**482.** *The Nature of the Co-ordinate Link. Part VIII.* Geometrical Isomerism and Simple Reactions of Ethylthio-bridged Complexes of Platinum(II) and of Palladium(II).*

By J. Chatt and F. A. Hart.

When dichlorobistri-*n*-propylphosphine-μμ′-dichlorodiplatinum (VII) is treated with an excess of ethanethiol, the two bridging chlorine atoms are replaced by SEt groups to yield a mixture of the *trans*- (IV) and *cis*-symmetrical isomers (V) of dichlorobistri-*n*-propylphosphine-μμ′-bisethylthio-diplatinum. Both isomers remain unchanged in benzene solution at room temperature, but the *trans*- changes into the *cis*-isomer in boiling benzene or under the catalytic influence of tri-*n*-propylphosphine. The above dithiol-bridged complexes are not attacked by amines in boiling benzene. The tetrachloro-compound (VII) reacts with the dithio-compounds (IV) and (V) to yield *cis*-SPS-*cis*-symmetrical-dichlorobistri-*n*-propylphosphine-μ-chloro-μ′-ethylthiodiplatinum † (VI). This is attacked in solution by amines as if it existed in equilibrium with a mixture of the above dithio-compounds and the tetrachloro-compound. The tetrachloro-compound has a *trans*-configuration, but in solution it exists in equilibrium with about 2% of its *cis*-isomer. This equilibrium appears to be established by a very slight reversible dissociation of the tetrachloro-compound at the bridge to give the configurationally unstable PPr$^n_3$PtCl$_2$. The corresponding mono- and bis-ethylthio-bridged palladium complexes also have *cis*-configurations. The surprisingly high stability of the *cis*-isomers relative to the *trans*-isomers when sulphur occupies one or both of the bridging positions is discussed. It is evidence of some strong directing influence in the Pt⎯S⎯Pt⎯S and Pd⎯S⎯Pd⎯S rings. The dipole moments of the above compounds, used to determine their configurations, are listed.

PFEIFFER, in 1923 (Werner and Pfeiffer, "Anorganische Chemie," 5th Edn., pp. 56, 170) suggested that the few platinous complexes of the type LPtX₂ [L = ligand, *e.g.*, CO, PCl₃, P(OEt)₃; X = halogen] which were then known would have halogen-bridged structures. He also noted that three isomeric forms are possible. These may be represented by (I), (II), and (III) :

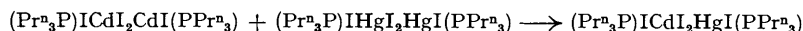| (I)	(II)	(III)
" *trans*-symmetrical "	" *cis*-symmetrical "	" unsymmetrical "
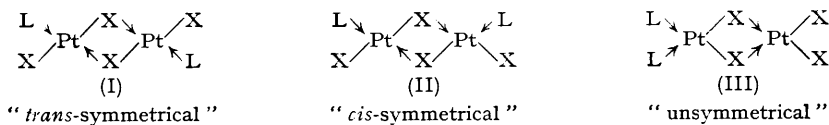
This isomerism is theoretically possible in similar complexes of any bivalent metal whether it be co-ordinated in a plane or tetrahedrally; yet out of the numerous bridged complexes now known, only *trans*-symmetrical forms (I) have been identified (*e.g.*, Mann and Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169). Of the 4-co-ordinated metals, platinum(II) forms the most robust complexes, hence geometrical isomerism is more probable among its bridged complexes than among those of any other metal. In Part II (Chatt, *J.*, 1951, 652) we briefly reviewed previous work and described the halogen-bridged platinous complexes of tri-*n*-propylphosphine, among which we failed to find geometrical isomerism. There are three possible causes for this failure : (1) The four methods of preparation we used yielded exclusively the *trans*-symmetrical isomer, by which it is implied that some other method might yield exclusively the *cis*-isomer. (2) The terminal X and L groups can interchange positions spontaneously so that an equilibrium mixture of isomers exists in solution. This suggestion has already been made with reference to the analogous palladous series of complexes (Mann, *Ann. Reports*, 1938, **35**, 150; Chatt and

Mann, *J.*, 1939, 1622). (3) In solution the complex is slightly dissociated at the bridge into two fragments, $LPtX_2$, which would be configurationally unstable. They thus yield an equilibrium mixture from which only the stable (usually *trans-*)bridged isomer can be isolated. Dissociation of this type has been suggested to explain reactions in the cadmium and mercury series of complexes (Mann and Purdie, *J.*, 1940, 1230) of the type :

$$(Pr^n{}_3P)ICdI_2CdI(PPr^n{}_3) + (Pr^n{}_3P)IHgI_2HgI(PPr^n{}_3) \longrightarrow (Pr^n{}_3P)ICdI_2HgI(PPr^n{}_3)$$

We suspected the third cause to be responsible for our failure to isolate geometrically isomeric forms of the halogen-bridged $(PPr^n{}_3)_2Pt_2Cl_4$. In the palladous series of complexes, the ethylthio-group is known to be much more strongly bridging than the halogen atom (Chatt and Mann, *J.*, 1938, 1949); we have, therefore, prepared the thio-bridged $(PPr^n{}_3)_2Pt_2(SEt)_2Cl_2$. The bridge in this compound has proved sufficiently stable to allow us to isolate two geometric isomers (IV) and (V), both of which are stable at room temperature. Surprisingly the *cis*-isomer (V) is the thermodynamically stable isomer in benzene solution. In consequence of this, we have examined the configuration of the bridged monothio-complex $(PPr^n{}_3)_2Pt_2(SEt)Cl_3$ and the bridged palladium complexes $(PPr^n{}_3)_2Pd_2(SEt)_2Cl_2$ and $(PPr^n{}_3)_2Pd_2(SEt)Cl_3$. All are *cis*-isomers of type (II), but the palladous complexes isomerise in benzene at 25° to yield equilibria in which the *cis*-isomers predominate.

The compounds which form the subject of this paper have been allocated structures as follows; all except (VII) are new and some of their physical properties are listed in Tables 1 and 2, p. 2367.

(IV) (V) (VI)

(VII) (VIII) (IX)
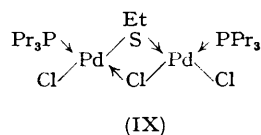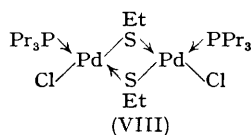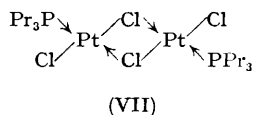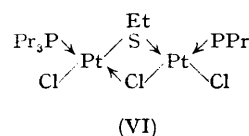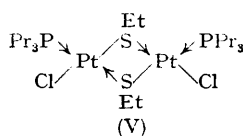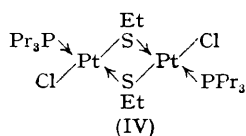
When ethanethiol in excess (4—8 mols.) was added to a solution of the tetrachloro-compound (VII), the colour changed immediately from orange to yellow. Evaporation now yielded a sticky mixture containing the monothio- (VI) and the dithio-compounds (IV) and (V). More prolonged action of ethanethiol (6 hr.) yielded only the dithio-compounds; no evidence of further substitution was obtained even after 3 days. The monothio-compound (VI) is best prepared by boiling the dithio-compounds, either (IV) or (V), with their equivalent of the tetrachloro-compound (VII) in benzene but may also be obtained by reaction of one molecule of ethanethiol with (VII).

Structure and Configuration of the Bridged Ethylthioplatinous Complexes.—The methods of synthesis, the analysis, and molecular weights indicate the formula $(PPr^n{}_3)_2Pt_2(SEt)_2Cl_2$ for the dithio-compounds (IV) and (V), and $(PPr^n{}_3)_2Pt_2(SEt)Cl_3$ for the monothio-compound (VI). These substances are non-electrolytes in nitrobenzene solution; thus they can only be formulated by bridged as opposed to ionic, *i.e.*, salt, structures.

Halogen-bridged platinous complexes are split at the bridge immediately on being mixed with amines in cold solvents (Part II, *loc. cit.*). Both *p*-toluidine and dipyridyl are
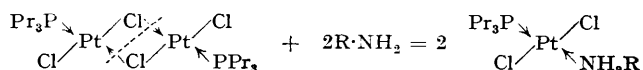
without action on the dithio-compounds either in cold or boiling solvents; hence the SEt groups occupy the bridging positions and stabilise the bridge as they do in the analogous palladous series of complexes (Chatt and Mann, *J.*, 1938, 1949). The monoethylthio-compound (VI) reacts only slowly with amines in boiling benzene; its reaction with 2 : 2′-

dipyridyl in nitrobenzene at room temperature requires some six days to go to completion. The bridge is thus intermediate in stability between the very reactive halogen bridge of the tetrachloro-compound (VII) and the stable dithiol bridges. This is consistent with a bridge containing both SEt and Cl as shown in formula (VI). The relative positions of the two tri-*n*-propylphosphine molecules and the chlorine atoms were determined by measuring the dipole moments of the compounds. *trans*-Symmetrical forms, type (I), will have zero dipole moments; *cis*-symmetrical forms, type (II), should have moments approximating to that of *cis*-$(PPr^n_3)_2PtCl_2$ which Jensen (*Z. anorg. Chem.*, 1936, **229**, 250) found to be 11·5 D; unsymmetrical forms, type (III), should have moments approaching twice this value, say 20 D. The moments listed in Table 1 (p. 2367) show that the dithio-compound of m. p. 156·5—157·5° is *trans*-symmetrical dichlorobistri-*n*-propylphosphine-μμ'-bisethylthiodiplatinum (IV), and the compound of m. p. 125·5—127° is its *cis*-isomer (V). The monothio-derivative (Table 2, p. 2367) is also a *cis*-symmetrical isomer and its appreciably higher dipole moment indicates that the most electropositive donors, phosphorus and sulphur, must be arranged along one edge of the molecule as formulated in (VI). No rules of nomenclature have yet been proposed to distinguish this structure from the structure (XIV) (p. 2368). We * have therefore adopted the proposal to prefix the name with *cis*-PSP- to indicate that these three atoms all lie on the same side of the planar molecule. The monothio-compound (VI) is thus *cis*-PSP-*cis*-symmetrical-dichlorobistri-*n*-propylphosphine-μ-chloro-μ'-ethylthiodiplatinum. The unknown compound of structure (XIV) would have the same name except that the prefix would be *cis*-PClP.

Besides the isomerism discussed above, it is possible for each of the dithio-compounds (IV) and (V) to exist in two geometrically isomeric forms because the three bonds from the sulphur atom are not planar, and the ethyl groups may be in *cis*- or *trans*-relation to each other about the Pt–S–Pt–S ring.† Such isomerism was sought by Bennett, Mosses, and Statham (*J.*, 1930, 1668) in complexes of type (X) (MX$_2$ = PdCl$_2$ or HgI$_2$) but was not observed, presumably because the sulphur atoms pass easily through the plane of the three attached groups. It would be possible to determine the relative configuration of the ethyl groups in the *trans*-dithio-compound (IV) if we could measure its dipole moment accurately. If the ethyl groups are in *trans*-positions the molecule would be centro-symmetrical and have zero moment; if they are in *cis*-positions the moment would be of the order 1 D.
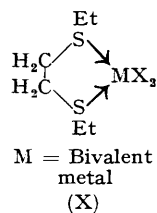
(structure diagram, labelled: Et, S, H$_2$C, H$_2$C, S, Et, MX$_2$; M = Bivalent metal; (X))

Unfortunately, it is not possible to determine the dipole moments of complex compounds which have small moments from measurements made on solutions of the compound. This arises because the atom polarisation in metallic complexes is large and cannot be estimated with any certainty (*e.g.*, see Part VII, *loc. cit.*). Jensen (*Z. anorg. Chem.*, 1936, **229**, 225) found that an atom polarisation of about 20% of the electron polarisation was generally necessary so that a number of completely symmetrical *trans*-complexes of the type (MR$_3$)$_2$PtCl$_2$ (M = P or As) should have zero moment. We find that an allowance for the atom polarisation of 15% of the electron polarisation is necessary if the *trans*-dithio-compound (IV) is to have zero moment. If the moment were greater than zero then the allowance must be less than 15%, which is rather low for compounds of this type. It is very probable, therefore, that the moment really is zero and the ethyl groups are in *trans*-relation about the Pt–S–Pt–S ring. Uncertainty regarding the atom polarisation does not affect the values of the order 10 D recorded for other compounds in this series, because the contributions of the atom polarisations to the total polarisations of these highly dipolar molecules is negligible.

Reactions of the Bridged Ethylthio-compounds (IV), (V), *and* (VI).—The *cis*-dithio-compound (V) is the more stable and it is recovered unchanged after 21 hr. in boiling benzene. The *trans*-isomer (IV) is stable in cold benzene but is slowly converted into the

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* We are indebted to the Editor for suggesting this logical extension of existing nomenclature.

† We have some evidence that the S–Pt–S–Pt ring is "aromatic" in character. The S–C bonds and the ring could thus be coplanar.

cis-isomer in boiling benzene. This isomerisation is not appreciably catalysed by the presence of 2 equivalents of *p*-toluidine or 2 : 2′-dipyridyl but occurs rapidly even in cold benzene on addition of a trace of tri-*n*-propylphosphine (cf. Chatt and Wilkins, *J.*, 1951, 3061). The *cis*-isomer is not changed even in presence of a trace of PPr^n_3, so the equilibrium between the two geometric isomers (IV) and (V) lies completely, or almost completely, on the *cis*-side.

The monoethylthio-compound (VI) reacts with amines as if there existed sluggishly established equilibria as follows :

$$\text{(VI)} \rightleftharpoons \text{(IV)} + \text{(V)} + \underbrace{\text{(VII)}}$$

EtOH(cold)– p-C$_7$H$_7$·NH$_2$ ↑↓ C$_6$H$_6$(hot)　　　Dipy　　　　　(Dipy = Dipyridyl)

(XI) 2 *trans*-*p*-C$_7$H$_7$·NH$_2$,PPr$^n_3$,PtCl$_2$　　　*trans*-(PPr$^n_3$)$_2$PtCl$_2$ (XII) + Dipy,PtCl$_2$ (XIII)
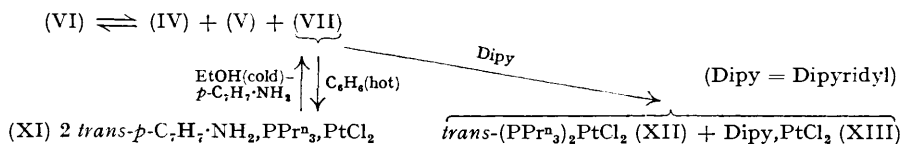
The evidence is :

(*a*) The dithio-compounds (IV) and (V) react with the tetrachloro-compound (VII) in boiling benzene to yield the monothio-compound (VI) quantitatively in less than an hour. At room temperature the reactions require about 3 days, even when the tetrachloro-compound is present in excess.

(*b*) One mol. of 2 : 2′-dipyridyl in a boiling benzene solution of the monothio-compound (VI) reacts slowly (36 hr.) to yield a mixture of (XII), (XIII), the dithio-compounds (IV) and (V), and the excess of dipyridyl. The tetrachloro-compound (VII) is known to react with dipyridyl to yield the salt [dipy,PPr$^n_3$,PtCl]$^+$[PPr$^n_3$PtCl$_3$]$^-$ (Chatt, *J.*, 1951, 652) which decomposes in boiling solvents to yield (XII) and (XIII), a reaction which is not reversible. By repeating the reaction in nitrobenzene at room temperature in a conductivity cell, the formation of a salt was observed. The non-conducting solution of the monothio-compound (VI) became conducting on addition of dipyridyl, and the conductivity continued to rise for 6 days after the addition.

(*c*) The monothio-compound (VI) reacts sluggishly with 2 mols. of *p*-toluidine in boiling benzene. After 23 hours' reaction, we isolated a trace of (VI), (XI), and the dithio-compound (V) with a small proportion of the *trans*-isomer (IV). The reverse reaction was demonstrated by dissolving 2 equivalents of (XI) in a saturated solution of the dithio-compound (IV) in ethanol at 35—40°. After 3 days at room temperature, a small quantity of the rather sparingly soluble monothio-compound (VI) had separated; (IV), (V), (VI), and (XI) were isolated from the alcoholic solution. Spectrophotometrically it was shown that in 10^{-5}M-ethanol solution the equilibrium lies entirely on the side of the free monothio-compound (VI) and *p*-toluidine. It is to be noted that in the reaction with amines, twice the quantity of amine necessary for the reactions which occurred was used, so that if a simple bridge-splitting reaction (p. 2364) had been possible there was sufficient amine to allow it to happen.

The chemistry of the bridged ethylthio-compounds (IV), (V), and (VI) is obviously closely analogous to that of the corresponding tri-*n*-butylphosphine *palladous* bridged ethylthio-compounds described by Chatt and Mann (*J.*, 1938, 1949). However, the above reactions of the platinous complexes, even when carried out in boiling solvents, are much slower than in the palladous series where even the slowest of the analogous reactions is complete in about an hour at room temperature.

Comparison of the Physical Properties of Simple and Bridged Geometrical Isomers in the Platinous Series of Complexes.—The dithio-compounds (IV) and (V) provide the first examples of bridged *trans*- and *cis*-complexes. Their more obvious physical properties are in marked contrast with those of their simple analogues, *trans*- and *cis*-(PPr$^n_3$)$_2$PtCl$_2$. The last two isomers differ markedly in melting point, colour, and solubility, whereas (IV) and (V) show a close resemblance to each other. The slight differences which do occur are in the opposite sense to the greater differences between the properties of members of the simple series (see Table 1).

Configuration of Ethylthio-bridged Palladous Complexes.—In view of the surprisingly high stability of the ethylthio-bridged platinous complexes (V) and (VI) of *cis*-configuration, it

was of interest to determine the configurations of the ethylthio-bridged palladous complexes $(PPr^n_3)_2Pd_2(SEt)_2Cl_2$ and $(PPr^n_3)_2Pd_2(SEt)Cl_3$. A comparison of X-ray powder photographs, for which we are indebted to Dr. P. G. Owston, shows that the dithiopalladous

TABLE 1. *A comparison of trans- and cis-$(PPr^n_3)_2PtCl_2$ with trans- and cis-symmetrical-$(PPr^n_3)ClPt(SEt)_2PtCl(PPr^n_3)$.*

	$(PPr^n_3)_2Pt_2(SEt)_2Cl_2$		$(PPr^n_3)_2PtCl_2$	
Property	*trans* (IV)	*cis* (V)	*trans*	*cis*
M. p.	156·5—157·5°	125·5—127°	85—86°	150·5—152°
Colour	Very pale yellow	Pale yellow	Pale yellow	Colourless
Solubility in organic solvents	Moderately soluble < (V)	Moderately soluble > (IV)	Very soluble —	Moderately soluble —
Dipole moment	~0	10·3D	~0	11·5D
Approx. equil. % of isomers	<1	>99	97	3

complex is isomorphous with the *cis*-dithioplatinous complex (V) and has the same unit-cell size, so must have a *cis*-configuration (VIII). This is confirmed by the dipole moments recorded in Tables 1 and 2. The *trans*-platinous isomer (IV) gives a different photograph. The monothio-platinous and -palladous complexes are also isomorphous and have identical unit-cell size, so these also have the same configurations (VI) and (IX).

TABLE 2. *Melting points, colours, and dipole moments of* (VI), (VIII), *and* (IX).

| $(PPr^n_3)_2Pt_2(SEt)Cl_3$ (VI) | $(PPr^n_3)_2Pd_2(SEt)_2Cl_2$ (VIII) | $(PPr^n_3)_2Pd_2(SEt)Cl_3$ (IX) |
220—221·5°	136·5—137°	224—224·5°
Pale yellow	Yellow	Yellow
13·0 D	10·7 D	8·3 D *

  * This is obviously a solution of an equilibrium mixture containing about 35% of related *trans*-complexes.

The dielectric constants of the benzene solutions of (VI) and (IX) at 25° were steady, but that of (VIII) fell slowly, reaching equilibrium after about 25 hr. If we assume, as is most probable, that this drop is caused by isomerisation to a mixture of palladium analogues of the dithio-compounds (IV) and (V), then the equilibrium mixture contains about 90% of the *cis*-isomer. This is the greatest amount of a palladous complex of *cis*-configuration ever recorded in a labile system (cf. Chatt and Wilkins, *J.*, 1953, 70). (IX) has rather poor solubility in pure benzene and slight warming was necessary to get it into solution. The rather low moment found corresponds to a solution containing about 65% of *cis*-isomers in equilibrium with *trans*-isomers. Since the dielectric constant of this solution did not vary with time, isomerisation must have been complete in the time necessary to prepare the solution for measurement. This isomerisation may also be accompanied by a small amount of disproportionation, yielding small quantities of (VIII) and the palladium analogue of (VII) (see Chatt and Mann, *J.*, 1938, 1949).

That the moment of the dithiopalladium compound (VIII) is slightly greater than that of its platinum analogue (V), if significant, is interesting, because it agrees with the expectation that double bonding between ligand and metal is greater in platinous than in palladous complexes. It is also interesting that, when the equilibria between *cis*- and *trans*-platinous complexes are compared with those between the corresponding palladous complexes, the equilibria lie much farther to the *trans*-side in the palladous series (Chatt and Wilkins, *loc. cit.*). The above bridged complexes show the same relation. We regard this as evidence that directing forces (*e.g.*, the *trans*-effect) are considerably weaker in palladous than in platinous complexes.

That the *cis*-configuration of the thio-bridged platinous complexes is preferred is evidence of some strong directing influence in the Pt–S–Pt–S ring. This influence is obviously much weaker when the sulphur is replaced by chlorine. The greater covalent character and polarisability of the sulphur ring system, and the non-planar arrangement of the bonds from the sulphur atoms (which confers some asymmetry on its electronic structure), are possible factors responsible for directing the PPr₃ group into *cis*-positions. Whatever may be the cause of the stability of the sulphur-bridged *cis*-isomers, it is of fundamental importance to any theory of substitution in complex compounds and in

establishing the nature of the co-ordinate link itself. That the configuration (VI) should be more stable than (XIV) is a simple manifestation of the *trans*-effect. We have shown in the previous four parts of this series that when a simple platinous complex contains
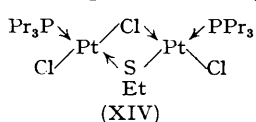
two groups of fairly high *trans*-influence then the *cis*-isomers have a greater bond energy than the *trans*. Both sulphur and phosphorus have a fairly high *trans*-influence. In (XIV) these atoms are in *trans*-positions about both platinum atoms whereas in (VI) they are in *cis*-positions. Thus (VI) should have the greater bond energy and in absence of any unusual entropy difference between (VI) and (XIV) should be the stable isomer. The monothio-platinum compound (VI) is a most unusual molecule in having all the electropositive atoms, P and S, along one edge and the three electronegative chlorine atoms along the opposite edge, giving us the very high dipole moment of 13·0 D, which demonstrates further the unexpectedly powerful directing influences in platinous complexes.

The Nature of the Equilibria in Solutions of Halogen-bridged Platinous and Palladous Complexes.—Mann and his co-workers (Mann, *Ann. Reports*, 1938, **35**, 148; Chatt and Mann, *J.*, 1939, 1622) reached the conclusion that halogen-bridged palladous complexes of trialkyl-phosphines and -arsines exist in solution as equilibrium mixtures of the symmetrical forms of types (I) and (II). There was no evidence for the existence of the unsymmetrical isomer of type (III). All attempts to prepare a compound of the last type by using chelating diarsines and disulphides as ligands had failed. Now we know that such a complex would have a moment of the order of 20 D, and a large amount of electrical energy would be stored in the molecule. It therefore seems very unlikely that any except the minutest quantity of an isomer of type (III) could exist in equilibrium with its symmetrical isomers even if it is capable of existence. Thus we need consider only types (I) and (II) as being present in the equilibrium. The only evidence that any of the *cis*-symmetrical type (II) exists in a solution of the *trans*-symmetrical isomer type (I) is provided by the small but definite apparent dipole moments of the *trans*-bridged complexes in benzene solution. These are too high to be accounted for by assuming a high but reasonable value for the atom polarisation. Mann and Purdie (*J.*, 1936, 873) recorded the dipole moment of $(PBu^n_3)_2Pd_2Cl_4$ as 2·34 D, but made no allowance for atom polarisation. Experience gained since 1936 indicates that 20% of the electron polarisation is a fair approximation to the atom polarisation (Jensen, *loc. cit.*); the moment recalculated on this basis is 1·9 D. We find the moment of $(PPr^n_3)_2Pt_2Cl_4$ to be 1·6 D. Thus in both the palladous and the platinous series of halogen-bridged complexes, we have small moments of the same order of magnitude. These can be accounted for by supposing (*a*) that in each case we have the *cis*-symmetrical isomer in equilibrium with its *trans*-isomer, (*b*) that partial reversible dissociation occurs, giving two highly dipolar fragments, thus : $(PPr^n_3)_2Pt_2Cl_4 \rightleftharpoons 2(PPr^n_3)PtCl_2$, or (*c*) that the compounds have atom polarisations of the order of 50% of the electron polarisations. If dissociation (*b*) were responsible for the observed moments then the observed total polarisation should vary with dilution of the solution. We find that it does not. An atom polarisation as high as 50% of the electron polarisation, as required by (*c*), is very improbable. It lies around 20% in all previously measured symmetrical platinous complexes and cannot be greater than 15% in the sulphur-bridged complex (IV). Supposition (*a*) provides the most probable explanation and has already been made with reference to the palladous complexes (Mann, *loc. cit.*, 1938; Chatt and Mann, *J.*, 1939, 1622). If we assume that the *cis*-symmetrical halogen-bridged complexes have moments of the same order as that found for the *cis*-dithio-compound (V), *viz.*, 10 D, then the equilibrium mixture need contain only about 2% of *cis*-isomer to account for the observed small moments.

The nature of the reactions by which the equilibria are established in the platinous series is also evident. The isomerisation could occur either by interchange of positions by the terminal singly bound ligands or through a very slight dissociation at the bridge into two configurationally unstable fragments, $PPr^n_3,PtCl_2$. If the former explanation were correct, then replacement of the bridging halogen atoms by sulphur atoms should increase the rate of isomerisation. This would be expected because all the terminal ligands are in

trans-positions relative to the bridging groups and sulphur has a greater *trans*-labilising effect than chlorine. If the second explanation were correct the rate of isomerisation should be decreased because the stronger sulphur bridge would be less dissociated than the halogen bridge. Since the latter is what we have found, the isomerisation of the halogen-bridged platinous complexes must occur through dissociation of the bridge. The dissociation is too small to be detected by molecular-weight determinations made in the usual manner (with a micro Swietoslawski apparatus and Beckmann thermometer) or to make a detectable contribution to the apparent dipole moment of the tetrachloro-compound (VII) at the concentrations we used.

The same explanation is probably correct in the case of the palladous bridged complexes because isomerisation of the dithiopalladium compound (VIII) is measurably slow, a most unusual phenomenon amongst palladous complexes containing only monodentate ligands. Such dissociation would account also for the ease with which the bridging halogen atoms can be replaced by many acid radicals, including even the bivalent oxalate radical (Chatt, Mann, and Wells, *J.*, 1938, 2086).

EXPERIMENTAL

Microanalyses are by Mr. W. Brown of these laboratories.

*Reaction of Dichlorobistri-*n-*propylphosphine-*μμ′-*dichlorodiplatinum* (VII) *with Ethanethiol.—*Ethanethiol (1·45 g.) was added to (VII) (5 g., 0·25 mol.) in acetone (150 c.c.). The solution which immediately changed colour was kept for 6 hr. and then evaporated under reduced pressure. The residual solid was recrystallised from ethanol, giving 4·48 g. of mixed isomers (IV) and (V). These were separated by allowing their solution in hot ethanol (200 c.c.) to cool slowly, giving needles (1·7 g.), m. p. 150—153·5°. The mother-liquor from these was evaporated to 70 c.c. and then on slow cooling yielded thick plate-like tablets (1·6 g.), m. p. 121—125·5°. The needles, recrystallised three times from acetone, yielded pure trans-*symmetrical-dichloro-bistri-*n-*propylphosphine-*μμ′-*bisethylthiodiplatinum* (IV) (0·96 g.), m. p. 156·5—157·5° (Found : C, 29·2; H, 5·8; S, 6·9%; *M*, ebullioscopically in 1·87% benzene solution, 896; in 2·81% solution, 923. C$_{22}$H$_{52}$Cl$_2$S$_2$P$_2$Pt$_2$ requires C, 29·2; H, 5·8; S, 7·1%; *M*, 904). The tablets, recrystallised four times from ethanol, yielded the pure cis-*symmetrical-isomer* (V) (0·86 g.), m. p. 125·5—127° (Found : C, 29·3; H, 5·82; S, 7·1%; *M*, ebullioscopically in 1·82% benzene solution, 919; in 3·13% solution, 884). Repetition of this reaction with only 0·125 mol. of (VII) and keeping the mixture for 3 days gave identical products. Repetition, except that the products were worked up immediately after mixing, yielded a gum from which we isolated cis-*PSP*-cis-*symmetrical-dichlorobistri-*n-*propylphosphine-*μ-*chloro-*μ′-*ethylthiodiplatinum* (VI) (1·8 g.), m. p. 220—221·5° (Found : C, 27·4; H, 5·55; S, 3·5%; *M*, ebullioscopically in 1·41% acetone solution, 911; in 1·81% solution, 914. C$_{20}$H$_{47}$Cl$_3$SP$_2$Pt$_2$ requires C, 27·3; H, 5·6; S, 3·65%; *M*, 878).

The monothio-compound (VI) was prepared quantitatively, and pure without recrystallisation, by boiling a solution of equivalent quantities of (VII) and the mixed isomers (IV) and (V) in benzene (1 g. of solid in 10 c.c.) for 1 hr.

Reaction of (VII) *with Pure* (IV) *and with Pure* (V) *in Cold Benzene.—*Solutions of (IV) (0·1 g.) and (V) (0·1 g.) were made up separately in benzene (1 c.c. each). To those were added (VII) (0·075 g., 0·8 mol.) in benzene (1 c.c.). Slow colour change was apparent within 10 min. of mixing; fine needles started to be deposited from (IV) after 1 hr., and heavier, thicker needles from (V) after 1·75 hr. Deposition continued from both solutions for about 3 days. The product from both reactions had m. p. 220—222° alone and mixed with authentic (VI).

*Preparation of Dichlorobistri-*n-*propylphosphine-*μ-*chloro-*μ′-*ethylthiopalladium* (IX) and *Dichlorobistri-*n-*propylphosphine-*μμ′-*bisethylthiodipalladium* (VIII).—Ethanethiol (1·28 g., 3 mols.) was added slowly to a solution of the palladium analogue of (VII) (5 g.) in acetone (200 c.c.). Crystals started to separate immediately and after 70 hr. were filtered off. These were pure *monothio*-derivative (IX) (2·9 g.), m. p. 224° (Found : C, 34·5; H, 7·0; S, 4·45. C$_{20}$H$_{47}$Cl$_3$SP$_2$Pd$_2$ requires C, 34·3; H, 6·8; S, 4·6%). The mother-liquor was evaporated, to yield a solid (1·71 g.) which was extracted with cold benzene leaving a slight residue of (IX). The *dithio*-derivative (VIII) (1 g.), m. p. 137°, was recovered from the benzene solution and was pure after three recrystallisations from methanol (Found : C, 36·5; H, 7·55; S, 8·9%; *M*, ebullioscopically in 1·48% benzene solution, 724; in 2·14% solution, 718. C$_{22}$H$_{52}$Cl$_2$S$_2$P$_2$Pd$_2$ requires C, 36·35; H, 7·2; S, 8·8%; *M*, 727).

*Conductivity.—*All the platinum complexes were tested for electrolytic properties by

measuring the conductivity of a solution of the complex (0·25 g.) in nitrobenzene (10 c.c.), using the cell and apparatus described in *J.*, 1951, 652. The conductivities observed were of the order 0—0·1 μmho, whereas a uni-univalent electrolyte should give a conductivity of about 800 μmhos.

Dipole Moments.—Dielectric constants (ε) were measured with a heterodyne beat capacity meter based on that of Hill and Sutton (see Everard and Sutton, *J.*, 1949, 2313) and a rhodium-plated cell of the same dimensions and design as that of Jenkins and Sutton (*J.*, 1935, 609). The refractive indices (n) were determined with a Pulfrich refractometer and specific volumes (v) with the usual U-shaped pyknometer. Small dipole moments were evaluated by the method of Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, **46**, 417). It was assumed, however, that the atom polarisation ($_AP$) is equal to 20% of the electron polarisation ($_EP$) and that $_EP$ is equal to the molar refractivity for the red hydrogen line (λ 6562·8 Å). These assumptions were made on good grounds by Jensen (*loc. cit.*) for a series of platinous complexes, and our moments are thus comparable with his. Large moments, of the order of 10 D, were calculated with sufficient accuracy by using Jensen's approximate formula (*Acta Chem. Scand.*, 1949, **3**, 479). The measurements are recorded in Table 3. w is the weight fraction of solute, $\Delta\varepsilon = \varepsilon_s - \varepsilon_B$ where ε_s = dielectric constant of solution, ε_B = dielectric constant of benzene, and similarly for Δn and Δv. All measurements were made in benzene solution at 25°. The value $\varepsilon_B = 2\cdot2727$ was used to calibrate the capacity meter (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 683).

TABLE 3.

10^3w	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-10^2\Delta v$	$_TP$	$_EP$	$_OP$	μ
trans-(PPr$_3$)$_2$Pt$_2$(SEt)$_2$Cl$_2$ (IV)							
11·38	5·438	—	—	—	—	—	—
17·92	8·168	—	1·0	—	—	—	—
43·90	—	2·798	—	—	—	—	—
33·44	—	2·012	—	—	—	—	—
19·75	—	1·125	—	236·8	205·6	−10	∼0
			If $_AP = 15\%$ of $_EP$, then μ is exactly 0.				
cis-(PPr$_3$)$_2$Pt$_2$(SEt)$_2$Cl$_2$ (V)							
20·90	281·7	—	1·20	—	—	2150 *	—
9·477	124·8	—	—	—	—	2180 *	—
3·935	51·28	—	—	—	—	2190 *	10·3 *
66·695	—	4·148	—	—	—	—	—
48·68	—	3·013	—	2426	199	2187	10·3
(PPr$_3$)$_2$Pt$_2$Cl$_4$ (VII)							
34·83	25·30	—	—	—	—	—	—
21·54	15·60	—	—	—	—	—	—
42·52	31·50	—	—	—	—	—	—
37·58	27·62	—	—	—	—	—	—
66·89	—	3·430	—	—	—	—	—
52·80	—	2·659	—	—	—	—	—
6·42	—	—	0·41	—	—	—	—
10·65	—	—	0·68	246·3	163·6	50·0	1·6
(PPr$_3$)$_2$Pt$_2$(SEt)Cl$_3$ (VI)							
2·87	60·96	—	—	—	—	3460 *	13·0 *
0·8407	17·44	—	—	—	—	3410 *	
(PPr$_3$)$_2$Pd$_2$(SEt)$_2$Cl$_2$ (VIII)							
7·441	129·1	—	—	—	—	2300 *	10·7 *
3·435	60·4	—	—	—	—	2370 *	
(PPr$_3$)$_2$Pd$_2$(SEt)Cl$_3$ (IX)							
0·7175	7·662	—	—	—	—	1400 *	8·3 *
0·638	7·045	—	—	—	—	1450 *	

* Calculated by Jensen's approximate formula. The benzene used had a d^{25} 0·8734. To convert the weight fractions into molar concentrations for substitution in Jensen's formula we assumed that the solution had the same density as the benzene. The error thus introduced is 0·02 D in moments of 10 D measured under the above conditions. The above moments are accurate to ±0·1 D.

Reactions of the cis-*Dithio*- (V), trans-*Dithio*- (IV), *and Monothio*- (VI) *compounds with Amines.* —Products were identified by mixed m. p. with authentic specimens.

(*a*) (V) *with* p-*toluidine.* *p*-Toluidine (0·241 g., 2 mols.) was refluxed with (V) (1 g.) in benzene (25 c.c.) for 16 hr., and the solution was then taken to dryness under reduced pressure. The residue (0·92 g.) washed with ethanol was almost pure (V), m. p. 122·5—123·5°. *p*-Toluidine (0·12 g.) was recovered from the alcoholic washings.

(b) (V) *with* 2 : 2'-*dipyridyl*. Experiment (a) was repeated, but with dipyridyl (0·173 g., 1 mol.) instead of p-toluidine, with similar results.

(c) (IV) *with* p-*toluidine*. The experiment was carried out exactly as (a). Mixed (IV) and (V), m. p. 138—143° (0·90 g.), were recovered and separated in almost pure condition by fractional crystallisation from alcohol, giving (IV) (0·22 g.), m. p. 154°, and (V) (0·08 g.), m. p. 127°. p-Toluidine (0·13 g.) was recovered.

(d) (IV) *with* 2 : 2'-*dipyridyl*. The experiment was carried out as (b), except that the reaction time was 22 hr. Mixed (IV) and (V) (0·98 g.), m. p. 133—137°, were recovered and separated as in (c). Dipyridyl (0·1 g.) was recovered.

(e) (VI) *with* p-*toluidine*. p-Toluidine (0·487 g., 2 mols.) was added to (VI) (2 g.) in boiling benzene (135 c.c.), and the whole refluxed for 23 hr. and then evaporated to dryness. The residue was extracted with ether and crude *trans*-p-toluidinetri-n-propylphosphinedichloro-platinum (XI) (0·85 g.) obtained by evaporation of the ethereal extract. Thrice recrystallised from methanol it had m. p. 111°. The residue (1·11 g.) from the ethereal extraction was mainly (V). It was extracted with hot alcohol, leaving 0·04 g. of unchanged (VI), and on cooling the alcohol deposited a yellow solid, m. p. 125—135°. The latter was fractionally recrystallised, to yield pure specimens of (IV) and (V).

(f) (VI) *with* 2 : 2'-*dipyridyl*. 2 : 2'-Dipyridyl (0·177 g., 1 mol.) was boiled with (VI) (1 g.) in hot benzene (65 c.c.) for 34 hr. Fine insoluble red and yellow needles of 2 : 2'-dipyridyldi-chloroplatinum (XIII) separated during the reaction and were filtered off (Found : C, 28·7; H, 1·9. Calc. for $C_{10}H_8Cl_2Pt$: C, 28·4; H, 1·9%). The benzene solution worked up as (e) yielded a mixture of (IV) and (V) (0·4 g.), m. p. 125—135°, and *trans*-$(PPr^n_3)_2PtCl_2$ (XII) (0·49 g. crude). Thrice recrystallised from methanol the last had m. p. 85°.

(g) *Reversal of reaction* (e). The compound (IV) (0·25 g.) and *trans*-p-$C_7H_7 \cdot NH_2, PPr^n_3, PtCl_2$ (XI) (0·295 g., 2 mols.) were dissolved in ethanol (50 c.c.) at 35—40° and kept at room temperature for 3 days, during which a few crystals (0·03 g.) of (VI) had separated. The alcoholic solution was taken to dryness; extraction of the residue with a little benzene left a further 0·01 g. of (VI) undissolved. These fractions of (VI), once recrystallised from benzene, had m. p. 221—222°. From the alcoholic solution was recovered a mixture of (IV) and (V), m. p. 130—135°, and a small quantity of unchanged *trans*-p-$C_6H_4Me \cdot NH_2, PPr^n_3, PtCl_2$. An attempt to investigate this equilibrium spectrophotometrically with a Unicam S.P. 500 instrument showed that, in very dilute solution (1·14 × 10⁻⁵M) even with 100% excess of p-toluidine, it lies entirely on the side of free p-toluidine. The absorption spectrum of a mixture of (VI) (0·57 × 10⁻⁵M) with 100% excess of p-toluidine (1·14 × 10⁻⁵M) in ethanol was identical with that calculated from the spectrum of the components, and remained unchanged for 18 hr., showing that no reaction had occurred. Further work along these lines is proceeding; our preliminary results indicate, however, that the reaction between p-toluidine and the tetra-chloro-compound (VII) is a fairly rapidly established equilibrium lying entirely on the side of free p-toluidine at low concentrations (10⁻⁵M).

Isomerisation of (IV) *and* (V).—The compound (IV) (0·25 g.) was boiled under reflux for 15 hr. and then taken to dryness, leaving a mixture, m. p. 138—148°, of (IV) and (V) containing about 35% of (V) (estimated spectrophotometrically in a 1·11 × 10⁻⁵M-solution in alcohol). Under the same conditions (V) (0·245 g.) was recovered almost unchanged. It had m. p. 123·5—124·5°, mixed m. p. 124—124·5°, and after one recrystallisation melted at 125—126°. A trace of tri-n-propylphosphine caused rapid isomerisation of (IV) in benzene at room temperature.

Isomerisation of (VIII).—The dielectric constant of a solution of (VIII) (0·4264 g.) in benzene (56·88 g.) was measured at 25° after various times. The dielectric constant (ε) decreased, approaching a constant value in about 25 hr. The value at zero time, found by extrapolation, was used to determine the dipole moment of (VIII) (t = time in min. from making up of the solution) :

t	0	15	20	37	43	55	66	85	104
ε	(2·4018)	2·4003	2·3997	2·3983	2·3979	2·3971	2·3965	2·3955	2·3947
t	136	190	19 hr.	25 hr.					
ε	2·3935	2·3923	2·3886	2·3884					

This change in dielectric constant is attributed to isomerisation in solution, to yield the *trans*-isomer, and corresponds to about 10% isomerisation in 25 hr.

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