527. *The Sulphito-compounds of Palladium*(II).

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The sulphito- and sulphito-ammine complexes of palladium(II) have been examined. They show strong similarities to known thiosulphato- but little to sulphato-complexes. It is concluded that they probably all contain sulphur-to-metal bonds. It is tentatively suggested that the anions of the disulphitopalladates are polymeric. The marked reactivity with carbon monoxide shown by some of these compounds appears to depend on the presence of readily replaceable aquo-groups.

THE sulphito-complexes of palladium have received little attention and only two compounds, $Na_6[Pd(SO_3)_4],2H_2O$ and $(NH_3)_3[PdSO_3Cl_3]$, have been reported.[1,2] Since Werner's time it has been generally assumed that sulphur–metal bonds are involved in such compounds, which may thus be regarded as salts of metal-sulphonic acids. Although there is little reason to doubt this for mercury or for most of the platinum-metal sulphites, yet the constitution of such compounds as $Na_2Pt(SO_3)_2$, in which the sulphito-groups apparently each occupy two co-ordination positions, remains puzzling, particularly for those metals which show a strong tendency to form M–S bonds. Sidgwick [3] suggested that these compounds contain the group (I) and that even when the sulphito-groups each

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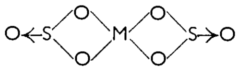
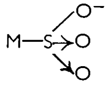
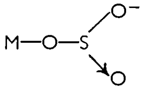
[1] Frerichs and Wohler, *Annalen*, 1872, **164**, 179.
[2] Rosenheim and Itzig, *Z. anorg. Chem.*, 1900, **23**, 28.
[3] Sidgwick, " Chemical Elements and their Compounds," Oxford, 1950, p. 910.

occupy only one position it is not possible to decide definitely between the formulæ (II) and (III).


(I)


(II)


(III)

This remains true, but the evidence to be adduced for sulphitopalladium(II) complexes, which show close affinities to the thiosulphato-complexes of palladium and platinum described by Riabtschikov [4] and but little to the few known sulphato-compounds, strongly favours the M–S view.

Sulphitotriaquopalladium(II) *and its Ammine Derivatives.*—The following series of compounds has been prepared (their molecular conductivities Λ in 0·001M-solution at 25° being shown):

	$[Pd(SO_3)(H_2O)_3]$,	$[Pd(SO_3)(H_2O)_2(NH_3)]$,	$[Pd(SO_3)(H_2O)(NH_3)_2]$, and	$[Pd(SO_3)(NH_3)_3]$
Λ	34	11	9	14

Tetramminepalladium(II) sulphite could not be isolated.

Sulphitotriaquopalladium(II) crystallises well but is thermally unstable and slowly decomposes at room temperature to palladium and sulphuric acid. The thermal stability in the series increases regularly with increasing ammine content, the triammine being stable in air at 200°. The stepwise replacement of aquo- by ammine-groups can be followed by titrating sulphitotriaquopalladium(II) with ammonia, both conductometrically (Fig. 1) and potentiometrically (Fig. 2). The parallel course (Fig. 1) of the curve for the addition of ammonia to water, with that for the addition of ammonia in excess of the triammine stage, shows that there is no tendency for the sulphito-group to be displaced to form tetramminepalladium(II) sulphite.

The existence of this series demonstrates that any tendency for a sulphito-group to assume a chelate arrangement must be feeble indeed, because to achieve this it would be necessary only to replace an aquo-group from each of the first three of the series, but water could not be removed without causing total decomposition. Moreover, since ammonia is unable to displace the sulphito-group, the single bond between this group and palladium is strong, in marked contrast to that between palladium and sulphato-groups in which oxygen-to-metal bonds must be assumed. Sulphatoaquodiamminepalladium(II) dissociated instantly on dissolution and hydrolysed rapidly. Its molecular conductivity in freshly prepared 0·001M-solution was about 200 mho, but sulphitoaquodiamminepalladium(II) has a molecular conductivity of 9 mho and its aqueous solutions may be boiled for hours without a trace of decomposition. It therefore seems reasonable to assume that the single link holding the sulphito-group to palladium is sulphur-to-metal in the above series.

The Disulphitopalladates.—The structure of the long-known series of compounds apparently having the general formula $M^{I}_{2}M^{II}(SO_3)_2$ has never been satisfactorily explained. Palladium also forms such complexes: *e.g.*, $K_2Pd(SO_3)_2$ and $Na_2Pd(SO_3)_2,H_2O$. These salts are slightly soluble in water but cannot be recrystallised from it. The conductivity of the solutions indicates dissociation into three ions, but the solutions are always slightly acidic at about pH 5·5. That this acidity is not caused by an impurity follows from potentiometric titration (Fig. 3), by use of a glass electrode, of palladous sulphite with sodium sulphite. A sharp end-point at about pH 5·5 was obtained when 1 molar equiv. of sodium sulphite had been added, corresponding to the disulphito-stage. There was also a less distinct end-point at the tri- but no trace of one at the tetra-sulphito-stage, although a solid tetrasulphitopalladate is known. Similar curves were obtained on using a palladium electrode.

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[4] Riabtschikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1938, **18**, 38; 1940, **27**, 690; 1943, **40**, 229; 1943, **40**, 169; *ibid.*, p. 209.

In solution, the disulphitopalladates behave as monobasic acids, $pK_a = 9$, and can be smoothly titrated potentiometrically with alkali (Fig. 4). This strongly suggests that in

FIG. 1. *Conductometric titration of* 0·2558 *g. of* $PdSO_3,3H_2O$ *in* 100 *ml. of solution with* 1·472N-*ammonia.*

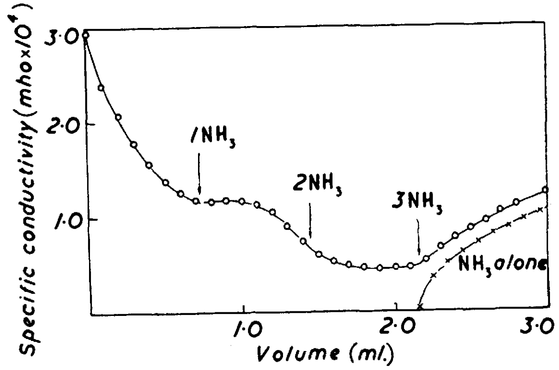


FIG. 2. *Potentiometric titration of* 0·3812 *g. of* $PdSO_3,3H_2O$ *in* 100 *ml. of solution with* 1·472N-*ammonia.*

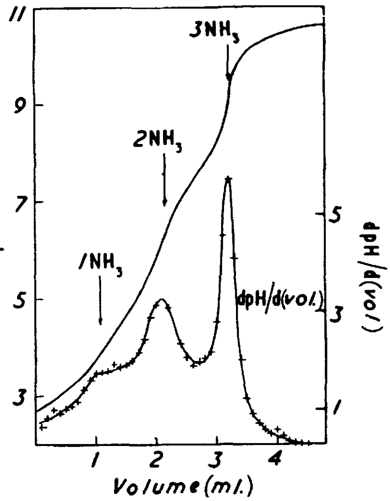


FIG. 3. *Potentiometric titration of* 0·246 *g. of* $PdSO_3,3H_2O$ *in* 100 *ml. of solution with* 0·975M-*sodium sulphite.*

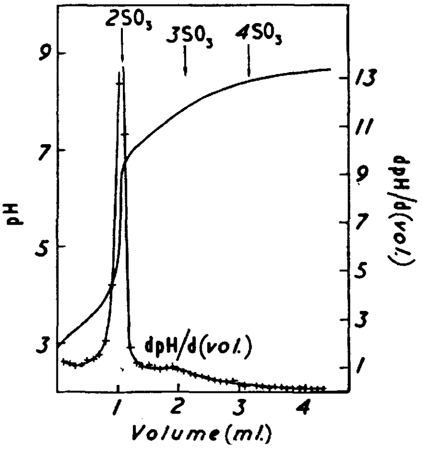
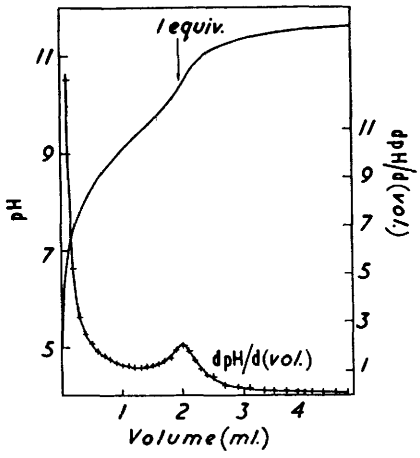


FIG. 4. *Potentiometric titration of* 0·3402 *g. of* $Na_2Pd(SO_3)_2,2H_2O$ *in* 100 *ml. of solution with* 0·5N-NaOH.



solution the anion contains at least one aquo-group and possibly two, dissociating as follows:

$$[2H_2O,Pd(SO_3)_2]^{2-} = [(OH)H_2O,Pd(SO_3)_2]^{3-} + H^+$$

That no inflexion corresponding to a second dissociation was found is not surprising because it would correspond to the fourth dissociation of the acid $H_4[(OH)_2Pd(SO_3)_2]$.

Since anions containing aquo-groups are rare, this again suggests that, if chelate sulphito-groups are present in the solid, one of the bonds must be extremely feeble. It seems that the ion $[Pd(SO_3)_2]^{2-}$ may not exist as such in solution and there is no proof that it does in the solid. It is tentatively suggested that, in the solid, the anions are polymeric, each sulphito-group forming a bridge between two palladium atoms, one being attached through sulphur and the other by oxygen. Lebedinskii and Shenderetskaya,[5] in their work on rhodium sulphito-complexes, commented on the enormous disparity in the strengths of the two bonds where chelate groups were assumed. This led them to postulate one link through sulphur and the other through oxygen. This, however, requires an improbable 3-ring arrangement with 60° valency angles for both sulphur and oxygen, which had been earlier rejected by Sidgwick.[3]

The Disulphitodiamminepalladates.—The disulphitodiamminepalladates(II) were found to exhibit *cis–trans*-isomerism in the anion. Tetramminepalladium dichloride reacts with excess of sodium sulphite, probably giving disodium *trans*-disulphitodiamminepalladate, $Na_2[Pd(SO_3)_2(NH_3)_2],6H_2O$, $\Lambda_\infty = 220$ mho. This, in cold solution, with one molar equiv. of tetramminepalladium dichloride immediately precipitates (presumably) *trans*-$[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2],1\frac{1}{2}H_2O$ as fine needles, $\Lambda_\infty = 285$ mho. This compound precipitates Vauquelin's salt from sodium chloropalladate(II) solution, showing the presence of the tetramminepalladium cation.

Apart from water of crystallisation, *trans*-$[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2]$ has the same empirical composition as the non-electrolyte, sulphitotriamminepalladium and is rapidly transformed into it in hot solutions. The change can be followed conductometrically at 25°. The molecular conductivity could be obtained only by following the decrease in conductivity and extrapolation to zero time. This change would be helped by the mutual *trans*-effect of the sulphito-groups, which, by making them labile, facilitates their attack on the tetramminepalladium cation:

$$[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2] = 2[PdSO_3(NH_3)_3]$$

Dipotassium disulphitopalladate(II) reacts with ammonia to give (probably) *cis*-disulphitodiamminepalladate(II), $K_2[Pd(SO_3)_2(NH_3)_2]$. This again with tetramminepalladium dichloride gives a salt $[Pd(NH_3)_4][Pd(SO)_2(NH_3)_2]$ as pale yellow granular anhydrous crystals, $\Lambda_\infty = 280$ mho. The *X*-ray powder diagram is quite different from that of the *trans*-salt. It also changes to $[PdSO_3(NH_3)_3]$ in solution but much more slowly, since the *trans*-effect of the sulphito-groups would tend to make NH_3 groups labile. In confirmation of this, the pH values of 0·005M-solutions of dipotassium *cis*-disulphitodiamminepalladate and disodium *trans*-disulphitodiamminepalladate were 8·7 and 8·0, respectively.

It can now be seen that the sulphito-chemistry of palladium is largely co-extensive with that of platinum, although crystalline sulphitotriaquoplatinum(II) and the corresponding monammine have not yet been reported. Sulphito- and thiosulphato-complexes of both palladium and platinum, having the following general formulæ are known:

$$M^{I}_6[M^{II}X],\ M^{II}_2[M^{II}X_2],\ M^{I}_2[M^{II}X_2(NH_3)_2],\ [(H_2O)M^{II}X(NH_3)_2] \text{ and } [M^{II}X(NH_3)_3]$$

where M^I is usually K, Na, or NH_4, M^{II} is Pd or Pt, and X is SO_3 or S_2O_3. The close similarity of the sulphito- and thiosulphato-complexes is striking. On the other hand, only a few sulphato- and no dithionato-compounds have been reported. Diammineplatinous sulphate and triammineplatinum sulphate were re-examined by King,[6] who showed the sulphato-groups to be loosely bound and completely replaced by aquo-groups in solution. As already mentioned, this is also true of diamminepalladous sulphate. With these ligands derived from sulphur oxyacids, it seems that strong links to the metal atom are only formed when there is a possibility of a sulphur-to-metal bond. Whatever may be true for sulphito-complexes of other elements, with palladium there is nothing inconsistent (notwithstanding alternative possibilities for the disulphito-palladates) with the view that a sulphito-group is never attached to the same palladium atom by more than one bond and, except where bridging between two palladium atoms may occur, this bond is sulphur-to-metal.

Reaction with Carbon Monoxide.—The original purpose of this investigation was to find an explanation for the exceptionally rapid reaction of potassium disulphitopalladate

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[5] Lebedinskii and Shenderetskaya, *J. Inorg. Chem. U.S.S.R.*, 1957, **2**, 1768.

[6] King, *J.*, 1938, 1338; 1948, 1912.

solutions with carbon monoxide. The sulphito-complex, absorbed on silica gel, had been used successfully as a detector for carbon monoxide. It was originally tried because, as pointed out by Welch,[7] sulphur-to-metal bonds are in general very susceptible to carbon monoxide. It now appears that, apart from any specific effect of the S–M link a major factor is the ability of sulphito-groups to stabilise weakly bound, and therefore readily replaceable, aquo-groups.

A comparison of the rates of reaction with carbon monoxide of solutions of the various compounds described showed that aquo-groups are most probably concerned. To complete the series, potassium disulphitoethylenediaminepalladate was included, because, with this strongly bound ligand, exchange with aquo-groups should not occur, as appears to happen with NH_3 groups.

The following order of decreasing reactivity towards carbon monoxide was found:

$$[PdSO_3(H_2O)_3] > [PdSO_3(NH_3)(H_2O)_2] = Na_2Pd(SO_3)_2 = K_2Pd(SO_3)_2 > [PdSO_3(H_2O)(NH_3)_2] >$$
$$\textit{trans-}\ [Pd(SO_3)_2(NH_3)_2]^{2-} = \textit{cis-}[Pd(SO_3)_2(NH_3)_2]^{2-} > [PdSO_3(NH_3)_3] =$$
$$[Pd(NH_3)_4]Cl_2 > [PdSO_3(NH_3)_3]\ \text{plus excess}\ NH_3 > Na_2[Pd\ (en)\ (SO_3)_2].$$

The range of reactivity was so wide that it was easy to place these in order by visual inspection alone. The first nine showed some reduction to metal as soon as the gas was passed, reduction of the first being extremely rapid. There was a delay of several minutes with the triammine in the presence of excess of ammonia and of ½ hr. with the ethylenediamine complex before any change could be seen.

The position in the series of the disulphitopalladates supports the view that in solution the anion is $[Pd(SO_3)_2(H_2O)_2]^{2-}$, while the effect of excess of NH_3 in suppressing dissociation of the *trans*-NH_3 in $[PdSO_3(NH_3)_3]$ is of interest. It was not, however, possible to distinguish between *cis*- and *trans*-$[Pd(SO_3)_2(NH_3)_2]^{2-}$, although one would have expected the *cis*-form to be the more reactive. In general, the results confirm that with those compounds that show extreme reactivity with carbon monoxide, the first step in the reaction is the replacement of an aquo-group to form a transient sulphito-carbonyl complex.

EXPERIMENTAL

(For molar conductivites Λ of the first four *compounds* in 0·001M-solution at 25°, see p. 2621.)

Sulphitotriaquopalladium(II).—*Method* 1. Palladous chloride (5 g.) was ground with water (5 ml.), silver sulphite (9 g.) being slowly added. More water (35 ml.) was stirred in, and the whole left overnight. The solids were filtered off and washed with a little cold water, and the combined filtrates were evaporated under reduced pressure over silica gel.

Method 2. Palladous hydroxide, precipitated from a solution of palladous chloride (2 g.) by a slight excess of sodium hydroxide, was washed by decantation and suspended in acetone (100 ml.). The mixture was saturated with sulphur dioxide, with cooling, left overnight, and then evaporated to dryness by sucking off the solvent at or below room temperature. If the product was tarry, the addition of more acetone and sulphur dioxide and re-evaporation gave a dry residue, which was broken up and stirred until the smell of sulphur dioxide had gone. The solid was extracted with cold water and crystallised as in method 1. Yields of thick orange needles were 70% by both methods but the first method was less tedious {Found: Pd, 44·3; S, 13·2. $[PdSO_3(H_2O_3)]$ requires Pd, 44·3; S, 13·3%}. Freezing-point depression in water gave molecular weights of 198 in 0·0163M- and 208 in 0·052M-solution (Calc.: 240·8).

Sulphitodiaquoamminepalladium(II).—Sulphitotriaquopalladium(II) (2 g.) was dissolved in cold water (15 ml.), and 4·5N-ammonia (1·75 ml., 0·95 equiv.) added. Golden-yellow needles (1·7 g.) separated and were recrystallised from hot water {Found: Pd, 44·5; NH_3, 6·8. $[PdSO_3(NH_3)(H_2O)_2]$ requires Pd, 44·5; NH_3, 7·1%}. Excess of ammonia (12%) raised the ammonia content to 7·4%. This compound was too insoluble to give a satisfactory freezing-point depression; the best result indicated a molecular weight of 190 (Calc.: 239·8).

Sulphitoaquodiamminepalladium(II).—*Method* 1. Dichlorodiamminepalladium(II) (4 g.) and silver sulphite (6 g.) were ground together in water (10 ml.) to a smooth paste. Water (60 ml.) was added, and the whole stirred for 20 min. on a boiling-water bath and filtered hot. The

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[7] Welch, *Ann. Reports*, 1941, **38**, 76.

residue was extracted twice with hot water (20 ml.) and the combined filtrates were evaporated to half bulk and cooled. *Sulphitoaquodiamminepalladium*(II) separated as yellow crystals (3·6 g.) {Found: Pd, 44·9; NH_3, 14·3. $[PdSO_3(NH_3)_2(H_2O)]$ requires Pd, 44·7; NH_3, 14·3%}.

Method 2. Sulphitotriaquopalladium(II) (1·12 g.) was dissolved in water (10 ml.), and 2·31N-ammonia (4 ml.) added. The mixture was heated with more water until all dissolved, filtered hot, and allowed to cool (Found: NH_3, 14·4%).

Method 3. Sulphitotriamminepalladium(II) (2·9 g.) in water (200 ml.) was steam-distilled until all had dissolved and the volume was about 150 ml. This took several hours. The solution was filtered hot and allowed to cool. The product (1·2 g.) was slightly paler than that from the other methods (Found: NH_3, 14·5%). The diammine was stable at 100° but decomposed at 150°. It dissolved in dilute sulphuric acid to give yellow solutions becoming orange when heated, without loss of sulphur dioxide, but in hydrochloric acid sulphur dioxide was evolved on heating, to give $[PdCl_2(NH_3)_2]$.

Sulphitotriamminepalladium(II).—*Method* 1. Sulphitotriaquopalladium(II) (1 g.) was dissolved in water, and ammonia added until the yellow colour was discharged. The white precipitate was dissolved in boiling water (200 ml.) containing excess of ammonia, and the solution allowed to cool and crystallise {Found: Pd, 44·7; NH_3, 21·3. $[PdSO_3(NH_3)_3]$ requires Pd, 44·9; NH_3, 21·5%}.

Method 2. Dichlorodiamminepalladium(II) (2 g.) was dissolved in water (10 ml.) by adding ammonia in slight excess. To the solution of tetramminepalladium dichloride thus obtained sodium sulphite heptahydrate (2·5 g.) was added, and the mixture warmed. The *triammine* separated as a white powder (2 g.) and was recrystallised from hot water (400 ml.) to which ammonia (*d* 0·880; 20 ml.) was added to give ivory-white, granular crystals (1·3 g.) (Found: Pd, 44·8; NH_3, 21·4%). The dry solid was stable up to 200°. The pH of a 0·001M-solution at 25° was 8·9. The rate of loss of ammonia from a boiling solution of the triammine (0·1953 g. in 200 ml.) was measured by titrating the distillate with hydrochloric acid (0·1003N). Loss of one NH_3 from the triammine should have required 8·19 ml. of acid. In Fig. 5 the plot of log $(8{\cdot}19 - x)$ against time, where x is the volume of acid consumed at a given time, is a straight line for most of its course, showing that the rate of loss of ammonia is proportional to the remaining triammine.

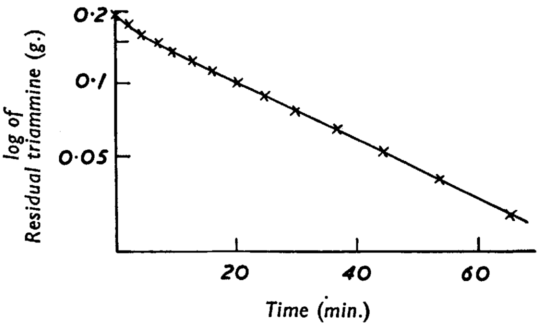

FIG. 5. *Rate of loss of ammonia from boiling solution of the triammine*: log (*residual triammine*) *against time.*

Sodium Disulphitopalladate(II).—Sulphitotriaquopalladium(II) (1 g.) in water (10 ml.) and sodium sulphite heptahydrate (1 g.) in water (5 ml.) were mixed. Addition of acetone precipitated an oil which solidified when stirred. The yellow powder (1·5 g.), dried *in vacuo* over silica gel, lost 6·6% when heated to constant weight at 100°, and was then analysed [Found: Pd, 32·3; Na, 13·6. $Na_2Pd(SO_3)_2,H_2O$ requires Pd, 32·25; Na, 13·9%]. Λ at 25° in 0·001M-solution was 191 mho, the pH value being 5·66.

Potassium Disulphitopalladate(II).—*Method* 1. Palladous chloride (2 g.) and potassium pyrosulphite (5 g.) were stirred together in water (20 ml.) until dissolved. The filtered solution was heated on a water-bath until no more sulphur dioxide was evolved, and the yellow precipitate (3·5 g.) washed with water and acetone and dried *in vacuo* [Found: K, 22·6; Pd, 30·5; S, 18·1. $K_2Pd(SO_3)_2$ requires K, 22·67; Pd, 30·9; S, 18·6%].

Method 2. Sulphitotriaquopalladium(II) (2 g.), dissolved in water (20 ml.), was mixed with potassium sulphite (1·5 g.), dissolved in a little water, to give a yellow precipitate (Found: K, 22·8; Pd, 30·5%). Λ at 25° in 0·001M-solution was 240 mho. In the preparation by method 1, an acid impurity was present which could not be removed by washing.

trans-*Sodium Disulphitodiamminepalladate*(II).—Dichlorodiamminepalladium(II) (2 g.) was converted into $[Pd(NH_3)_4]Cl_2$ in water (20 ml.) by adding ammonia. Sodium sulphite in excess (>5 g.), dissolved in water (10 ml.), was added. Any initial precipitate was dissolved by warming, and the whole allowed to crystallise. trans-*Sodium disulphitodiamminepalladate*(II) separated as large, pale yellow tablets {Found: Na, 10·2; NH_3, 7·4; Pd, 23·4; H_2O, 23·7. $Na_2[Pd(SO_3)_2(NH_3)_2],6H_2O$ requires Na, 10·1; NH_3, 7·5; Pd, 23·4; H_2O, 23·75%}. Λ at 25° 0·001M-solution was 199 mho, and Λ_∞ was 220 mho.

trans-*Tetramminepalladium Disulphitodiamminepalladate*(II).—*Method* 1. Dichlorodiamminepalladium(II) (5 g.) was converted into $[Pd(NH_3)_4]Cl_2$ in water (25 ml.) by adding ammonia. Finely ground disodium sulphite heptahydrate (6 g.) was stirred into the cold solution. Pale yellow needles (3·1 g.) separated, which were filtered off, washed with a little cold water and acetone, and dried *in vacuo* {Found: Pd, 42·5; NH_3, 20·4. $[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2],1{\cdot}5H_2O$ requires Pd, 42·45; NH_3, 20·3%}.

Method 2. Dichlorodiamminepalladium(II) (1 g.) was dissolved in water (5 ml.) by adding ammonia and mixed with a solution of $Na_2[Pd(SO_2)_2(NH_3)_2],6H_2O$ (2·2 g. in 25 ml.). Similar crystals separated (Found: NH_3, 19·9; H_2O, 5·2. $[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2],1{\cdot}5H_2O$ requires NH_3, 20·3; H_2O, 5·4%). Since this salt changes in solution to a non-electrolyte, the triammine, in order to find the molecular conductivity it was necessary to follow the change in conductivity and extrapolate to zero time. The plot of Λ against (concentration) $^{0{\cdot}5}$ gave $\Lambda_\infty = 285$, and 250 mho in 0·001M-solution.

cis-*Potassium Disulphitodiamminepalladate*(II).—Potassium disulphitopalladate(II) (1·9 g.) was suspended in water (5 ml.) and dissolved by adding 1·54N-ammonia (7·2 ml.). The filtered solution was precipitated with acetone. cis-*Potassium disulphitodiamminepalladate*(II) (2 g.) separated as nearly colourless needles that lost water of crystallisation readily {Found: K, 18·8; NH_3, 7·95; Pd, 24·9; H_2O, 9·5. $K_2[Pd(SO_3)_2(NH_3)_2],2H_2O$ requires K, 18·8; NH_3, 8·2; Pd, 24·7; H_2O, 8·7%}. Λ at 25° was 260 mho in 0·001M-solution, and Λ_∞ was 290 mho.

cis-*Tetramminepalladium Disulphitodiamminepalladate*(II).—Dichlorodiamminepalladium(II) (1 g.) was converted into the tetrammine in water (5 ml.) by adding a slight excess of ammonia and mixed with *cis*-$K_2[Pd(SO_3)_2(NH_3)_2]$ (1·8 g.) dissolved in water (5 ml.) at 0°. cis-*Tetramminepalladium disulphitodiamminepalladate*(II) separated as short, pale yellow prisms (2 g.) {Found: Pd, 44·6; NH_3, 21·2. $[Pd(NH_3)_4][Pd(SO_3)_2(NH_3)_2]$ requires Pd, 44·9; NH_3, 21·5%}. At 25° the change to the triammine was slow and was ignored in determining the conductivity: $\Lambda_{1000} = 206$, $\Lambda_\infty = 280$ mho. The change in molecular conductivity with concentration was greater with the *cis*- than with the *trans*-salts. Possibly the overall dipole moment of the *cis*-anions favours association.

Sodium Disulphitoethylenediaminepalladate(II).—Ethylenediamine rapidly displaces ammonia from sulphitodiamminepalladates. $Na_2[Pd(SO_3)_2(NH_3)_2],6H_2O$ (2 g.) and ethylenediamine (0·27 g., 1 : 1) were dissolved in water (3·5 ml.) by warming. On cooling, yellow crystals of *sodium disulphitoethylenediaminepalladate* separated {Found: Na, 10·5; Pd, 24·0; H_2O, 16·15. $Na_2\,[Pd(SO_3)_2(en)],4H_2O$ requires Na, 10·3; Pd, 24·0; H_2O, 16·2%}.

Sulphatoaquodiamminepalladium(II).—Dichlorodiamminepalladium(II) (6 g.) and silver sulphite (9 g.) were ground together in water. The precipitated silver chloride was filtered off, and acetone added to precipitate sulphatoaquodiamminepalladium(II) (5 g.) as a yellow powder {Found: NH_3, 13·3; Pd, 42·4; SO_4, 36·2. Calc. for $[PdSO_4(NH_3)_2(H_2O)]$: NH_3, 13·6; Pd, 41·9; SO_4, 37·7%}. It gave clear yellow solutions in cold water that slowly precipitated palladium hydroxide. A freshly made 0·001M-solution had Λ = 196 mho which increased to 200 mho after 24 hr. The pH remained unchanged during this period at 4·43.

Electrochemical Measurements.—These call for little comment except that most were made in an atmosphere of nitrogen. Platinised electrodes could not be used for conductance determinations because the readings drifted, there being some local action. Bright platinum electrodes with a current of frequency 1 kc./sec. gave no trouble.

X-*Ray Powder Diffraction Photographs*.—These, taken for most of the compounds, mainly to establish identity or otherwise of compounds prepared by different procedures, were taken in a 19 cm.-diam. camera with Cu-K_α radiation.

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