compound can be shown to have an acid rather than a basic reaction,⁸ it is clear that the mixture of *mono*- and *tri*-methyl-hydroxides should form a salt $[\text{TeMe}_3]^+ [\text{Me} \cdot \text{TeO} \cdot \text{O}]^-$. The correctness of this alternative view can be established from measurements of conductivity,⁸ which show that the ' β -base' gives a curious series of values ranging from $\Lambda_{32}^{25} = 31$ to $\Lambda_{512}^{25} = 37$. These can be explained by assigning to the cation $[\text{TeMe}_3]^+$ a mobility of 50, as in the case of $[\text{NMe}_4]^+$, and to the anion $\text{CH}_3 \cdot \text{TeO} \cdot \text{O}$ a mobility of 30, as in the case of the acetate ion $\text{CH}_3 \cdot \text{CO} \cdot \text{O}$, giving a limiting conductivity of 80 for the salt, or 40 for each atom of tellurium, in close agreement with the data recorded above.

It is important to point out that whilst the *stereoisomerism* of Vernon's theory has been disproved, the *isomerism* indicated by his experiments may still be valid for some of the compounds of this series. In particular, crystallographic evidence suggests that the α -di-iodide is itself a complex compound, with a structure that is very similar to that of the β -di-iodide; there are therefore clear indications that the α -dihalides may form complex molecules of the type $[\text{TeMe}_2\text{I}]^+ [\text{TeMe}_2\text{I}_3]^-$ which would be isomeric with $[\text{TeMe}_3]^+ [\text{TeMeI}_4]^-$, although they are evidently more readily dissociated into molecules or ions containing only a single atom of tellurium.

The abrupt disappearance of the only evidence which justified the representation of quadrivalent tellurium by a planar model at once raises the question whether the analogous configurations for quadrivalent platinum and palladium are likely to survive. In a matter of this kind, prediction is dangerous, but it can at least be said that the planar formulae for palladium and platinum are supported by a greater variety of evidence and are therefore much less likely to collapse under a single blow. The evidence cited by Werner in 1893⁹ corresponds closely with that obtained by Vernon. So long ago as 1828, Magnus,¹⁰ by the action of ammonia on platinous chloride, obtained a compound which is still known as *Magnus' green salt*. This has the empirical composition $\text{PtCl}_2 \cdot 2\text{NH}_3$, but behaves as a complex salt of the formula, $[\text{Pt} \cdot 4\text{NH}_3]^{++} \text{PtCl}_4^{--}$. When boiled with ammonia it is converted into *Reiset's salt*,³ $[\text{Pt} \cdot 4\text{NH}_3]^{++} \text{Cl}_2^{--}$, which on heating to 250° ¹¹, or on boiling with concentrated hydrochloric acid,¹² is converted into two isomeric forms of the non-valent diammine $[2\text{NH}_3 \cdot \text{PtCl}_2]$. These two isomers, which can be prepared more readily by the action of ammonia on ammonium platino-chloride,¹³ $(\text{NH}_4)_2\text{PtCl}_4$, are distinguished, for no very obvious reason, as platosammine chloride and platosemidiammine chloride.

The two compounds, which differ in colour and in solubility, were formulated somewhat arbitrarily by Werner¹⁴ as follows:

On account of their limited solubility, their molecular

weights were not determined precisely until 1926, when Reihlen and Nestle¹⁵ made a series of observations on the vapour pressures of solutions in liquid ammonia. These showed that the *cis* compound had a normal molecular weight, whilst that of the *trans*-compound was twice as great. On the other hand, Grünberg¹⁶ has obtained normal values for solutions in acetone of both forms of the thiocyanate, $[2\text{NH}_3 \cdot \text{Pt}(\text{CNS})_2]$; Hantzsch¹⁷ has obtained normal molecular weights for solutions in phenol of both forms of the dipyridyl-compound $[2\text{C}_5\text{H}_5\text{N} \cdot \text{PtCl}_2]$; and Kraus and Brodkorb¹⁸ have obtained normal values for the two forms of $[2\text{C}_5\text{H}_5\text{N} \cdot \text{PdCl}_2]$ and $[2\text{EtNH}_2 \cdot \text{PdCl}_2]$, as well as for one form of $[2\text{NH}_3 \cdot \text{PdCl}_2]$, the other being hydrolysed too readily to permit of accurate measurements.

Up to this point the story is an almost exact duplicate of the recent observations on tellurium, since the mere multiplication of examples of α - and β -compounds does not rule out the possibility of an alternative explanation of the supposed isomerism in either case; and the repeated determinations of molecular weights have again provided conflicting evidence. It is also open to question whether the occurrence of the same isomerism in tetrammines of the type $[2\text{C}_5\text{H}_5\text{N} \cdot \text{Pt} \cdot 2\text{NH}_3]\text{Cl}_2$, might not stand or fall with that of the diammines. Fortunately, however, physical evidence is now available which appears to be decisive on the point at issue. Thus crystallographic observations have shown that the double cyanides, $\text{K}_2[\text{Zn} \cdot 4\text{CN}]$, $\text{K}_2[\text{Cd} \cdot 4\text{CN}]$, $\text{K}_2[\text{Hg} \cdot 4\text{CN}]$, crystallise in the *cubic* system, and X-ray analysis¹⁹ confirms the obvious deduction that the anion has a tetrahedral configuration, such as has already been found in the molecules of $[\text{SnI}_4]$, although the ion $[\text{SnCl}_6]^{--}$ has an octahedral configuration. On the other hand, the two pallado chlorides, $\text{K}_2[\text{PdCl}_4]$ and $\text{Am}_2[\text{PdCl}_4]$, and the platinochloride $\text{K}_2[\text{PtCl}_4]$ all crystallise in the *tetragonal* system, and X-ray analysis²⁰ confirms the deduction that the anion has the same symmetry as the crystal and must be represented with the four halogens at the corner of a square of which the metal occupies the centre. The planar configuration which Werner assigned to this group of compounds thirty-five years ago is therefore now established by a process of mensuration, which does not encourage any hope of its disestablishment by less direct chemical methods.

¹⁵ Reihlen and Nestle, *Ann.*, **447**, 211; 1926.

¹⁶ Grünberg, *Zeit. anorg. Chem.*, **157**, 299; 1926.

¹⁷ Hantzsch, *Ber.*, **59**, 2761; 1926.

¹⁸ Kraus and Brodkorb, *Zeit. anorg. Chem.*, **165**, 73; 1927.

¹⁹ Dickinson, *J. Amer. Chem. Soc.*, **44**, 774; 1922.

²⁰ Dickinson, *J. Amer. Chem. Soc.*, **44**, 2404; 1922.

University and Educational Intelligence.

LONDON.—Dr. Harold Raistrick has been appointed as from Aug. 1 to the University chair of biochemistry tenable at the London School of Hygiene and Tropical Medicine, where he will also hold the position of Director of the Division of Biochemistry and Chemistry as applied to Hygiene. Dr. Raistrick is a graduate of Leeds and Cambridge. From 1915 until 1920 he was engaged on research work on the biochemistry of micro-organisms for the Medical Research Committee in Sir Frederick Hopkins's laboratory at Cambridge, and since 1921 he has been on the research staff of Messrs. Nobel's Explosives Company, Ayrshire, where he organised and equipped a new Biochemical Research Department.

THE National Union of Teachers held its annual conference this year at Llandudno on Mar. 30. The

⁸ Gilbert and Lowry, *J. Chem. Soc.*, 1997-2010; 1928.
⁹ Werner, *Zeit. anorg. Chem.*, **3**, 310; 1893.
¹⁰ Magnus, *Pogg. Ann.*, **14**, 204; 1828.
¹¹ Reiset, *Compt. rend.*, **10**, 870; 1840; **11**, 711; *Ann. Chim. Ph.* [3] **11**, 417; 1844.
¹² Peyrone, *Ann. Chim. Ph.* [3] **12**, 193; 1844; **16**, 462; 1846.
¹³ Jørgensen, *Zeit. anorg. Chem.*, **24**, 181; 1900.
¹⁴ Werner, *Zeit. anorg. Chem.*, **3**, 310; 1893.