

On the Complex Formation of Palladium with Dimethylglyoxime

KÁLMÁN BURGER* and DAVID DYRSSEN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

The distribution of radioactive palladium between chloroform and 1 M (H,Na)(ClO₄,OH,Cl) has been determined at 25°C as a function of the concentrations of dimethylglyoxime (HA), H⁺, Cl⁻ and OH⁻. The distribution constant of PdA₂ was determined to be $\log \lambda_2 = 1.85 \pm 0.08$. At pH > 7.5 the distribution decreases with increasing [OH⁻] due to the formation of PdA₂OH⁻ in the aqueous phase. The formation constant of this complex was determined as $\log K_{OH} = 5.50$. At high chloride concentrations the distribution decreases with increasing [H⁺] and decreasing [HA]. From measurements of the solubility of ^{110m}AgCl with increasing palladium concentration $K_1 = [\text{PdCl}^+][\text{Pd}^{2+}]^{-1}[\text{Cl}^-]^{-1}$ was calculated to be $\log K_1 = 3.88 \pm 0.09$ and from spectrophotometric measurements at 222 and 279 m μ $K_4 = [\text{PdCl}_4^{2-}][\text{PdCl}_3^-]^{-1}[\text{Cl}^-]^{-1}$ was determined as $\log K_4 = 1.34 \pm 0.02$. On the basis of these determinations we could estimate $\kappa_2 = [\text{PdA}_2][\text{Pd}^{2+}]^{-1}[\text{A}^-]^{-2}$ as $\log \kappa_2 = 34.1$. This extremely large complexity constant explains the formation of PdA₂ in very acid solutions. The formation of PdA₂OH⁻ explains the solubility of the complex in alkaline solutions.

Dimethylglyoxime has been used for more than 50 years for the detection and determination of palladium(II)¹. Palladium(II) is quantitatively precipitated by dimethylglyoxime (HA) from solutions of dilute mineral acids (pH \approx 2). It dissolves, however, in basic solutions (pH > 9–10). The complex has the composition of PdA₂, its structure is known from X-ray measurements^{2,3}. The stability of the complex has not yet been reported.

The nickel complex of dimethylglyoxime has the same composition, is isomorphous and also nearly isostructural^{2,3}. It is formed, however, in neutral or ammoniacal solution, but dissolves in acids. This fact makes possible the analytical separation of palladium and nickel.

According to X-ray measurements^{2,3} the PdA₂ molecule is less symmetrical than the NiA₂. It has two slightly different Pd–N and two slightly different

* On leave from the Institute for Inorganic and Analytical Chemistry of the L. Eötvös University, Budapest.

N—O distances. The hydrogen bonded O—O distance and the Pd—N distance are greater than the corresponding distances in NiA_2 ; the metal-metal bond length is also slightly greater⁴ in the palladium complex. Both complexes are diamagnetic⁵.

On the basis of the crystal structures or magnetic properties it does not seem possible to explain the different behavior of the palladium and nickel dimethylglyoximes in solution. For the clarification of these differences it might be of interest to determine the stability constant of the palladium complex.

The stability constants of some transitional metal dioximes have been determined potentiometrically⁶⁻¹⁰. From the stability constants it was possible to show the stabilization effects of the strong ligand field, the hydrogen bridge and the donor π -bond in these complexes¹⁰.

The solution chemistry of copper and nickel dimethylglyoximes has been studied by solvent extraction^{11,12}. From these measurements it was concluded that the large difference in the solubility (in water) and in the distribution ($\text{CHCl}_3/\text{H}_2\text{O}$) of these two complexes can only be explained by the fact that the copper complex is solvated in the aqueous phase¹². This conclusion is confirmed by the difference in the heat of solution of the two complexes in water¹³⁻¹⁵.

The low solubility of the palladium complex made the application of the potentiometric method for the determination of the stability constant impossible. It can be extracted however, with organic solvents such as chloroform. One should therefore be able to use solvent extraction for the determination of the stability constant.

EXPERIMENTAL

Chemicals. Chloroform (Merck p.a.) was washed repeatedly with an equal volume of distilled water to remove the 1% abs. alcohol and to saturate the solvent with water. Dimethylglyoxime (Merck p.a.) was used without further purification; solutions of 1.0 M NaClO_4 + 0.0001 M HClO_4 were saturated with dimethylglyoxime by filtering the solutions through a column with a bed of reagent 6–8 cm thick at a flow rate of about 1 cm/min. The solubility of dimethylglyoxime in this solution has been found to be 5.00×10^{-3} M.

NaClO_4 was prepared from p.a. perchloric acid and p.a. sodium carbonate (both chloride free). HClO_4 Merck p.a. was used. It was very important to make sure that the HClO_4 was really chloride free. This was accomplished with a radioactive silver chloride ($^{109}\text{mAgCl}$) column, using the solubility decreasing effect of chloride for determining the chloride content of the solution. A chloride concentration as low as 5×10^{-6} M caused a measurable solubility decrease, and as our solutions gave no such decrease it maybe safe to state that they contained less than 10^{-6} M chloride.

The palladium-109 isotope (half-life 13.6 h) was prepared by irradiation of p.a. palladium metal in the R1 reactor in Stockholm. The irradiated palladium metal was dissolved in fuming nitric acid. Most of the nitric acid was removed by evaporation to 0.5–1 ml. It was important not to evaporate to dryness, because the residue (hydrous oxide) is not soluble in nitric acid. To the nitric acid solution NaOH was added to a hydroxide concentration of 1 M. The palladium was thereby transformed to the hydroxo complex. Practically nitrate free hydrous palladium oxide was precipitated from this solution with 1 M HClO_4 . For quantitative precipitation of palladium the solution should be neutralized to a pH of 6–7. The quantitateness of the precipitation was checked by measuring the activity of the mother liquid. The palladium oxide precipitate was washed three times with distilled water and once with 0.1 M HClO_4 , then dissolved in a few ml of 70% HClO_4 . The solution was diluted until $[\text{Pd}^{2+}] \leq 0.002$ M and $[\text{H}^+] = 1$ M.

In accordance with the experiments of Berecki-Biedermann¹⁶ we found that with this method it was possible to prepare a chloride free palladium(II) solution even from PdCl₂. It is important never to boil palladium(II)-perchlorate solutions, because chloride ions may be formed by reduction of ClO₄⁻.

The chloride content of the palladium solution can be checked by measuring the light absorption at 420 mμ; 5 × 10⁻⁵ M chloride causes a significant extinction increase — in the case of 1.3 × 10⁻⁴ M Pd²⁺ and 1 cm cells from 0.03 to 0.06. Judged by this test, our palladium solutions contained less than 10⁻⁵ M chloride.

Together with ¹⁰⁹Pd, ¹¹¹Ag (half life 7.5 d) is produced by the irradiation. To remove this radioactive silver we tried to exchange the radioactive silver in the solution with inactive silver from a silver chloride precipitate¹⁷. For this purpose we used freshly prepared silver chloride, thoroughly washed to eliminate excess chloride and silver and recrystallized from hot water. The exchange reached equilibrium rather slowly, and a reaction was observed between the palladium(II) and the silver chloride precipitate.

Under these circumstances, and since under our experimental conditions silver ions do not react with dimethylglyoxime, it seemed to be preferable to correct for the activities caused by the silver contamination. Every activity measurement was therefore repeated after one palladium-109 half time and the activity decrease was used for determining the palladium content (*e.g.*, the distribution coefficient).

Analytical measurements. The palladium(II) solutions were analyzed by precipitating the palladium and measuring it in the form of PdA₂. For the analysis of dimethylglyoxime in 1 M NaClO₄ solution, the dimethylglyoxime was reacted with an excess of nickel sulfate in ammoniacal solution. The complex was extracted into chloroform and the UV light absorption was measured at 365 mμ.

Distribution experiments. Equal total volumes (15 ml) of the aqueous and organic phases were equilibrated in 50 ml stoppered centrifuge tubes. The phases were mixed by repeated slow inversion of the tubes at 25°C in a thermostated room. The two phases were made up in the following way. The organic phase was chloroform saturated with water. Dimethylglyoxime was added as a saturated solution in 1 M NaClO₄. The hydrogen ion concentration of the aqueous layer was adjusted with different buffer solutions containing HClO₄, NaOH, NaCH₃CO₂ or Na₂B₄O₇. The acetate or borate concentration never exceeded 0.01 M. The samples were shaken over night, and centrifuged. Two ml of both phases were taken for measurement of the γ-activity and 10 ml of the aqueous phase for measurement of its -log [H⁺]. The measurements of the γ-activity of the solutions were made with a Tracerlab Compu/Matic V scaler connected with a Tracerlab well scintillation counter. The value of -log [H⁺] was measured with a Radiometer pH meter Type PHM 3i using Beckman glass electrode type 40498 or Radiometer glass electrode Type G 202 B and a "Wilhelm" reference bridge. The glass electrodes were standardized against a solution of 0.01 M HClO₄ + 0.99 M NaClO₄ (-log [H⁺] = 2.00) or 0.01 M NaOH + 0.99 M NaClO₄ (-log [OH⁻] = 2.00).

From the measurements of the potential *E* of these standards, we could determine the constants *E*_{H⁺}⁰ and *E*_{OH⁻}⁰ in the following relations:

$$\begin{aligned} E &= E_{\text{H}^+}^0 - 59.154 \log [\text{H}^+] + 51 [\text{H}^+] \text{ mV} \\ E &= E_{\text{OH}^-}^0 + 59.154 \log [\text{OH}^-] - 24 [\text{OH}^-] \text{ mV} \end{aligned}$$

The last terms for the liquid junction potential were estimated from measurements¹⁸ in 3 M NaClO₄. For acid solutions below -log [H⁺] = 1, [H⁺] was calculated from the amount of HClO₄ and HCl added in the aqueous phase.

For pH values below 8, [HA], the free concentration of dimethylglyoxime in the aqueous phase, was calculated from [HA]_{tot} with the following equation

$$[\text{HA}] = \frac{[\text{HA}]_{\text{tot}}}{K_d + 1} - 2 \cdot \frac{[\text{Pd}^{2+}]_{\text{tot}}}{q + 1}$$

*K*_d = 0.0788 was obtained by dividing the solubility of dimethylglyoxime in CHCl₃ saturated with water (3.94 × 10⁻⁴ M) by that in 1.0 M NaClO₄ + 0.0001 M HClO₄ (5.00 × 10⁻³ M).

Solubility experiments. The radioactive crystalline silver chloride used in the solubility experiments for determining the first stability constant of palladium chloride (*K*₁ = [PdCl⁺][PdCl²⁺]⁻¹[Cl⁻]⁻¹) was prepared from p.a. AgNO₃ and p.a. HCl. First an

Table 1. Distribution of radioactive Pd between chloroform and 1 M (H,Na) (Cl,ClO₄) containing dimethylglyoxime. The initial Pd conc. in the aqueous phase was between 2.25×10^{-6} and 9.02×10^{-6} . [HA] is calculated free conc. of dimethylglyoxime in the aqueous phase at equilibrium.

| $-\log [\text{Cl}^-]$ | $-\log [\text{H}^+]$ | $-\log [\text{HA}]$ | $\log q$ |
|-----------------------|----------------------|---------------------|----------|
| 3.398 | 2.208 | 4.255 | + 1.863 |
| 3.398 | 2.088 | 4.255 | + 1.920 |
| 3.398 | 1.863 | 4.255 | + 1.819 |
| 3.398 | 1.516 | 4.255 | + 1.839 |
| 3.398 | 1.092 | 4.255 | + 1.832 |
| 3.398 | 0.688 | 4.255 | + 1.672 |
| 3.398 | 0.132 | 4.255 | + 1.187 |
| 3.825 | 0.331 | 3.430 | + 1.824 |
| 2.780 | 0.331 | 3.430 | + 1.896 |
| 1.137 | 1.126 | 4.255 | + 1.730 |
| 1.137 | 0.688 | 4.255 | + 1.477 |
| 1.137 | 0.470 | 4.255 | + 1.327 |
| 0.972 | 2.191 | 4.255 | + 1.938 |
| 0.972 | 2.047 | 4.255 | + 1.921 |
| 0.972 | 1.493 | 4.255 | + 1.858 |
| 0.972 | 1.084 | 4.255 | + 1.654 |
| 0.972 | 0.470 | 4.255 | + 1.197 |
| 0.972 | 0.132 | 4.255 | + 0.731 |
| 0.943 | 2.201 | 4.255 | + 1.973 |
| 0.943 | 1.107 | 4.255 | + 1.675 |
| 0.943 | 0.688 | 4.255 | + 1.435 |
| 0.943 | 0.470 | 4.255 | + 1.184 |
| 0.943 | 0.132 | 4.255 | + 1.004 |
| 0.560 | 0.876 | 3.306 | + 1.521 |
| 0.560 | 0.876 | 4.757 | + 0.619 |
| 0.560 | 0.876 | 3.896 | + 1.143 |
| 0.560 | 0.331 | 5.402 | - 0.189 |
| 0.560 | 0.180 | 4.425 | + 0.523 |
| 0.560 | 0.180 | 5.130 | - 0.087 |
| 0.513 | 2.171 | 4.255 | + 2.036 |
| 0.513 | 2.101 | 4.255 | + 1.924 |
| 0.513 | 1.905 | 4.255 | + 1.654 |
| 0.513 | 1.692 | 4.255 | + 1.891 |
| 0.513 | 1.177 | 4.255 | + 1.723 |
| 0.513 | 0.688 | 4.255 | + 0.938 |
| 0.513 | 0.269 | 4.255 | + 0.300 |
| 0.460 | 0.876 | 4.282 | + 1.132 |
| 0.460 | 0.876 | 4.578 | + 0.934 |
| 0.460 | 0.876 | 4.882 | + 0.609 |
| 0.460 | 0.876 | 5.442 | - 0.021 |
| 0.460 | 0.876 | 5.501 | - 0.199 |
| 0.460 | 0.876 | 5.535 | - 0.243 |
| 0.137 | 0.132 | 4.255 | + 1.091 |
| 0.076 | 2.177 | 4.255 | + 2.140 |
| 0.076 | 1.090 | 4.255 | + 1.409 |
| 0.076 | 0.688 | 4.255 | + 0.435 |
| 0.076 | 0.269 | 4.255 | - 0.072 |
| 0.076 | 0.132 | 4.255 | - 0.174 |

inactive silver chloride precipitate was prepared by precipitating from a boiling 1 M AgNO₃ solution with small excess of 1 M HCl. The chloride excess was washed out thoroughly. This precipitate was dissolved in conc. NH₃, and mixed with a solution containing ^{110m}Ag in the form of AgNO₃. The silver chloride was precipitated from the hot solution with chloride free conc. nitric acid. After washing with distilled water the silver chloride was recrystallized from hot water. For determining the specific activity of the precipitate a weighed amount of the dried AgCl was dissolved in conc. NH₃ and its γ -activity measured.

The solubility column and method used have been described previously by Dyrssen and Tyrrell¹⁹. The concentration of the palladium(II) perchlorate solutions circulated in the column varied between 1.21×10^{-3} and 4.84×10^{-5} . The ionic strength of the solutions was kept constant at 1 M with HClO₄.

Knowing the specific activity of silver chloride used in the column we could determine the silver concentration in the samples by measuring the γ -activity. The palladium concentration in this sample was checked spectrophotometrically. The absorption of the PdCl₄²⁻ complex was measured in 1 M HCl at 280 m μ .

Spectrophotometric measurements were made with Hilger H700 photoelectric spectrophotometer, with quartz absorption cells of 1 or 4 cm. The light source in the UV was a hydrogen lamp, in the visible range a tungsten lamp.

All experiments were carried out at 25°C in a constant temperature room. The solubility measurements in a $25.0 \pm 0.05^\circ\text{C}$ thermostated water bath. The ionic strength of the aqueous solutions was kept constant at 1 M (except for the data reported in Fig. 1) using NaClO₄ and HClO₄.

SYMBOLS AND EQUILIBRIUM CONSTANTS

| | | |
|------------------------------------|---|--------|
| HA | = dimethylglyoxime CH ₃ C(:NOH)C(:NOH)CH ₃ | |
| K _a | = [H ⁺][A ⁻][HA] ⁻¹ | (I) |
| K _d | = [HA] _{org} [HA] ⁻¹ | (II) |
| α_2 | = [PdA ₂][Pd ²⁺] ⁻¹ [A ⁻] ⁻² | (III) |
| λ_2 | = [PdA ₂] _{org} [PdA ₂] ⁻¹ | (IV) |
| \bar{K} | = [PdA ₂][H ⁺] ² [Pd ²⁺] ⁻¹ [HA] ⁻² = $\alpha_2 K_a^2$ | (V) |
| K _n | = [PdCl _n ²⁻ⁿ][PdCl _n ³⁻ⁿ] ⁻¹ [Cl ⁻] ⁻¹ | (VI) |
| β_n | = [PdCl _n ²⁻ⁿ][Pd ²⁺] ⁻¹ [Cl ⁻] ⁻ⁿ | (VII) |
| φ | = $\sum \beta_n [Cl-]n$ | (VIII) |
| K _{s0} | = [Ag ⁺][Cl ⁻] | (IX) |
| K _{s1} | = [AgCl] | (X) |
| K _{s2} | = [AgCl ₂ ⁻][Cl ⁻] ⁻¹ | (XI) |
| K _{OH} | = [PdA ₂ OH][PdA ₂] ⁻¹ [OH ⁻] ⁻¹ | (XII) |
| q | = net distribution ratio (org/aq) | |
| [HA] _{tot} | = initial total dimethylglyoxime concentration in aqueous phase | |
| [Pd ²⁺] _{tot} | = initial total concentration of palladium(II) in the aqueous phase | |
| I | = molar ionic strength. | |

Complex formation of PdA₂

We tried to apply the method of Dyrssen *et al.*^{11,12}, used for the study of complex formation of nickel and copper with dimethylglyoxime. We found that the extraction of palladium dimethylglyoxime into chloroform is inde-

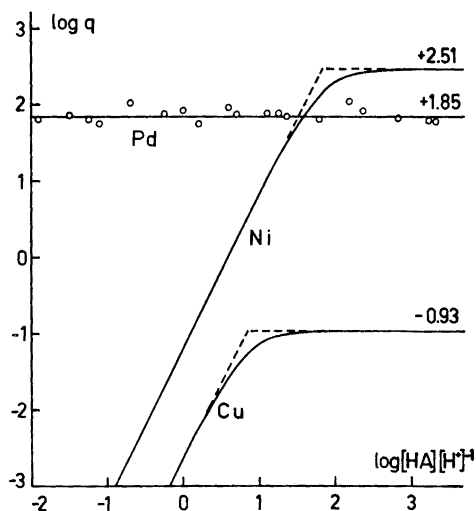


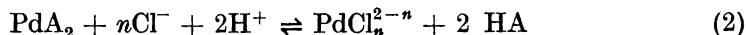
Fig. 1. The distribution ratios of Ni(II), Pd(II), and Cu(II) between chloroform and 0.1 M (H,Na)ClO₄ as a function of [HA][H⁺]⁻¹. The distribution curves of Ni and Cu were determined previously.

pendent of the pH, between pH 0 and 7. This shows that the complex is extremely strong and that the distribution ratio is

$$q = \frac{[\text{PdA}_2]_{\text{org}}}{[\text{PdA}_2]} = \lambda_2 = 10^{1.85 \pm 0.08} \quad (1)$$

In Fig. 1 is given the distribution of palladium-, nickel-, and copper dimethylglyoxime between chloroform and 0.1 M NaClO₄ as a function of log [HA] - log [H⁺]. It shows that palladium(II) can be separated from nickel and copper in the form of the dimethylglyoxime complex by extraction with chloroform. This makes possible the selective determination of palladium(II).

For obtaining the λ_2 value for palladium(II) dimethylglyoxime the distribution of the complex was determined as a function of the chloride concentration of the solution. According to our investigations the following reaction takes place:



where n depends on the chloride concentration.

The experiments have given no evidence for the presence of any appreciable amounts of mixed complexes (such as PdA₂Cl) in either phase or other species (e.g. PdA⁺ or Pd²⁺) than PdA₂ and PdCl_{*n*}^{2-*n*} in the aqueous phase (cf. eqn. 1). In 1 M H(Cl,ClO₄) the distribution ratio is then

$$q = \frac{[\text{PdA}_2]_{\text{org}}}{[\text{PdA}_2] + \Sigma[\text{PdCl}_n^{2-n}]} \quad (3)$$

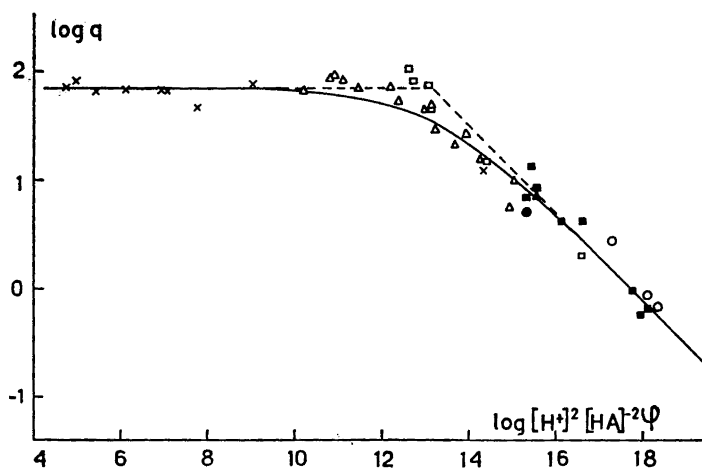


Fig. 2. The distribution ratio of Pd(II) between chloroform and 1 M (H,Na)(Cl,ClO₄) as a function of $[H^+]^2[HA]^{-2}\varphi$, where $\varphi = \sum_1^4 \beta_n [Cl^-]^n$. The symbols represent different chloride concentration in the aqueous phase: O 0.9 to 0.4 M, □ 0.4 to 0.2 M, △ 0.2 to 0.01 M, × 0.01 to 0.0006 M. Filled symbols are $[HA] < 5 \times 10^{-5}$ M.

or

$$q = \frac{\lambda_2}{1 + K^{-1}[H^+]^2[HA]^{-2}\varphi} \quad (4)$$

where φ is defined above (VIII) and calculated from experiments below.

To find the unknown constant we plotted the experimental data as $\log q$ against $\log [H^+]^2[HA]^{-2}\varphi$ (Fig. 2) and compared it with the standardized curve

$$Y = -\log(1 + v); X = \log v \quad (5)$$

where

$$v = [H^+]^2[HA]^{-2}\varphi \quad (6)$$

From the positions of the coordinate axes at the best fit we obtained from (4) and (6)

$$\log q - Y = \log \lambda_2; \log ([H^+]^2[HA]^{-2}\varphi) - X = \log K = 13.20 \quad (7)$$

From (I), (III) and (V) we obtained

$$\kappa_2 = KK_a^{-2} \quad (8)$$

or using $\log K_a = -10.46$

$$\log \kappa_2 = \log K - 2 \log K_a = 34.12 \quad (9)$$

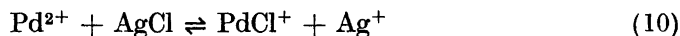
The rather good fit of the data in Fig. 2 with the normalized curve (eqn. 5) demonstrates that the assumptions underlying eqn. (4) are permissible.

Table 2. Reported K_n values for the complex formation between Pd^{2+} and Cl^- .

| | Fernelius <i>et al.</i> ²⁰ | Shukarev <i>et al.</i> ²¹ | Jørgensen ^{25,26} | This work |
|------------------|--|---|----------------------------|-----------------|
| $\log K_1$ | 6.2 ± 0.1 | 4.34 | | 3.88 ± 0.09 |
| $\log K_2$ | 4.7 ± 0.1 | 3.54 | | 3.03 |
| $\log K_3$ | 2.5 ± 0.1 | 2.68 (2.79) | | 2.18 |
| $\log K_4$ | 2.6 ± 0.1 | 1.68 (1.83) | 0.8 | 1.34 ± 0.02 |
| I M | 0.440 | 0.8 | 1.0 | 1.0 |
| $[\text{H}^+]$ M | 0.208 | 0.6 | | 1.0 |
| $^\circ\text{C}$ | 21 | 20 | | 25 |

Formation of PdCl^+

From VIII it can be seen that for obtaining φ in eqn. (4) we had to know β_n . The values have been determined photometrically by Fernelius and coworkers²⁰ and by Shukarev and coworkers²¹. The constants are given in Table 2. The contradiction in these results forced us to deal with the determination of them. We used for the determination of K_1 the miniature solubility column of Dyrssen and Tyrrell¹⁹ filled with crystalline silver chloride containing $^{110\text{m}}\text{Ag}$. The following reaction between palladium(II) and silver chloride was studied:



Palladium(II) solutions with different palladium concentration were circulated in the column and the solubility of the silver chloride in these solutions were determined by measuring the γ -activity.

The equilibrium constant K_1 (eqn. VI) has been determined as follows:

$$[\text{Pd}^{2+}]_{\text{tot}} = [\text{Pd}^{2+}] + [\text{PdCl}^+] \quad (11)$$

$$[\text{Ag}^+]_{\text{tot}} = [\text{Ag}^+] + [\text{AgCl}] = [\text{Ag}^+] + K_{s1} \quad (12)$$

$$[\text{Cl}^-]_{\text{tot}} = [\text{AgCl}] + [\text{PdCl}^+] + [\text{Cl}^-] \quad (13)$$

$$[\text{Ag}^+]_{\text{tot}} = [\text{Cl}^-]_{\text{tot}} \quad (14)$$

The complex AgCl_2^- can be neglected in eqns. (12) and (13). From eqns. (12), (13), and (14) we obtained

Table 3. Solubility of $^{110\text{m}}\text{AgCl}$ in 1 M HClO_4 as a function of the Pd conc.

| $[\text{Pd}^{2+}]_{\text{tot}} \times 10^4$ | $[\text{Ag}^+]_{\text{tot}} \times 10^5$ | $K_1 \times 10^{-3}$ |
|---|--|----------------------|
| 12.1 | 4.27 | 7.50 |
| 12.1 | 4.35 | 7.82 |
| 12.1 | 4.28 | 7.56 |
| 10.1 | 3.57 | 5.92 |
| 7.26 | 3.89 | 10.3 |
| 4.84 | 2.68 | 6.06 |
| 4.84 | 2.59 | 5.55 |
| 4.84 | 2.81 | 7.10 |
| 2.42 | 2.45 | 9.62 |
| 2.42 | 2.08 | 5.57 |
| 1.21 | 2.02 | 10.5 |

Mean value of $K_1 = (7.59 \pm 1.55) \times 10^3$, or $\log K_1 = 3.88 \pm 0.09$.

$$[\text{PdCl}^+] = [\text{Ag}^+] - [\text{Cl}^-] \quad (15)$$

From (11) and (VI)

$$[\text{Pd}^{2+}]_{\text{tot}} = [\text{PdCl}^+](K_1^{-1}[\text{Cl}^-]^{-1} + 1) \quad (16)$$

From (15), (16), and (IX)

$$[\text{Pd}^{2+}]_{\text{tot}} = ([\text{Ag}^+] - K_{s0}[\text{Ag}^+]^{-1})(K_1^{-1}[\text{Ag}^+]K_{s0}^{-1} + 1) \quad (17)$$

$$K_1 = \frac{[\text{Ag}^+]^2 K_{s0}^{-1} - 1}{[\text{Pd}^{2+}]_{\text{tot}} - [\text{Ag}^+] + K_{s0}[\text{Ag}^+]^{-1}} \quad (18)$$

Eqns. (12), (18), $K_{s0} = 1.82 \times 10^{-10}$, and $K_{s1} = 4.61 \times 10^{-7}$ (Refs.^{22,23}) were used for the calculation of K_1 from $[\text{Pd}^{2+}]_{\text{tot}}$ and $[\text{Ag}^+]_{\text{tot}}$.

Table 3 shows the experimental data and the calculated values of K_1 . The mean value is

$$\log K_1 = 3.88 \pm 0.09$$

As may be seen from Table 2, this value is not far from the K_1 reported by Shukarev *et al.*²¹ In our opinion, however, reliable K_n values cannot be obtained from spectrophotometric measurements around 400 $m\mu$.

Formation of PdCl_4^{2-}

Except for some work by Sundaram and Sandell²⁴ all previous investigations of the complex formation between Pd^{2+} and Cl^- agree that the maximum coordination number is 4. For the spectrophotometric determination of the stability constants Fernelius *et al.*²⁰ and Shukarev *et al.*²¹ both used wavelengths around 400 $m\mu$ where Pd^{2+} as well as all PdCl_n complexes absorb light with rather small extinction coefficients. Jørgensen²⁵ has reported that PdCl_4^{2-} has two maxima at 279 ($\epsilon_4 = 10\,500$) and 223 $m\mu$ ($\epsilon_4 = 30\,000$). He also reports²⁶ a value of $\log K_4 = 0.8$ in 1 M HClO_4 .

We measured the extinction at 210, 222, 235, and 279 $m\mu$ with different chloride concentrations and a total concentration of palladium of 1.31×10^{-4} M (Table 4). From the measurements at both 222 and 279 $m\mu$ we could easily

Table 4. Spectrophotometric measurements of 1.31×10^{-4} Pd(II) at various chloride concentrations.

| [Cl ⁻] M | Extinction values at $m\mu$ wave-lengths | | | |
|-------------------------|--|-------|-------|-------|
| | 210 | 222 | 235 | 279 |
| 4×10^{-1} | 1.241 | 1.434 | 1.209 | 1.042 |
| 10^{-1} | 1.297 | 1.224 | 1.273 | 0.797 |
| 4×10^{-2} | 1.314 | 0.986 | 1.280 | 0.563 |
| 10^{-2} | 1.368 | 0.665 | 1.219 | 0.265 |
| 4×10^{-3} | 1.362 | 0.560 | 1.097 | 0.161 |
| 10^{-3} | 1.265 | 0.478 | 0.691 | 0.064 |
| 5×10^{-4} | 1.190 | 0.454 | 0.506 | 0.049 |
| 10^{-4} | 0.858 | 0.300 | 0.183 | 0.033 |
| 5×10^{-5} | 0.733 | 0.222 | 0.140 | 0.023 |
| 0 | 0.422 | 0.124 | 0.056 | 0.026 |
| Cell length, cm | 1 | 0.5 | 1 | 1 |

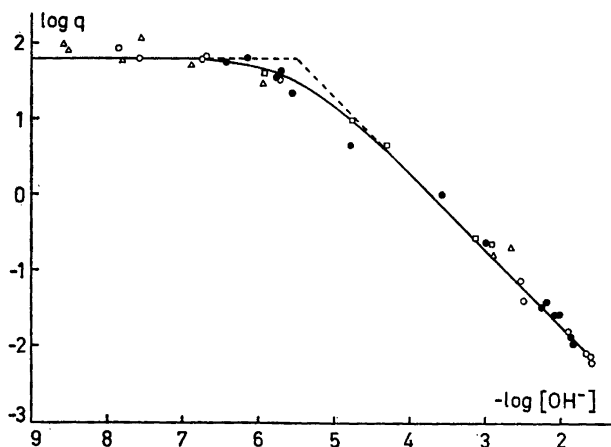


Fig. 3. The distribution ratio of Pd(II) between chloroform and 1 M Na(ClO₄, OH) as a function of $-\log [\text{OH}^-]$. The symbols represent different initial concentrations of dimethylglyoxime in the aqueous phase: ● 3.33×10^{-4} M, ○ 1.66×10^{-5} M, □ 8.40×10^{-5} M, △ 4.20×10^{-4} M

calculate $K_4 = 22 \pm 0.5$. While the absorption at 279 $m\mu$ belongs only to one complex (most probably PdCl_4^{2+}), the absorption at 210, 222, and 235 $m\mu$ seems to belong to several species (not unlikely to all of the chloride complexes as well as Pd^{2+}). In our opinion only a very extensive spectrophotometric work at the lower wave-lengths could enable the calculation of the seven parameters ϵ_0 , ϵ_1 , ϵ_2 , ϵ_3 , K_1 , K_2 , and K_3 ; one additional difficulty is that the free chloride must be calculated from the amount chloride bound to Pd^{2+} . Because such an investigation was beyond the scope of this work we have preferred to estimate K_2 and K_3 from our values of K_1 and K_4 using the two-parameter approximation by Dyrssen and Sillén²⁷. In this approximation the ratio of adjacent complexity constants is assumed to be equal, *i.e.* no complex predominates. (The assumption is close to the statistical distribution of the complexes.) From eqns (11) and (12) in Ref.²⁷ we obtain

$$\log K_1 = a + 3b = 3.88 \quad (19)$$

$$\log K_4 = a - 3b = 1.34 \quad (20)$$

$$\log K_n = a + b(5 - 2n) \quad (21)$$

$$\log \beta_n = an + bn(4 - n) \quad (22)$$

From these eqns we calculated $b = 0.423$ and $a = 2.61$. With these two parameters and eqns (21) and (22) we calculated the values of K_n given in Table 2 and the values of φ .

If in the future more reliable values of β_n will be found it is possible to calculate new values of $[\text{H}^+]^2[\text{HA}]^{-2}\varphi$ and thus refine the value of κ_2 .

Formation of the PdA_2OH^-

To study the "hydrolysis" of the dimethylglyoxime complex of palladium(II), we plotted the distribution coefficients as a function of $-\log [\text{OH}^-]$

Table 5. Distribution of radioactive Pd between chloroform and 1 M Na(ClO₄,OH) containing dimethylglyoxime. The initial conc. of Pd in aqueous phase was 9.02×10^{-6} M. [A]_{tot} is the initial total conc. of dimethylglyoxime in the aqueous phase.

| $-\log [\text{OH}^-]$ | $[\text{A}]_{\text{tot}} \times 10^4$ | $\log q$ |
|-----------------------|---------------------------------------|----------|
| 8.53 | 0.42 | + 1.913 |
| 7.87 | 1.66 | + 1.927 |
| 7.59 | 1.66 | + 1.806 |
| 6.77 | 1.66 | + 1.784 |
| 6.72 | 1.66 | + 1.805 |
| 6.45 | 3.33 | + 1.744 |
| 6.16 | 3.33 | + 1.813 |
| 5.94 | 0.84 | + 1.615 |
| 5.79 | 3.33 | + 1.549 |
| 5.74 | 1.66 | + 1.639 |
| 5.58 | 3.33 | + 1.340 |
| 4.79 | 0.84 | + 0.997 |
| 4.75 | 1.66 | - 0.051 |
| 4.32 | 0.84 | + 0.656 |
| 3.59 | 3.33 | - 0.001 |
| 3.14 | 0.84 | - 0.556 |
| 2.93 | 0.84 | - 0.629 |
| 2.89 | 0.42 | - 0.799 |
| 2.56 | 1.66 | - 1.136 |
| 2.52 | 1.66 | - 1.470 |
| 2.21 | 3.33 | - 1.405 |
| 2.12 | 3.33 | - 1.570 |
| 2.05 | 3.33 | - 1.653 |
| 1.92 | 1.66 | - 1.793 |
| 1.89 | 3.33 | - 1.839 |
| 1.85 | 3.33 | - 1.866 |
| 1.69 | 1.66 | - 2.074 |
| 1.63 | 1.66 | - 2.188 |

(Fig. 3). According to our experiments above both the organic phase and the acid aqueous phase contained PdA₂. Furthermore, the distribution of the complex is independent of the concentration of dimethylglyoxime over the entire pH range. The decrease in $\log q$ with slope 1 above pH 9 can then only be explained by the following reaction:



When no Cl⁻ is present, the distribution ratio for the entire pH range 0–12.5 is then

$$q = \frac{[\text{PdA}_2]_{\text{org}}}{[\text{PdA}_2] + [\text{PdA}_2\text{OH}^-]} = \frac{\lambda_2}{1 + K_{\text{OH}}[\text{OH}^-]} \quad (24)$$

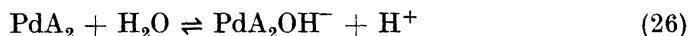
To obtain K_{OH} we may compare the $\log q$ ($-\log [\text{OH}^-]$) curve with the same normalized curve as before (eqn. 5) where $v = [\text{OH}^-]$. From the position of best fit we obtain

$$\log [\text{OH}^-] - X = -\log K_{\text{OH}} = -5.50 \quad (25)$$

These experiments exclude the formation of PdD₂²⁻ (H₂D = HA) in alkaline solutions. This complex has been suggested by Feigl and Suter²⁸.

CONCLUSIONS

The stability constant of the palladium(II) dimethylglyoxime complex has been determined. It has been shown that the stability of this complex is extremely large ($\log \kappa_2 = 34.1$). This is the reason why the complex is formed even in solutions with fairly high acidity. Its distribution coefficient is nevertheless smaller than that of the nickel complex, which has a smaller stability constant (Fig. 1). This can be explained by the greater tendency of PdA_2 to coordinate water molecules. The tendency of palladium(II) to coordinate with more ligands than two oxime groups is also shown by the formation of PdA_2OH^- . This "hydrolysis", which can not be observed in the case of the nickel complex, is the reason for the solubility of PdA_2 in basic solutions. The fact that on increasing the pH the stronger PdA_2 complex will release one proton and not the weaker NiA_2 , indicates that this is not a proton from one of the two strong hydrogen bridges, but a product of the "hydrolysis" of the complex:



where the water molecule is most probably coordinatively bound to the palladium. The same conclusion was made in a previous study¹² of CuA_2OH^- and agrees with the well-known lack of reactivity of the hydroxyl groups in MA_2 complexes.

Acknowledgements. We wish to thank the head of the department, Professor Lars Gunnar Sillén, for helpful discussions and Dr Tomas Spiro for revising the English text. The work has been supported by the *Swedish Council for Atomic Research*.

REFERENCES

1. Welcher, F. J. *Organic analytical reagents*, Vol. III, D. Van Nostrand Comp., New York 1947.
2. Panattoni, C., Frasson, E. and Zannetti, R. *Gazz. Chim. Ital.* **89** (1959) 2132.
3. Williams, D. E., Wohlaue, G. and Rundle, R. E. *J. Am. Chem. Soc.* **81** (1959) 755.
4. Banks, C. V. and Barnum, D. W. *J. Am. Chem. Soc.* **80** (1958) 3579.
5. Banks, C. V., Vander Haas, R. W. and Wander Val, R. P. *J. Am. Chem. Soc.* **77** (1955) 324.
6. Charles, R. G. and Freiser, H. *Anal. Chim. Acta* **11** (1954) 101.
7. Van Uitert, L. G. and Fernelius, W. C. *J. Am. Chem. Soc.* **76** (1954) 375.
8. Bochkova, V. M. and Peshkova, V. M. *Zhur. neorg. Khim.* **3** (1958) 1131.
9. Peshkova, V. M. and Bochkova, V. M. *Nauchnye Doklady Vysshei Shkoly* **1** (1958) 62.
10. Burger, K. and Ruff, I. *Talanta* **10** (1963) 329.
11. Dyrsen, D., Krašovec, F. and Sillén, L. G. *Acta Chem. Scand.* **13** (1959) 50.
12. Dyrsen, D. and Hennichs, M. *Acta Chem. Scand.* **15** (1961) 47.
13. Fleischer, D. *Thesis* Univ. Pittsburgh 1959. *Univ. Microfilms* 59-2396 Ann Arbor, Michigan.
14. Fleischer, D. and Freiser, H. *J. Phys. Chem.* **66** (1962) 389.
15. Rundle, R. E. and Banks, C. V. *J. Phys. Chem.* **67** (1963) 508.
16. Berecki-Biedermann, C. *Proc. TCCC.* (1962) 161.
17. Sunderman, D. N. and Meinke, W. W. *Anal. Chem.* **29** (1957) 1578.
18. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand.* **11** (1957) 1034.
19. Dyrsen, D. and Tyrrell, V. *Acta Chem. Scand.* **15** (1961) 393.
20. Droll, H. A., Block, B. P. and Fernelius, W. C. *J. Phys. Chem.* **61** (1957) 1000.

21. Shukarev, S. A., Lobanova, D. A., Ivanova, M. A. and Kononova, M. A. *Vestn. Leningr. Univ.* **10** (1961) 152.
22. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants*, Part II, The Chemical Society, London 1958.
23. Fomin, V. V. *Zhur. Fiz. Khim.* **29** (1955) 1728.
24. Sundaram, A. K. and Sandell, E. B. *J. Am. Chem. Soc.* **77** (1955) 855.
25. Jørgensen, C. K. *Absorption spectra and chemical bonding in complexes*, Pergamon Press, London 1962.
26. Jørgensen, C. K. *Final Techn. Report DA-91, 508-EUC-247*, 1958.
27. Dyrssen, D. and Sillén, L. G. *Acta Chem. Scand.* **7** (1953) 663.
28. Feigl, F. and Suter, H. A. *J. Chem. Soc.* **1948** 378.

Received February 21, 1963.