

49. *The Structure of the Thio-ether Compounds of Platinous and Palladous Chlorides.*

By E. G. COX, H. SAENGER, and W. WARDLAW.

IN order to study further the thio-ether compounds of platinous and palladous chlorides by chemical and X-ray methods we have prepared the dimethyl sulphide derivatives, $[\text{Pt}(\text{Me}_2\text{S})_2\text{Cl}_2]$ and $[\text{Pd}(\text{Me}_2\text{S})_2\text{Cl}_2]$.

Blomstrand (*J. pr. Chem.*, 1888, **38**, 352) and Klason (*Ber.*, 1895, **28**, 1477; 1904, **37**, 1349; *J. pr. Chem.*, 1903, **67**, 1) state independently that bisdimethylsulphineplatinous chloride may exist in three isomeric forms, but it was shown by Tschugaev and his co-workers (*Z. anorg. Chem.*, 1913, **82**, 420; *et seq.*) and confirmed by ourselves that their third, pink, compound of similar composition was in reality the plato-salt $[\text{Pt}(\text{Me}_2\text{S})_4][\text{PtCl}_4]$. Like the isomerides which diethyl sulphide forms with platinous chloride (Angell, Drew, and Wardlaw, *J.*, 1930, **33**, 349), the dimethyl sulphide analogues are unimolecular and show a marked difference in physical properties. The α - is deeper in colour than the β -isomeride and recrystallises from chloroform in orange monoclinic plates with no solvent of crystallisation, whilst the β - recrystallises from this solvent in citron-yellow tetragonal plates with one molecule of chloroform of crystallisation, which it quickly loses on exposure to air. From acetone they both crystallise without solvent of crystallisation, the α - (as before) in orange monoclinic plates but the β - in transparent citron-yellow monoclinic prisms.

Their solubilities in cold water also show a difference; the α - is insoluble whereas the β - dissolves to a small extent. The molecular conductivity of the β -form was measured in this solvent and indicates that it is ionised to about 63% at $v = 1000$, if $u_\infty = 100$. This result suggests that the β -dichloride in aqueous solution is either a polar substance or alternatively easily undergoes hydrolysis.

The two dichlorides are readily interconvertible. The α - was completely converted into the β -dichloride on being dissolved in boiling water and almost completely by treatment with further aqueous dimethyl sulphide, but, in solution in chloroform or on melting, either dichloride tends to pass into an equilibrium mixture of both; warming the chloroform solution favours the formation of the α -form.

The most striking difference between these isomeric dihalides, however, is shown by their interaction with silver oxide in presence of water. The β -dichloride reacts in a few minutes with the production of silver chloride and a markedly basic yellowish-brown varnish-like substance which Blomstrand (*loc. cit.*) seems to have obtained by the action of baryta on the sulphate, $\text{Pt}(\text{Me}_2\text{S})_2\text{SO}_4$; this base is hygroscopic and dissolves in water forming an alkaline solution which is neutralised by acid with the precipitation of pure β - $\text{Pt}(\text{Me}_2\text{S})_2\text{Cl}_2$. The α -dichloride, on the other hand, reacts only very slowly, with evolution of dimethyl sulphide, formation of silver chloride, and precipitation of platinum as hydroxide or oxide; the filtrate is quite neutral to litmus and no solid is precipitated on addition of hydrochloric acid.

On treatment of the chloroform solutions of the dichlorides with chlorine, a different tetrachloride was produced in each case. As expected, these compounds differ in properties as profoundly as do the isomeric dihalides. The α -tetrachloride is very soluble in chloroform and separates slowly from its solution in thick, irregular, orange plates, whereas the β -tetrachloride is very slightly soluble in this solvent, separating in aggregates of very small yellow prisms.

Werner was of opinion that the chlorides had a planar structure and that the α - had the *cis*- and the β - the *trans*-configuration. The existence of two tetrachlorides $\text{PtCl}_4 \cdot 2\text{Me}_2\text{S}$ is in accordance with this view, but the reaction with silver oxide and the conductivity of aqueous solutions of the β -compound are difficult to reconcile with this hypothesis. Some time ago, Angell, Drew, and Wardlaw (*loc. cit.*) expressed doubt as to the correctness of Werner's views and proposed alternative structures. Since then new physical and chemical evidence has been obtained by us which proves conclusively that α - $\text{PtCl}_2 \cdot 2\text{Me}_2\text{S}$

has a *trans*-planar structure, not a *cis*-planar structure, as proposed by Werner, or a tetrahedral configuration, as surmised by Angell, Drew, and Wardlaw. The crystallographic examination shows definitely that in α -PtCl₂·2Me₂S there is a planar distribution of valencies around the platinum atom, the sulphide groups occupying *trans*-positions. The chemical reactions with ethylenediamine fully confirm this finding. Whilst the β -chloride dissolves readily in aqueous ethylenediamine and gives with potassium chloroplatinite a pure plato-salt, [Pt en (Me₂S)₂][PtCl₄], the α -chloride reacts in a noteworthy manner. This reaction proceeds much more slowly than in the case of the β -chloride, dimethyl sulphide is evolved, and the plato-salt [Pt₂en][PtCl₄] is isolated. Moreover, if ethylenediamine is added to an acetone solution of the α -chloride, dimethyl sulphide is again evolved and the compound Pt en₂Cl₂ is precipitated. These results indicate quite clearly that in the β -compound the sulphur atoms are in *cis*-positions and that the chelate group en is readily co-ordinated to the platinum atom. The difficulty of reaction of the α -chloride, the loss of the thio-ether, and the formation of the tetrammine Pt en₂Cl₂ are fully in harmony with the X-ray findings that the α -compound has a *trans*-planar structure. It should be emphasised, however, that no deduction of a positive nature relating to the configuration of the chlorides can be made from the chemical evidence alone. The X-ray results in the case of the α -chloride are definite, but the β -chloride is less easily investigated. It has a more complicated and unsymmetrical structure and the detailed configuration cannot be deduced with certainty at present. Nevertheless, from the preliminary results of the physical examination and the detailed results from the chemical experiments it seems most likely that the sulphur atoms are in *cis*-positions, and moreover, the fact that the density of the β -isomeride is appreciably less than that of the α - (2·50 as against 2·56) lends support to the view that this substance is ionised in the solid state. The reactions with silver oxide and the conductivity data relating to aqueous solutions of the β -chloride indicate that in solution this salt is ionised.

With regard to the thio-ether compounds of palladous chloride, in each case only one derivative is known; the detailed examination which we have made of bisdimethylsulphinepalladous chloride shows it to be completely isomorphous with the α -Pt(Me₂S)₂Cl₂, so there is no doubt that this compound also has a planar *trans*-configuration.

EXPERIMENTAL.

The Preparation of the Isomeric Bisdimethylsulphineplatinous Chlorides.—Potassium chloroplatinite (4·0 g.), dissolved in water (80 c.c.) and cooled in ice, was mixed with dimethyl sulphide (1·6 c.c.) and placed in an ice-chest over-night. Pink and yellow solids were deposited, which, after being filtered from the mother-liquor, washed with cold water, and dried in a vacuum over phosphoric oxide, were separated by extraction with cold chloroform, the pink (A) remaining undissolved, whilst both α - and β -Pt(Me₂S)₂Cl₂ separated on evaporation of the extract.

The α , m. p. 159°, is insoluble in water, cold alcohol, light petroleum, and benzene, but readily soluble in acetone and chloroform, separating from either of these solvents in orange, transparent, monoclinic plates without solvent of crystallisation [Found: Pt, 49·78; *M*, in boiling acetone (0·15 g./29 c.c.; *e* 0·03°), 383. Calc. for Pt[(CH₃)₂S]₂Cl₂: Pt, 50·01%; *M*, 390·4].

The β , m. p. 159°, is insoluble in alcohol and light petroleum, slightly soluble in benzene, but soluble in water (0·0936 g. in 100 c.c. at 15°), acetone, and chloroform, separating from the last with one molecule of chloroform of crystallisation in citron-yellow, transparent, tetragonal plates. It quickly loses this molecule of chloroform, becoming opaque and distorted (Found: Pt, 50·25%). On recrystallisation from acetone, it separates in citron-yellow, transparent, monoclinic prisms with no solvent of crystallisation {Found: Pt, 49·87; *M*, in boiling acetone (0·17 g./25 c.c.; *e* 0·04°), 377. Calc. for Pt[(CH₃)₂S]₂Cl₂: Pt, 50·01%; *M*, 390·4}. The β -form is more soluble in acetone than the α -form.

The pink substance (A) was found to be [Pt(Me₂S)₄][PtCl₄] (Found: Pt, 50·15. Calc.: Pt, 50·01%). It is insoluble in alcohol, but slightly soluble in chloroform and alcohol-chloroform (1:1), undergoing transformation to the β -Pt(Me₂S)₂Cl₂. Further, it breaks down to a mixture of both isomeric disulphines on standing at room temperature, warming at 85°, or dissolving in excess aqueous dimethyl sulphide (boiling). On warming in water, this plato-salt changes into a mixture of the isomeric thio-ethers, finally dissolving to a yellow solution, from which solely β -Pt(Me₂S)₂Cl₂ separates in pale yellow needles on cooling (Found: Pt, 50·21. Calc.:

Pt, 50.01%). Thinking that this pink product (A) might be the trisulphine plato-salt $[\text{Pt}(\text{Me}_2\text{S})_3\text{Cl}]_2[\text{PtCl}_4]$, we treated it with the theoretical quantity of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ in aqueous solution either by warming or allowing it to react for several days at room temperature with frequent agitation. Green salt of Magnus was deposited, and a further precipitate of this compound was obtained from the filtrate on treatment with aqueous potassium chloroplatinite, signifying that the reaction was not practicable quantitatively owing to the partial decomposition of the pink compound into the dichlorides. However, in general confirmation of earlier work, when dimethyl sulphide (2 mols.) was mixed with a 5% aqueous solution of chloroplatinic acid (1 mol.) at room temperature, a yellow precipitate was immediately deposited, which, on recrystallisation from chloroform, gave the characteristic crystals of α - $\text{Pt}(\text{Me}_2\text{S})_2\text{Cl}_4$ and α - and β - $\text{Pt}(\text{Me}_2\text{S})_2\text{Cl}_2$, thus indirectly confirming the existence of $[\text{Pt}(\text{Me}_2\text{S})_4][\text{PtCl}_4]$.

When the original dried mixture of pink and yellow solids was warmed with a small quantity of water, it turned yellow. This yellow substance, dried and extracted with chloroform, gave an insoluble residue, which on recrystallisation from boiling acetone proved to be pale yellow $[\text{Pt}(\text{Me}_2\text{S})\text{Cl}_3]\text{H}$ (Found: Pt, 53.63. Calc.: Pt, 53.53%).

The Interconversion of the Isomeric Dichlorides.—The α -dichloride is completely converted into the β -isomeride on being dissolved in boiling water, and almost completely by treatment with further aqueous dimethyl sulphide. It is only partially transformed on recrystallisation from chloroform or on melting, the solidified melt remelting at 154–161°. The β -dichloride is partially converted into the α -isomeride on recrystallisation from chloroform, especially after the solution has been warmed for some time, or on melting, the solidified melt remelting at 154–161°. (N.B. An approximately equimolecular mixture of both thio-ethers melts at 154–161°.) The conversion of either dichloride into the other is very slight in acetone, even on warming the solution. It is interesting to record that, unlike the diethyl sulphines, the dimethyl sulphide analogues appear to be stable on keeping.

Action of Moist Silver Oxide on the Isomeric Dichlorides.—The α -dichloride, on being shaken with an aqueous suspension of silver oxide for 20 minutes or longer in the cold or warm, was decomposed into dimethyl sulphide, silver chloride, and platinum oxide or hydroxide. The filtrate had the properties described on p. 182.

The β -dichloride under the same conditions gave a faint yellow filtrate reacting alkaline to litmus and leaving a yellowish-brown varnish-like solid, too hygroscopic for analysis, when evaporated to dryness over phosphoric oxide in a vacuum. This substance, which is most probably the β -base $\text{Pt}(\text{Me}_2\text{S})_2(\text{OH})_2$, dissolves readily in water, the original β -dichloride being precipitated from the solution on neutralisation with dilute hydrochloric acid (Found: Pt, 49.89. Calc.: Pt, 50.01%).

The pink substance (A) breaks down in aqueous silver oxide suspension to the dichlorides, thus acting similarly to the β -isomeride with the exception that dimethyl sulphide is liberated as in the case of the α -isomeride.

Action of Silver Nitrate on the Isomeric Dichlorides.—The solution of β -dichloride, obtained by shaking this isomeride in cold water for several minutes, immediately precipitates silver chloride on addition of silver nitrate solution in the presence of nitric acid. No precipitate was obtained on treating the α -dichloride in a like manner.

The Tetrachlorides.—The α -tetrachloride was prepared by passing a slight excess of chlorine at ordinary temperature into a chloroform solution of the α -dichloride. Orange-coloured crystals separated on standing, and crystallised from chloroform in thick irregular plates {Found: Pt, 42.17; 42.06. Calc. for $\text{Pt}[(\text{CH}_3)_2\text{S}]_2\text{Cl}_4$: Pt, 42.32%}. This substance, on heating, changes in appearance at 136°, darkens rapidly at 188°, and melts between 219° and 229° (decomp.).

The β -tetrachloride was prepared in a similar manner, being precipitated immediately in aggregates of very small prisms (Found: Pt, 42.09; 42.07%); it has a minute solubility in hot water, chloroform, and benzene, but is insoluble in light petroleum. On heating, it changes in appearance at 150°, darkens rapidly at 176°, and melts between 215° and 226° (decomp.).

Preparation of Bisdimethylsulphine-ethylenediaminoplatinous Chloride.—The plato-salt $[\text{Pt}(\text{Me}_2\text{S})_2\text{en}][\text{PtCl}_4]$ was prepared by dissolving β - $\text{Pt}(\text{Me}_2\text{S})_2\text{Cl}_2$ in water containing a drop of ethylenediamine, and immediately adding aqueous potassium chloroplatinite to the colourless solution {Found: Pt, 54.78; 54.47. Calc. for $\text{Pt}[(\text{CH}_3)_2\text{S}]_2[\text{C}_2\text{H}_4(\text{NH}_2)_2][\text{PtCl}_4]$: Pt, 54.49%}. This plato-salt crystallises in microscopic, rose-coloured, monoclinic prisms which are unstable on standing in water.

Under similar conditions, the α -isomeride reacted much less readily; dimethyl sulphide was evolved and only the compound $[\text{Pt}(\text{en})_2][\text{PtCl}_4]$ was produced. In cold acetone as

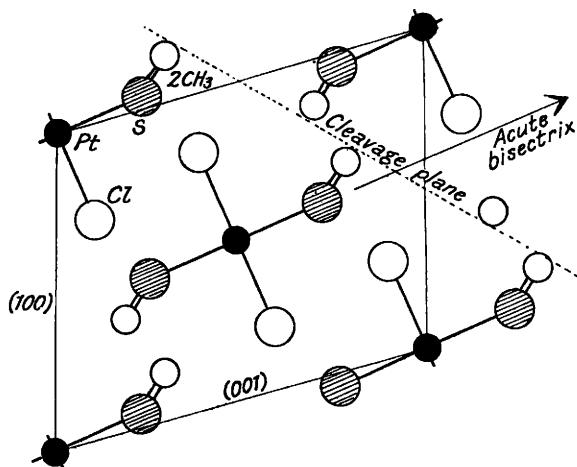
solvent, immediate reaction occurred, with evolution of dimethyl sulphide and precipitation of $[\text{Pt}(\text{en})_2]\text{Cl}_2$, identified by formation of its plato-salt in the usual way {Found : Pt, 59.81. Calc. for $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2][\text{PtCl}_4]$: Pt, 59.85%}.

Crystallographic Measurements.

α-Bisdimethylsulphineplatinous Chloride.—This substance has been described by Weibull (Groth, "Chemische Krystallographie," I, 270) as occurring in monoclinic prismatic crystals with $a : b : c = 1.8788 : 1 : 1.4060$; $\beta = 120^\circ 11'$, the forms observed being $c\{001\}$, $r\{201\}$, $p\{110\}$, and $o\{\bar{1}11\}$, with perfect cleavage parallel to $c\{001\}$. These results have been confirmed, but in accordance with T. V. Barker's system, the orientation has been changed by means of the transformation

$$\begin{array}{cccc} c(001) & r(20\bar{1}) & o(\bar{1}11) & p(110) \\ R(\bar{1}01) & r'(\bar{1}0\bar{1}) & q(0\bar{1}\bar{1}) & m'(\bar{1}\bar{1}0) \end{array}$$

The axial ratios thus become $a : b : c = 1.689 : 1 : 1.4060$; $\beta = 105^\circ 52'$. The optical properties were incorrectly reported by Weibull. We find them to be as follows: Double refraction positive, plane of the optic axes perpendicular to $\{010\}$, acute bisectrix nearly perpendicular to $\{201\}$. $2H$ (in liquid of $n = 1.69$) = 25° approx. Dispersion $\rho > \nu$.



X-Ray examination by the rotation method gave the following values : $a = 10.16$, $b = 6.01$, $c = 8.48$ Å.U.; $\beta = 105^\circ 55'$. With two molecules in the unit cell the calculated density from these figures is 2.58 g./c.c. (Found : by flotation, 2.56). Oscillation photographs indicate that the space-group is either $P2_1/m$ or $P2_1/c$ (C_{2h}^2 or C_{2h}^5). A rotation photograph about the $[111]$ axis shows extremely weak odd layer lines, indicating that the lattice is very nearly body-centred. Thus each molecule of $\alpha\text{-Pt}(\text{Me}_2\text{S})_2\text{Cl}_2$ has very nearly full C_{2h} symmetry, *i.e.*, a plane and a two-fold axis, so that, at any rate to a close approximation, the four valencies to the platinum atom must be coplanar, with the thio-ether groups in trans-positions. The deviation from exact C_{2h} symmetry is probably due to the interaction between chlorine and sulphur atoms in neighbouring molecules. That distortion might arise on this account can be seen from the figure, which shows a projection of the probable structure on (010) . This structure is in harmony with the observed cleavage and optical properties. The interatomic distances in the figure are not to scale.

The α -bromide is completely isomorphous with the chloride.

β-Bisdimethylsulphineplatinous Chloride.—This substance was described by Weibull (*loc. cit.*) as crystallising with one molecule of chloroform in tetragonal plates. This was confirmed, but together with the tetragonal crystals other (superficially identical) square plates were found, apparently orthorhombic, showing diagonal extinction and negative birefringence. The acute bisectrix is perpendicular to the plate; $2E = 33^\circ$ approx. These two forms were not investigated further on account of the rapidity with which they lose chloroform. It was difficult to obtain good crystals of this isomeride free from solvent of crystallisation; the best

were obtained from acetone in the form of monoclinic prisms showing the forms $a\{100\}$, $R\{101\}$, $b\{010\}$, $m\{110\}$, and $q\{011\}$, and usually elongated along the a -axis. Combined X -ray and goniometric examination gave for the cell dimensions: $a = 9.3$, $b = 13.2$, $c = 8.7$ Å.U.; $\beta = 105^\circ$ approx. The unit cell so defined contains four molecules (density by flotation, 2.50 g./c.c.). The crystals were not sufficiently good to enable more precise measurements to be made; in addition, they lost their transparency on continual exposure to X -rays. However, the fact that there are four molecules in the cell (which is not face-centred or even approximately so) shows that the molecular symmetry is less than in the case of the α -isomeride—the molecule of β -Pt(Me₂S)₂Cl₂ cannot possess more than one element of symmetry. Thus the probability of an ionised structure with the sulphur atoms in *trans*-positions is very remote.

α -Bisdiethylsulphineplatinous Chloride.—This substance also was described by Weibull (*op. cit.*, p. 273); we have confirmed his angular measurements, but not his axial ratios, cleavage, and optical orientation. The correct description is: monoclinic prismatic, showing the forms: $a\{100\}$, $c\{001\}$, $r\{101\}$, $R\{10\bar{1}\}$, $m\{110\}$; $a : b : c = 1.588 : 1 : 1.013$; $\beta = 93^\circ 56'$. (These axial ratios are recalculated from Weibull's angular measurements.) Cleavage parallel to $R\{\bar{1}01\}$. Double refraction negative, optic axial plane perpendicular to $b\{010\}$, acute bisectrix nearly perpendicular to $R\{101\}$. X -Ray measurements give $a = 12.0$, $b = 7.9$, $c = 7.7$ Å.U. There are two molecules in the unit cell (density by flotation, 2.08 g./c.c.).

Bisdimethylsulphinepalladous Chloride.—This substance was prepared from potassium chloropalladite and dimethyl sulphide (see Ardell, *Z. anorg. Chem.*, 1897, **14**, 143; Phillips, *J. Amer. Chem. Soc.*, 1901, **23**, 255; Drew, Preston, Wardlaw, and Wyatt, *J.*, 1933, 1296). It has m. p. 128° and undergoes slow decomposition (Found: Pd, 35.5, 35.0. Calc.: Pd, 35.4%). The crystals are deep red but otherwise precisely similar in appearance and properties to α -Pt(SMe₂)₂Cl₂ with which they are isomorphous. The density is 1.99 g./c.c. Goniometric examination gave the following results. Monoclinic prismatic; $a : b : c = 1.719 : 1 : 1.419$; $\beta = 105^\circ 42'$. Angular measurements: $r(101) : R(\bar{1}01) = 79^\circ 26'$; $r(101) : m(110) = 67^\circ 08'$; $R(\bar{1}01) : m(110) = 105^\circ 19'$; $R(\bar{1}01) : q(011) = 65^\circ 49'$ (calc. $65^\circ 59'$). The complete isomorphism of Pd(SMe₂)₂Cl₂ with Pt(SMe₂)₂Cl₂ leaves no doubt that the former also has a planar *trans*-configuration.

UNIVERSITY OF BIRMINGHAM, EDGBASTON.

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