

261. *The Nature of the Co-ordinate Link. Part X.\* The Effect of Ligands on the Redox Potentials of Non-ionic Platinous Complexes and the Evidence it gives for the Effect of Dative  $\pi$ -Bonding on the Total Transfer of Charge in Co-ordinate Bonds.*

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The redox potentials of some systems of the type  $L_2PtCl_4-L_2PtCl_2$  have been measured in a mixed aqueous solvent (Table I). When  $L = PPr^a_3$ , the redox potential of the *cis*-isomer system is higher than that of its *trans*-analogue. Our results indicate that both inductive withholding and mesomeric withdrawal of electrons from the metal by the ligand stabilises the lower-valent state of the metal against oxidation. This work, in conjunction with earlier evidence, indicates that with *metals in their usual valency states* and with ligands such as the alkyls of the elements of Groups V and VI, the total electron transfer between ligand and metal is not greatly affected by dative  $\pi$ -bonding; but that the mesomeric release of electrons from the metal to the ligand in dative  $\pi$ -bonding induces an almost compensating inductive release of electrons from the ligand to the metal in the  $\sigma$ -bond. In this way the metal-to-ligand bond is significantly strengthened by double bonding, but its electrical asymmetry is only slightly affected, so that the bond retains the high dipole moment usually associated with co-ordinate bonds.

DURING a study of olefin complexes<sup>1</sup> of platinous chloride it was suggested that the difference between the redox potentials of corresponding *cis*- and *trans*-couples of the type  $L_2PtCl_4-L_2PtCl_2$  in a series of compounds having different uncharged ligands, L, would give some measure of the relative double-bonding tendencies of the uncharged ligands. This conclusion was based on the consideration that in a series of simple analogous redox reactions such as (1) the redox components are uncharged and entropy effects will be roughly constant. Therefore the only important factor which would change in passing

\* Part IX, *J.*, 1954, 4403.

<sup>1</sup> Chatt and Duncanson, *J.*, 1953, 2939.

from one couple,  $L_2PtCl_4-L_2PtCl_2$ , to another,  $L'_2PtCl_4-L'_2PtCl_2$ , would be the electron affinity of the metal atom, as it is adjusted by the electron affinities of the ligands.



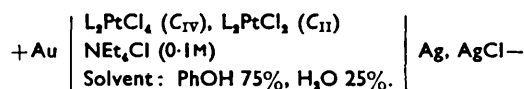
If the ligands tend to withhold or withdraw electrons from the metal atom, it will accept electrons more readily, *i.e.*, it will be more easily reduced, and the lower-valent state will become stabilised against oxidation. Withholding of electrons can occur through poor donation of electrons from ligand to metal in the  $\sigma$ -bond; withdrawal of electrons can occur from the  $d$ -orbitals of the metal atom in the formation of a dative  $\pi$ -bond.<sup>2</sup> Thus the electron-withholding or -withdrawal may be inductive and mesomeric in character.<sup>3,4</sup> When we consider two corresponding redox systems of *cis*- and *trans*-configurations in which all the ligands are the same, the withholding due to the inductive effect, since it is electrostatic in character, should be nearly equal in both systems. On the other hand, the mesomeric release of electrons from the metal to the ligands will depend on the configuration of the complex. When there are ligands which have strong double-bonding properties in *trans*-positions to each other they compete for electrons from the same  $d$ -orbitals. Mesomeric withdrawal will then be less than when they are in *cis*-positions where they can withdraw electrons from different  $d$ -orbitals.<sup>5</sup> Thus the *cis*- should have a greater resistance to oxidation than the *trans*-complex, *i.e.*, the *cis*-redox couple should have the higher potential. Since mesomeric electron withdrawal is the same phenomenon as dative  $\pi$ -bonding in these complexes, the greater the difference between the dative  $\pi$ -bonding tendencies of the ligands, L, and the chloride ion, the greater the difference in redox potentials between the *cis*- and the *trans*-couple. Unfortunately we have not yet been able to obtain suitable corresponding *cis*- and *trans*-couples to use the method to determine the relative double-bonding tendencies of uncharged ligands containing different donor atoms, but the difference between the potentials of the one *cis*- and *trans*-pair of couples which we have been able to examine accords with the above reasoning.

The difficulties in using the method are caused by the following factors.

(1) The platinum complexes are non-ionic and insoluble or very sparingly soluble at 25° in water and in most aqueous organic solvents. The platinic complexes are in general the less soluble and it was very difficult to find a solvent which would dissolve both them and the neutral salt necessary to provide an ionic medium. Aqueous methanol, ethanol, acetone, dioxan, acetic acid, and tetrahydrofurfuryl alcohol all proved useless, and finally aqueous phenol containing 25% of water was used. Tetraethylammonium chloride (0.1M) was used as the neutral salt, because inorganic salts caused the solvent to separate into two phases.

(2) It must be possible to isolate all four complexes of each set. The redox electrode requires 1—5 days to reach equilibrium with the solutions, presumably because the redox components are covalent and uncharged. The complexes must remain unchanged in solution for that length of time. Many platinic complexes of the type *cis*-[ $L_2PtCl_4$ ] isomerise spontaneously in solution, and from our experience of them only the amine and the tertiary phosphine complexes are likely to remain essentially unchanged sufficiently long. A number of amine complexes were tried, but all proved too insoluble for measurements except that of 4-*n*-pentylpyridine (pepy), and here we did not obtain the *cis*-platinous isomer.

The cell used was :



<sup>2</sup> Chatt, *Nature*, 1950, **165**, 637.

<sup>3</sup> Chatt, Duncanson, and Venanzi, *J.*, 1955, **4456**; *Chem. and Ind.*, 1955, 749.

<sup>4</sup> *Idem*, *J.*, 1955, **4461**.

<sup>5</sup> See Chatt and Wilkins, *J.*, 1952, **4300**, and previous references quoted therein.

The potentials measured are redox potentials of the complex compound system because the e.m.f.,  $E$ , of the cell obeyed Nernst's law,  $E = E_0 + 29.58 \log C_{IV}/C_{II}$  (at 25°;  $E$  in mv), when the concentrations of the platinum complexes,  $C_{IV}$  and  $C_{II}$ , were changed. Here  $E_0$  includes the constant potential of the Ag,AgCl electrode. The cell was sensitive to light and so all measurements were made in the dark. The values of  $E_0$  for the complexes examined are listed in Table 1.

TABLE 1. Difference ( $\Delta E_0$ ) between the redox potentials (mv) of the systems  $L_2PtCl_4$ - $L_2PtCl_2$ .

L	(a) PPr <sup>n</sup> , <i>cis</i>	(b) PPr <sup>n</sup> , <i>trans</i>	(c) Pr <sup>n</sup> <sub>2</sub> S <i>trans</i>	(d) pepy <i>trans</i>
Configuration .....				
$E_0$ .....	367	349	441	475
$\Delta E_0$ .....		18	92	34

The values of  $E_0$  have no absolute significance, but the differences should be almost equal to the differences between the standard redox potentials of the couples concerned: to be exactly equal, the ratio of the activity coefficients of the platinic to the platinous complexes should be the same in all systems examined. This must be almost so since measurements were made in practically the same medium throughout, and also because the redox components are themselves uncharged molecules whose activity coefficients should be very close to unity, whatever the medium. Nevertheless, the total e.m.f. of the cell should be very dependent on the activity of the chloride ion. This activity may be changed by altering either the solvent or the neutral salt used to provide the chloride ion. Thus the couple (b) in Table 1 had  $E_0 = 400$  mv when tetramethyl- was used instead of tetraethyl-ammonium chloride (0.1M).

The sign convention used in this paper is such that the more positive is the redox potential, the more resistant to oxidation is the Pt(II) complex. From the  $E_0$  values which we have measured it appears that Pt(II) is stabilised by electron withdrawal into the ligand, whether the withdrawal is mesomeric in the dative  $\pi$ -bond, or inductive in the  $\sigma$ -bond. In general, the two effects should operate together and our observations give distinct evidence of both of them.

The difference (18 mv) between the redox potentials of *cis*-(Pr<sup>n</sup><sub>3</sub>P)<sub>2</sub>PtCl<sub>4</sub>-*cis*-(Pr<sup>n</sup><sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> and the corresponding *trans*-couple (a and b in Table 1) must be caused by the difference in mesomeric electron withdrawal as explained above (p. 1380). The differences between the redox potentials of the *trans*-systems (b, c, and d in Table 1) must be caused by inductive withholding of electrons in the  $\sigma$ -ligand-to-metal bond. This is evident because mesomeric electron withdrawal would increase in the order of donor atoms N < S < P, so raising the redox potentials in that order.<sup>4</sup> Actually the potentials increase in the reverse order, which is the order of increasing electronegativities of the donor atoms.

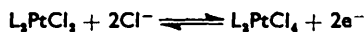
These very few experiments indicate a simple general scheme for the influence of ligands on the redox potentials of covalent or inner-orbital complexes. Electron-withholding or -withdrawal by the ligand, whether inductive or mesomeric, increases the electron affinity of the metal, and so stabilises the lower relative to the higher oxidation state. Ewens<sup>6</sup> has already observed the same correlation between the redox potentials of substituted trisphenanthroline-ferrous complexes and the electron-attracting or -releasing properties of the substituents. The more electron-withdrawing the substituent the higher the redox potential.

Nevertheless, the scheme appears to be at variance with the common observation that the most electronegative co-ordinating atoms fluorine and oxygen bring out the highest valency states of elements with which they are combined. This apparent anomaly arises

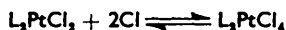
<sup>6</sup> Ewens, *Nature*, 1945, 155, 398; see Brandt, Dwyer, and Gyarfás, *Chem. Rev.*, 1954, 54, 1000, for further references.

because in this work we are comparing the relative oxidisabilities of our complexes using the same oxidant in every case, and the only variant is the ligand, L.

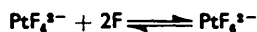
The reactions may each be written :



or



In saying that the higher-valent states of metals are stabilised, *e.g.*, by fluorine, the comparison is actually between such reactions as



and



In these examples the oxidants are different as well as the ligands attached to the platinum atom. Thus the comparison is not between the relative oxidisability of  $PtF_6^{3-}$  and  $PtCl_6^{3-}$  but between some combination of this and the relative oxidising powers of fluorine and chlorine. In other words, fluorine stabilises metals in high-valent states because the element is a good oxidising agent (*i.e.*, is a good electron-acceptor), and it does not necessarily follow that fluoro-complexes with metals in low-valent states are easily oxidised (*i.e.*, that they give up electrons readily).

In this connection it may be worth noting that the redox potentials of the systems  $[Fe(CN)_5NH_3]^{3-} - [Fe(CN)_5NH_3]^{2-}$  and  $[Fe(CN)_5H_2O]^{2-} - [Fe(CN)_5H_2O]^{3-}$  have been estimated, although not with certainty, under comparable conditions.<sup>7</sup> The redox potential appears to be raised from 374 to 491 mv (*i.e.*, the lower-valent state is stabilised) when nitrogen as donor atom is replaced by the more electronegative oxygen atom.

In comparing a series of complexes of a particular metal with a number of donor molecules, covering a great range in electronegativity, it must not be overlooked that sometimes a sudden discontinuity in properties occurs because of a complete change in hybridisation of the metal atom. In this paper we are considering only the more subtle changes produced by the ligands in inner-orbital complexes and not complete changes of that type.

It was shown previously<sup>4</sup> that the uncharged organic ligands may be placed in a series—amines, sulphides, selenides, tellurides, arsines, phosphines, stibines, phosphites, and olefins—such that certain properties of their  $PtCl_2$  complexes change regularly. From the amines to the arsines the properties were determined largely by the electronegativities of the donor atoms; beyond the arsines the mesomeric effects of the ligands became significant, increasing to ethylene. It appears that the redox potentials of the couples *trans*- $L_2PtCl_4$ -*trans*- $L_2PtCl_2$  also fit that general pattern. The potentials which we have measured for amine, sulphide, and phosphine complexes are determined mainly by the electronegativities of the donor atom, but we know that  $[C_2H_4PtCl_3]^-$ , in which there is strong dative  $\pi$ -bonding between the metal and olefin, is virtually incapable of being oxidised. On the other hand,  $[NH_3PtCl_3]^-$  can be oxidised readily.<sup>1,8</sup> It thus seems that if we could obtain the measurements to permit us to draw a graph of the standard redox potentials ( $E^\circ$ ) of the systems *trans*- $L_2PtCl_4$ -*trans*- $L_2PtCl_2$  against donor atoms in the sequence of ligands, L, corresponding to that on page 4465 of ref. 4 it would appear somewhat as in the Figure.

*The Effect of Dative  $\pi$ -Bonding on the Polarity of Co-ordinate Bonds.*—Since the redox potentials give us some direct relative measure of the electron affinities of the platinum atoms in the complexes, these results, although few, are of considerable significance for the indication they give of the relative importance of electron-donation in the  $\sigma$ -bond and back-donation in the  $\pi$ -bond. We now have definite evidence, mainly from work previously reported, that dative  $\pi$ -bonding is of very minor importance so far as electron transfer in the ligand-metal bond is concerned, in the case of all the common donor atoms N, S, Se, Te, As, P, and Sb in their alkyl derivatives.

<sup>7</sup> Davidson, *J. Amer. Chem. Soc.*, 1928, **50**, 2622.

<sup>8</sup> Hel'man and Ryabchikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 462.

The evidence is: (1) The close correlation of the N-H stretching frequencies of the complexes of the type *trans*-[L,amine PtCl<sub>2</sub>] with the electronegativities of the donor atoms in L, and the smooth relation between the frequency and intensity of the absorption bands, where L is an alkyl derivative of the above donor atoms.<sup>4</sup>

(2) The high dipole moments (~11 D) of such complexes as *cis*-[(MR<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>], where M = P, As, or Sb.<sup>5,9</sup> Since the Pt-Cl bond moment is probably of the order 2 D,<sup>10</sup> the PtCl<sub>2</sub> part of the molecule will contribute about 3 D to the total moment, and so the M-Pt bond moment must be of the order 5.5 D. When we compare this with the moment<sup>11</sup> (7.03 D) of the molecule PMe<sub>3</sub>.BCl<sub>3</sub>, where dative π-bonding cannot occur and the BCl<sub>3</sub> part of the molecule will contribute about 2 D to the moment, it is evident that the M-Pt bond, so far as gross electron transfer is concerned, is essentially a single co-ordinate bond.<sup>5</sup>

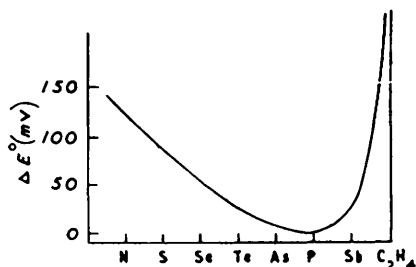
(3) The redox potentials, which indicate that the electron density on the platinum atom is lower in the amine and sulphide complexes than in the phosphine and arsine complexes, which we consider to contain the stronger π-type bonds.

It is now fairly certain that in the platinous complexes of the alkyls of the atoms, N, P, As, Sb, S, Se, and Te, the electron transfer in the co-ordinate bond, and its variation in a series of analogous compounds containing one or other of the above donor atoms, is largely inductive.

It seems reasonable to take the capacity of metal salts to form thermally stable carbonyl and olefin complexes, as a measure of the tendency of the acceptor atoms to form dative π-bonds. Metals in their *normal valency states* being considered, this criterion indicates that platinum(II) has one of the strongest tendencies to co-ordinate by double bonds; yet even in platinum(II) complexes the electron transfer due to the π-type bond is rather small compared with the range of inductive effects of the various donor atoms. This is true even of the complexes of the trialkyl-phosphines and -arsines. Nevertheless, the π-type bond appears to be able to make a significant contribution to the metal-ligand bond strength in favourable circumstances. As evidence of this we have the difference in total bond strengths between *cis*- and *trans*-[(MR<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>] (M = P, As, or Sb; R = alkyl), which is<sup>5</sup> of the order of 10 kcal.

This paradox may be explained if we suppose that the release of electrons from metal to ligand in the dative π-bond, by decreasing the electronegativity of the ligand, induces an *almost equal* release of electrons from ligand to metal in the σ-bond. In this way the metal-ligand bond will be strengthened, but its electrical asymmetry will remain high. This seems to be the situation in most complex compounds of metals in their usual valency states when double co-ordinate bonding occurs.

Only exceptionally does the π-type co-ordinate bond appear to affect significantly the total transfer of charge between ligand and metal. The exceptional cases occur when the metal which must have filled *d*-orbitals is in an unusually low oxidation state, and/or when the donor atom which must have suitable vacant orbitals for dative π-bond formation is attached to very electronegative atoms or groups. This is evident from the low moments of such bonds as CO-Pt and PF<sub>3</sub>-Pt.<sup>12</sup> Even in ethylene complexes, where dative π-bonding appears to be essential for stability but the carbon atoms are not attached to electronegative groups, the C<sub>2</sub>H<sub>4</sub>-Pt bond is still fairly dipolar, perhaps about 4 D. Here back-donation in the π-type bond is far from neutralising the forward-donation in the σ-bond.



<sup>9</sup> Jensen, *Z. anorg. Chem.*, 1936, 229, 250.

<sup>10</sup> Chatt and Wilkins, *J.*, 1952, 273.

<sup>11</sup> Phillips, Hunter, and Sutton, *J.*, 1945, 146.

<sup>12</sup> Chatt and Williams, *J.*, 1951, 3061.

The stabilisation of the exceptionally low oxidation states of metals with filled *d*-orbitals by such ligands as CO, PhNC, and PF<sub>3</sub> is undoubtedly due to the very poor availability of their lone pairs of electrons, together with their capacity to form strong dative  $\pi$ -bonds. Thus it is the result of a combination of very strong inductive withholding and mesomeric withdrawal of electrons from the metal atom by the ligands. However, when dative  $\pi$ -bonding is weak (*e.g.*, because the metal has not got all its *d*-orbitals filled, or the ligand has no suitable vacant orbitals), stabilisation of low-valency states against oxidation must generally be greatest in the case of complexes containing the most electronegative ligands which it is possible to attach to the metal in the low-valent state concerned. These ligands must often be amines, and undoubtedly [V(dipyridyl)]<sub>3</sub><sup>0</sup>,<sup>13</sup> and the unstable [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>0</sup>,<sup>14</sup> and [Ir(NH<sub>3</sub>)<sub>5</sub>]<sup>0</sup><sup>15</sup> are somewhat stabilised by the inductive withholding of electrons from the metal atom. This will also be assisted by mesomeric withdrawal in the manner suggested by Burstall and Nyholm<sup>16</sup> in the case of [V(dipyridyl)]<sub>3</sub><sup>0</sup>.

#### EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

The tri-*n*-propylphosphine complexes were prepared as described by Chatt and Wilkins,<sup>17</sup> and the di-*n*-propyl sulphide complexes as described by Rudelius.<sup>18</sup> The 4-*n*-pentylpyridine complexes were prepared as follows.

**4-*n*-Pentylpyridinium Chloroplatinite**, [pepy H]<sub>2</sub>[PtCl<sub>4</sub>].—This salt was obtained as a pink precipitate by warming a solution of potassium chloroplatinite (5 g.) and 4-*n*-pentylpyridinium chloride (5 g.) in water (50 c.c.) for a few minutes. It was removed, washed with water, ethanol, and ether, and dried (7.3 g.), m. p. 175—178° (decomp.), sinters at 172—175° (Found : C, 37.8; H, 4.9. C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>Cl<sub>4</sub>Pt requires C, 37.7; H, 5.1%).

**trans-Di-(4-*n*-pentylpyridine)dichloroplatinum**, *trans*-[pepy<sub>2</sub>PtCl<sub>2</sub>].—A suspension of the above chloroplatinite (7.0 g.) in di-*n*-butyl ether (100 c.c.) was boiled under reflux for 3 hr. The hot yellow solution was treated with a little charcoal, filtered, and allowed to cool. The product (3.5 g.) separated in thick yellow needles. Repeatedly recrystallised from carbon tetrachloride it had m. p. 140—141° (Found : C, 42.5; H, 5.2. C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>Cl<sub>2</sub>Pt requires C, 42.5; H, 5.35%). It is a non-electrolyte in nitrobenzene and its obvious physical properties together with a rough measurement of its dipole moment confirm its *trans*-configuration.

**trans-Di-(4-*n*-pentylpyridine)tetrachloroplatinum**, *trans*-[pepy<sub>2</sub>PtCl<sub>4</sub>].—The preceding *trans*-salt (3.9 g.) in carbon tetrachloride (250 c.c.) was treated at 0° with chlorine (0.36 g.) in carbon tetrachloride (10 c.c.). A yellow solid separated. After 1 hr. the solid (2.5 g.) was removed. Repeatedly recrystallised from acetone (charcoal), then from ethyl acetate it had m. p. 250—251° (Found : C, 37.8; H, 4.7. C<sub>30</sub>H<sub>30</sub>N<sub>2</sub>Cl<sub>4</sub>Pt requires C, 37.8; H, 4.8%). It is a non-electrolyte in nitrobenzene. It is better obtained by reactions exactly analogous to those used to prepare the platinous derivative. **4-*n*-Pentylpyridinium chloroplatinate**, [pepy H]<sub>2</sub>[PtCl<sub>6</sub>] (4.5 g.), was obtained as an orange precipitate on mixing aqueous solutions (25 c.c. each) of sodium chloroplatinate (3 g.) and 4-*n*-pentylpyridinium chloride (2.5 g.). It sinters at 200—210° and melts with gas evolution 213—220° (Found : C, 34.1; H, 4.5. C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>Cl<sub>6</sub>Pt requires C, 33.9; H, 4.55%). It (5.7 g.) was decomposed by boiling its xylene (250 c.c.) suspension under reflux for 22 hr. The brown solution was treated with charcoal, filtered, and taken to dryness at 15 mm. The residue, repeatedly recrystallised from ethyl acetate, gave pure *trans*-[pepy<sub>2</sub>PtCl<sub>4</sub>] (2 g.), m. p. 251—252.5°.

Pyridine and ammonia complexes were prepared, but they were too insoluble in the aqueous phenol solvent to make any measurements with them.

**Measurements of the Redox Potentials.—Solutions.** The solvent (phenol 75%, water 25%) was prepared from dried "AnalaR" phenol (colourless, m. p. 40.9°) and distilled water. Two preparations of tetraethylammonium chloride were used; analysed by an ion-exchange method they had equiv. 235.5 and 235.9 (Calc. for C<sub>8</sub>H<sub>20</sub>NCl<sub>4</sub>H<sub>2</sub>O : equiv., 237.8). This salt was made

<sup>13</sup> Herzog, *Naturwiss.*, 1956, **43**, 35.

<sup>14</sup> Watt, Walling, and Mayfield, *J. Amer. Chem. Soc.*, 1953, **75**, 6175.

<sup>15</sup> Watt and Mayfield, *ibid.*, p. 6178.

<sup>16</sup> Burstall and Nyholm, *J.*, 1952, 3570.

<sup>17</sup> Chatt and Wilkins, *J.*, 1951, 2532.

<sup>18</sup> Rudelius, *Acta Univ. Lund*, 1885—6, **22**, Part 2, Paper 4.

up to 0.1M in the above solvent. Standard solutions of the platinum complexes were prepared in the above salt solution, 0.008M in the case of the less soluble Pt(IV) complexes and 0.024M in the case of the Pt(II) complexes. These solutions were mixed in the desired proportions to provide the electrolyte for the redox cell.

**Redox cell.** The redox electrodes were of platinum foil plated at a current density of 1 mA/cm.<sup>2</sup> for 1—2 hr. in a gilding solution, prepared as described by Popoff, Kunz, and Snow.<sup>19</sup> The reference electrodes, Ag,AgCl, were prepared according to Brown's method.<sup>20</sup> The cell consisted of a small glass vessel containing two sets of electrodes, a nitrogen inlet tube, and an outlet tube. It was maintained at 25°. The solutions were mixed initially by bubbling pre-saturated nitrogen through them, then during the remainder of the experiment nitrogen was passed over them.

**Measurements.** The potentials of the two sets of electrodes were measured by a Tinsley Type 3126 B Vernier Potentiometer. The gold electrode was the positive electrode. The cell was sensitive to daylight; its e.m.f. increased with the strength of illumination, but its response to increased illumination was rather sluggish. The redox electrode must have been the source of light sensitivity, because when the Ag,AgCl electrodes were replaced by a salt bridge to an external calomel electrode the cell remained sensitive to light. All the following experiments were carried out in the dark or in dull artificial light, with the cell wrapped in tin foil.

The e.m.f. of the cell was very slow in reaching its equilibrium value (1—5 days). This was certainly due to the slow equilibration of the redox electrodes and the solution, because equilibrium was established equally slowly after the Ag,AgCl electrode had been replaced by an external calomel electrode. Bright platinum foil in place of the gold electrode was equally slow in coming to equilibrium. Platinised platinum electrodes appeared to catalyse some

TABLE 2. Variation with time of the e.m.f. of the cell containing *trans*-[(Pr<sup>n</sup><sub>2</sub>S)<sub>2</sub>PtCl<sub>4</sub>] (0.0074M) and *trans*-[(Pr<sup>n</sup><sub>2</sub>S)<sub>2</sub>PtCl<sub>2</sub>] (0.0062M).

Time (hr.)	0	0.42	0.58	5.0	16	29.5	47	65.5	87.5	96	112	136	144	160
E.m.f. (mv)	—	335.0	344.4	395.2	413.8	421.3	426.5	430.5	433.9	434.9	437.3	439.3	439.5	438.8

TABLE 3. Equilibrium potentials (*E*) and redox potentials (*E*<sub>0</sub>).

(C<sub>IV</sub> = molarity of Pt(IV) complex, C<sub>II</sub> = molarity of Pt(II) complex.)

System: *cis*-[(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>PtCl<sub>4</sub>]-*cis*-[(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>]. System: *trans*-[(Pr<sup>n</sup><sub>2</sub>S)<sub>2</sub>PtCl<sub>4</sub>]-*trans*-[(Pr<sup>n</sup><sub>2</sub>S)<sub>2</sub>PtCl<sub>2</sub>].

Expt.	Electrode		10 <sup>3</sup> C <sub>IV</sub>	10 <sup>3</sup> C <sub>II</sub>	<i>E</i>	<i>E</i> <sub>0</sub>	Expt.	Electrode		10 <sup>3</sup> C <sub>IV</sub>	10 <sup>3</sup> C <sub>II</sub>	<i>E</i>	<i>E</i> <sub>0</sub>	
	pair							pair						
IA	1		7.4	6.15	370	368	IA	1		6.0	6.0	439	439	
	2		7.4	6.15	371	369		2		6.0	6.0	442	442	
IB	1		4.95	12.3	351	363	IB	1		4.8	9.6	434	443	
	2		4.95	12.3	354	366		2		4.8	9.6	432	441	
II	1		6.0	6.0	362	362	II *	1		6.0	6.0	440	440	
	2		6.0	6.0	363	363								
III	1		6.0	6.0	372	372								
	2		6.0	6.0	373	373								
					Mean <i>E</i> <sub>0</sub>	367								

\* Electrode 2 of experiment II did not work.

System: *trans*-[(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>PtCl<sub>4</sub>]-*trans*-[(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>]. System: *trans*-[pepy<sub>3</sub>PtCl<sub>4</sub>]-*trans*-[pepy<sub>3</sub>PtCl<sub>2</sub>].

Expt.	Electrode		10 <sup>3</sup> C <sub>IV</sub>	10 <sup>3</sup> C <sub>II</sub>	<i>E</i>	<i>E</i> <sub>0</sub>	Expt.	Electrode		10 <sup>3</sup> C <sub>IV</sub>	10 <sup>3</sup> C <sub>II</sub>	<i>E</i>	<i>E</i> <sub>0</sub>			
	pair							pair								
IA	1		6.0	6.0	350	350	IA	1		6.0	6.0	477	477			
	2		6.0	6.0	350	350		2		6.0	6.0	471	471			
IB	1		4.8	9.6	340	349	IB	1		4.8	9.6	472	481			
	2		4.8	9.6	339	348		2		4.8	9.6	463	472			
					Mean <i>E</i> <sub>0</sub>	349										
															Mean <i>E</i> <sub>0</sub>	475

reaction in the solution leading to a very rapid decrease in the e.m.f. The addition of a trace (<1 mm) of ferrous salt in an attempt to promote equilibration between gold electrode and solution was also unsuccessful.

After the cell had been made up, both pairs of electrodes registered potential differences

<sup>19</sup> Popoff, Kunz, and Snow, *J. Phys. Chem.*, 1928, **32**, 1056.

<sup>20</sup> Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

50—100 mv lower than those finally obtained. The e.m.f.s increased for a few days, the two pairs of electrodes recording different e.m.f.s and showing different rates of potential drift, but both finally approached the same value within a few mv of their final value after 1—5 days. New electrodes reached equilibrium more rapidly than used ones, but reached the same equilibrium potential in the same solution. Old electrodes finally became poisoned and then the potentials drifted comparatively rapidly and erratically; they were then discarded. Sometimes the potential of the cell overshot the equilibrium potential by a few mv, so that equilibrium was finally approached from the higher potential side; such behaviour is indicative of the presence of a minute amount of a minor redox system.<sup>21</sup> In spite of the sluggish behaviour of the cell the final potentials obeyed Nernst's law and gave different  $E_0$  values for the different pairs of complexes, indicating that the equilibrium potentials were indeed redox potentials governed by the main redox components. A typical example showing the slow approach to constant e.m.f. is given in Table 2 and the results of our measurements in Table 3.

In Table 3, experiments IB were conducted with the same cell as IA, but with the addition of a further quantity of the solution of the Pt(IV) complex after equilibrium had been reached in experiment IA. A change of Roman numeral in the first columns denotes that fresh solutions were used.

The authors thank Miss J. H. Norwood and Mr. P. F. Todd for experimental assistance with the preparation of the platinum complexes.

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[Received, August 24th, 1956.]

<sup>21</sup> Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 137.

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