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Palladium(II) Halide Complexes. I. Stabilities and Spectra of Palladium(II) Chloro and Bromo Aqua Complexes

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Stability constants, β_n, n = 1, 2, 3, 4, for the chloro and bromo complexes of palladium(II) have been calculated, using a least squares programme, from spectrophotometric measurements at 222, 234.5 and 279 nm (chloride) and at 247, 265, and 332 nm (bromide). The following values of $\lg(\beta_n/M^{-n})$ were obtained: 4.47±0.01, 7.76±0.04, 10.17±0.07, and 11.54±0.09 (chloride) and 5.17±0.02, 9.42±0.04, 12.72±0.06, and 14.94±0.08 (bromide). Spectra of the species $PdX_n(H_2O)_{4-n}^{2-n}$, n = 0, 1, 2, 3, 4; X = Cl, Br, have been determined in the wave length region 210 to 600 nm. The temperature was 25.0°C and the ionic medium 1.00 M *perchloric acid.*

Introduction

Stability constants of palladium(II) chloro complexes have been published previously.[1-18] However, due to difficulties of finding reversible electrodes for palladium[12] and of preparing pure solutions of palladium(II) perchlorate,[4,19,20] most of these previous studies are incomplete and their results discordant.

Very little has been reported about the stabilities of palladium(II) bromo complexes. Only a few values of the stepwise stability constants K_1[14,21] and K_4[9,13,21] and the overall constant β_4[2,6,12,21,22] have appeared in the literature. The agreement between these few published constants is poor. The low solubility of $PdBr_2$ has complicated spectrophotometric and potentiometric studies on this system.

The maximum coordination number of the palladium(II) halide complexes has been disputed. Early studies[3,23,24] indicated the formation of six complexes, but these results have been disproved later.[4,11]

In connection with stopped-flow studies on the kinetics of the stepwise halide anations and acid hydrolyses of the palladium(II) chloro and bromo aqua complexes, which will be described in subsequent papers in this series,[25,36] it appeared necessary to determine the stepwise stability constants K_n for the reactions:

$$PdX_{n-1}(H_2O)_{5-n}^{3-n} + X^- \rightleftarrows PdX_n(H_2O)_{4-n}^{2-n} + H_2O$$

$$K_n = \frac{[PdX_n(H_2O)_{4-n}^{2-n}]}{[PdX_{n-1}(H_2O)_{5-n}^{3-n}][X^-]}; \qquad (1)$$

X = Cl, Br; $n = 1,2,3,4$;

These constants and the spectra of the complexes involved in each equilibrium (1) are necessary for the interpretation of the kinetic measurements. In eqn. (1), $PdX_2(H_2O)_2$ stands for an equilibrium mixture of *cis*- and *trans*-$PdX_2(H_2O)_2$ (*cf. Figure* 6).

Experimental Section

Palladium(II) Perchlorate. The most common method of preparation has been precipitation of palladium hydroxide from chloride or nitrate solutions followed by dissolution of the washed hydroxide in perchloric acid.[1,3,5,7,8,9,13,15,21] Solutions prepared by this method may contain polynuclear hydrolysis products or even colloidal species.[20] The methods used by Jørgensen *et al.*[20] and by Sandell *et al.*[23] give solutions containing much smaller concentrations of such species.

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Stock solutions (5 to 50 mM) of palladium(II) perchlorate were prepared by dissolving, quantitatively, weighed amounts (1 to 10 g) of spectrographically standardized palladium sponge (Johnson and Matthey) in 200 to 400 ml of hot, fuming nitric acid (Merck's *p.a.*, 1.52 kg l^{-1}). The nitric acid was removed by several evaporations (*Caution!*) with concentrated perchloric acid (Baker's *p.a.*, 70-72 %). Finally, the volume was reduced to about 160 ml, and the solution transferred quantitatively to a volumetric flask and diluted by water to 2000 ml. The concentration of perchloric acid was determined by titration with standard alkali and the volume of the solution adjusted to a perchloric acid concentration of 1.00 M.

The stock solutions were standardized gravimetrically for palladium using dimethyl glyoxime. They were tested for chloride by silver nitrate, after precipitation of the palladium as metal by hydrazine sulphate. No chloride was detected.

The absorption spectra of different preparations were identical between 210 and 600 nm (Fig. 1). Even after boiling of the perchlorate for 30 min. with concentrated perchloric acid, its spectrum was unchanged. Thus, there was no indication of an oxidation of the palladium(II) by the hot perchloric acid used in the syntheses, as has been claimed by some authors.[7] The colour of the solutions was yellow (5 mM) to bright red (50 mM).

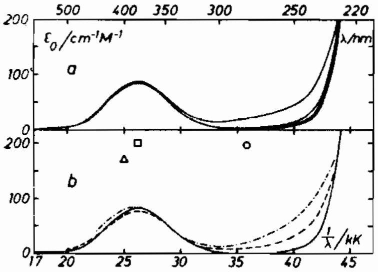

Figure 1. *a*. Spectra of 2 mM palladium perchlorate solutions with ionic strength 1.00 M ($NaClO_4 + HClO_4$). The acid concentration ($HClO_4$) was, from below, 1.00, 0.50 (these curves coincide), 0.20, 0.04 and 0.02 M. In the latter solution, a precipitate of palladium hydroxide was formed slowly. *b*. Spectra of the palladium(II) tetraaqua ion according to different authors: Ref. 3 △, Ref. 7 ○, Ref. 9 —·—·—, Ref. 19 □, Ref. 20 ----, this paper ———.

Figure 1*a* indicates that formation of hydroxo complexes increases the absorbance of palladium(II) perchlorate solutions in the region 230 to 330 nm. High molar absorptivities in this region have also been reported in the literature (Fig. 1 *b*). For instance, Burger and Dyrssen[7] gave $\varepsilon_o^{420} = 230$ cm^{-1} M^{-1}, $\varepsilon_p^{279} = 198$ cm^{-1} M^{-1} and $\varepsilon_o^{235} = 427$ cm^{-1} M^{-1}. A deep and wide minimum at 280 nm ($\varepsilon_o^{280} = 1.102$ cm^{-1} M^{-1} for our solutions) indicates low concentrations of hydrolysis products.

Other solutions. Ligand solutions were prepared from perchloric acid (Bakers's *p.a.*) and hydrochloric acid (Merck's *p.a.*) or hydrobromic acid (Merck's *p.a.*). The hydrobromic acid was distilled immediately before use. The water was doubly distilled from quartz vessels. All solutions had an ionic strength of 1.00 M with perchloric acid as supporting electrolyte. A hydrogen ion concentration of 1M is sufficient to suppress the protolysis of the aqua complexes, including the tetraaqua ion[26] (*cf.* also Fig. 1 *a*).

Apparatus. Spectra were recorded by a Cary 15 Recording Spectrophotometer. A Beckman DU Quartz Spectrophotometer and 4.00 to 0.1000 cm Quartz Suprasil cells (Hellma) were used for the equilibrium measurements.

Measurements. Series of solutions, each having a constant concentration of palladium, C_{Pd}, and varying total concentrations of ligand, C_X, were equilibrated in water thermostats at (25.00±0.01) °C. For the chloride system, 189 solutions, having the following concentrations, were mixed: $C_{Pd} = 4.76\times10^{-5}$ M, 1.000×10^{-4} $M \leqslant C_{Cl} \leqslant 0.500$ M; $C_{Pd} = 9.52\times10^{-5}$ M, 1.000×10^{-5} $M \leqslant C_{Cl} \leqslant 0.500$ M; $C_{Pd} = 2.38\times10^{-4}$ M, 1.000×10^{-3} $M \leqslant C_{Cl} \leqslant 0.300$ M; $C_{Pd} = 4.76\times10^{-4}$ M, 1.000×10^{-5} $M \leqslant C_{Cl} \leqslant 1.000\times10^{-2}$ M; $C_{Pd} = 9.52\times10^{-4}$ M, 1.000×10^{-5} $M \leqslant C_{Cl} \leqslant 3.00\times10^{-3}$ M; $C_{Pd} = 4.70\times10^{-3}$ M, 1.000×10^{-5} $M \leqslant C_{Cl} \leqslant 4.00\times10^{-3}$ M. For the bromide system, 207 solutions were used: $C_{Pd} = 2.35\times10^{-5}$ M, 2.00×10^{-5} $M \leqslant C_{Br} \leqslant 0.1000$ M; $C_{Pd} = 4.76\times10^{-5}$ M, $1.250\times10^{-5} \leqslant C_{Br} \leqslant 0.100$ M; $C_{Pd} = 9.40\times10^{-5}$ M, 1.250×10^{-5} $M \leqslant C_{Br} \leqslant 0.100$ M; $C_{Pd} = 2.38\times10^{-5}$ M, 1.250×10^{-5} $M \leqslant C_{Br} \leqslant 0.1000$ M; $C_{Pd} = 9.40\times10^{-5}$ M, 1.000×10^{-5} $M \leqslant C_{Br} \leqslant 1.000\times10^{-3} M$. No precipitation of $PdBr_2$ occurred in these solutions . The solubility product of $PdBr_2$ is about $3\times10^{-13}M^3$ (Ref. 22).

The absorbance of each solutions was measured at three wave lenghts. With a few exceptions, the

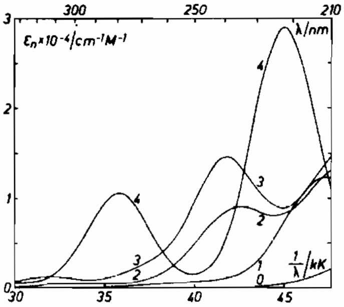

Figure 2. Spectra of the complexes $PdCl_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4 in the UV.

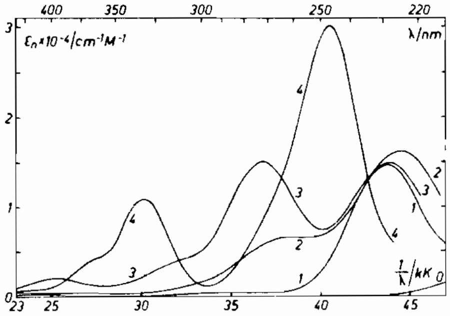

Figure 3. Spectra of the complexes $PdBr_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4 in the UV.

absorbances used for the calculations varied between 0.3 and 0.8. The blank was water. A complete table, containing concentrations and absorbances at the three wave lenghts for each of the 396 solutions is available from this institute. Reviews are given in Figures 4 and 5.

Figures 2 and 3 show resolved spectra of the complexes involved. The two charge transfer bands of $PdCl_4^{2-}$ at 222 and 279 nm and the isosbestic point at 234.5 nm ($\varepsilon_4 = \varepsilon_3$) were used for the chloride system. The bromide system was studied at the corresponding wave lenghts 247, 332 and 265 nm. The high molar absorptivities at these wave lengths (*cf.* Table II) made it possible to use very low concentrations of palladium. This was necessary for the bromide system in order to prevent precipitation of $PdBr_2$.

Spectra. Spectra were recorded at 25.0 °C of 30 solutions containing palladium (9.50×10^{-5} or 4.70×10^{-3} M) and chloride and of 39 solutions containing palladium (4.76×10^{-5}, 4.70×10^{-4} or 4.70×10^{-3} M) and bromide and having varying mean ligand numbers, $\bar{n}$. From these spectra and the stability constants of Table I, the molar absorptivities, ε_n, of the chloro aqua and bromo aqua complexes were calculated at 2.5 nm intervals in the region 210 to 300 nm and at 5 nm intervals in the region 305 to 605 nm. ε_2 represents the molar absorptivity of an equilibrium mixture of *cis-* and *trans-*$PdX_2(H_2O)_2$ (*cf.* Figure 6). A computer and a least squares programme were used for these calculations. The accuracy was good, as a rule within a few percent. The spectra are given in Figures 7 and 8.

Table I. Stepwise stability constants, K_n, and overall stability constants, β_n (given as $^{10}\lg\beta_n$), of the complexes $PdX_n(H_2O)_{4-n}^{2-n}$ at 25°C and $I = 1.00$ M.

Constant	X = Cl	X = Br
$K_1\times10^{-4}/M^{-1}$	2.98 ± 0.06	14.7 ± 0.6
$K_2\times10^{-3}/M^{-1}$	1.92 ± 0.13	18.0 ± 1.0
$K_3\times10^{-2}/M^{-1}$	2.6 ± 0.2	20.0 ± 1.0
$K_4\times10^{-1}/M^{-1}$	2.37 ± 0.10	16.3 ± 0.6
$\lg(\beta_1/M^{-1})$	4.47 ± 0.01	5.17 ± 0.02
$\lg(\beta_2/M^{-2})$	7.76 ± 0.04	9.42 ± 0.04
$\lg(\beta_3/M^{-3})$	10.17 ± 0.07	12.72 ± 0.06
$\lg(\beta_4/M^{-4})$	11.54 ± 0.09	14.94 ± 0.08

Results and Discussion

Stabilities. Figures 4 and 5 review the experiments. ε_{Pd} is defined as $\varepsilon_{Pd} = e/C_{Pd}$, where e is the absorptivity (cm^{-1}). For low values of C_X, the curves for the different C_{Pd}'s are well separated. In these regions ($0<\bar{n}<2$), graphical calculations using the method of corresponding solutions[27] gave preliminary values of the stepwise constants K_1 and K_2. For higher values of C_X, the curves coincide, since $C_X \gg C_{Pd}$, and therefore $C_X \approx [X^-]$. It was necessary to use such low concentrations of palladium, compared to ligand, because of the high molar absorptivities of the third and fourth complex at the wave lengths used, and because of the low solubility of $PdBr_2$.

The stability constants β_1 to β_4 were calculated using the UNIVAC 1108 computer at Lund and the spectrophotometric version of Sillen's least squares programme, « Letagrop ».[28] The following start values of the stability constants were used for these calculations: K_1 and K_2 obtained the method of corresponding solutions, K_4 determined from kinetic studies on the fourth complex formation step,[25] and K_3 obtained by interpolation.

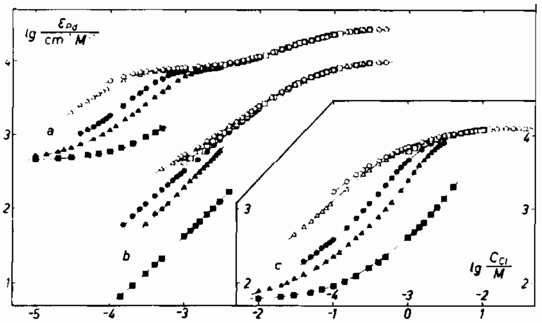

Figure 4. Equilibrium measurements. The palladium(II) chloride system at 222 (a), 279 (b) and 234.5 nm (c). C_{Pd}/M was 4.76×10^{-5} (○), 9.52×10^{-5} (△), 2.38×10^{-4} (□), 4.76×10^{-4} (●), 9.52×10^{-4} (▲) and 4.70×10^{-3} (■). The full-drawn curves were calculated by the computer from the values of K_n and ε_n given in the tables.

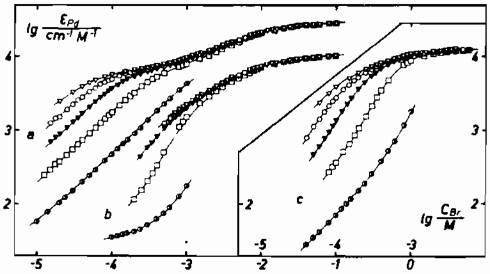

Figure 5. Equilibrium measurements. The palladium(II) bromide system at 247 (a), 332 (b) and 265 nm (c). C_{Pd}/M was 2.35×10^{-5} (▽), 4.76×10^{-5} (○), 9.40×10^{-5} (▼), 2.38×10^{-4} (□) and 9.40×10^{-4} (◑). The full-drawn curves were calculated by the computer from the values of K_n and ε_n given in the tables.

The molar absorptivities of $PdCl_4^{2-}$, $PdBr_4^{2-}$, $Pd(H_2O)_4^{2+}$, Cl^- and Br^- were determined separately (Table II) and given as constants in the calculations. The molar absorptivities of the intermediate complexes were allowed to vary. The obtained stability constants are given in Table I and the molar absorptivities in Table II. The full-drawn curves of Figures 4 and 5 have been calculated by the computer using these parameters. Obviously, they describe the experiments fairly well. The standard deviation for the relative differences between experimental and calculated ε_{Pd} was 1.6% for both systems.

The experiments give no evidence for the formation of a fifth or a sixth complex in the concentration ranges used ($[Cl^-]<0.5$ M; $[Br^-]<0.1$ M.)

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(28) L.G. Sillén and B. Warnqvist, *Arkiv Kemi*, *31*, 377 (1969).

Table II. Molar absorptivites of the complexes $PdX_n(H_2O)_{4-n}^{2-n}$, ε_n, and of the free ligands, ε_{Cl} and ε_{Br}, at the wave lengths used for the equilibrium measurements.

	X=Cl			X=Br		
	222	234.5	279	247	265	332
$\varepsilon_0/cm^{-1}\ M^{-1}$	441±4	58.6±0.5	1.09±0.01	11.2±0.1	1.94±0.02	28.1±0.3
$\varepsilon_1/cm^{-1}\ M^{-1}$	7 600±100	1 670±20	194±2	4 520±30	593±10	93±3
$\varepsilon_2/cm^{-1}\ M^{-1}$	8 300±300	8 970±100	465±10	6 670±100	6 050±100	436±20
$\varepsilon_3/cm^{-1}\ M^{-1}$	8 900±300	13 300±200	1 500±30	8 220±100	13 200±200	1 990±60
$\varepsilon_4/cm^{-1}\ M^{-1}$	29 000±200	12 300±200	10 500±70	29 700±200	12 800±200	10 900±100
$\varepsilon_{Cl}/cm^{-1}\ M^{-1}$	0.01	0	0	—	—	—
$\varepsilon_{Br}/cm^{-1}\ M^{-1}$	—	—	—	0.16	0.06	0

The stability constants obtained for the chloride system agree excellently with those calculated by Weed[11] from spectrophotometric measurements at 410 to 440 nm using the concentration interval 0.2 $mM < C_{Pd} < 5\ mM$. The values of $\lg K_4$ published by Burger and Dyrssen[7,8] (1.34±0.02), Shlenskaya and Biryukov[9] (1.38±0.02) and Levanda[16] (1.43±0.05) also agree with our results.

For the bromide system, few comparisons can be made. Shlenskaya and Biryukov[9,13] have published spectrophotometrically determined values of $\lg K_4$ (2.20 to 2.30) which are consistent with the present results. On the other hand, the $\lg K_l$ values given by Schukarev[21] (4.37) and by Grinberg[14] (6.8) disagree.

Recent potentiometric determinations[12,15] gave $\lg\beta_4$ 11.8±1 and 11.4±0.2 for the chloride system and 14±1 for the bromide system. These values give further support to the present results.

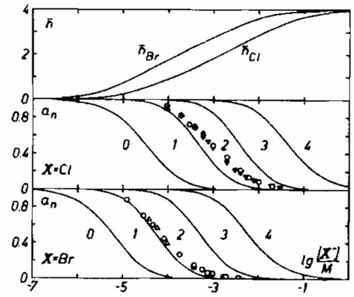

Figure 6. The formation curves and the distribution of palladium between the species $PdX_n(H_2O)_{4-n}^{2-n}$; $n = 0,1,2,3,4$, calculated from the stability constants of Table I. The experimental points denote the fraction $\alpha_0+\alpha_1+\alpha_{trans}$, obtained from kinetic measurements described subsequently.[36] They indicate a *cis/trans* ratio for $PdX_2(H_2O)_2$ of about 2 for the chloride system and about 6 for the bromide system.

Figure 6 gives the graphical representation of the systems. As to be expected for a soft (or *b*) acceptor like palladium, the bromo complexes are stronger than the chloro complexes. The present constants give $\beta_{4Br}/\beta_{4Cl} = 2500\pm200$. Newman and Srivastava[29] have calculated a ratio of 14000±4000 from a spectrophotometric study of the mixed chloro-bromo complexes at the ionic strength 4.5 *M*. The difference between their result and the present value is probably due to medium effects.

Spectra. Whereas spectra of $PdCl_4^{2-}$, $PdBr_4^{2-}$ and $Pd(H_2O)_4^{2+}$ have been described previously,[20,30,31] only one spectrum of a mixed chloro aqua complex (the *d-d* spectrum of $PdCl_2(H_2O)_2$) as been found in the literature.[20]

The charge transfer spectra of these halide complexes are due to transitions of electrons from the ligands to molecular orbitals, localized mainly on the metal. The spectra for the chloro aqua complexes are given in Fig. 7. For $PdCl_4^{2-}$, two bands appear at 35.8 and 45.0 kK. The former is somewhat irre-

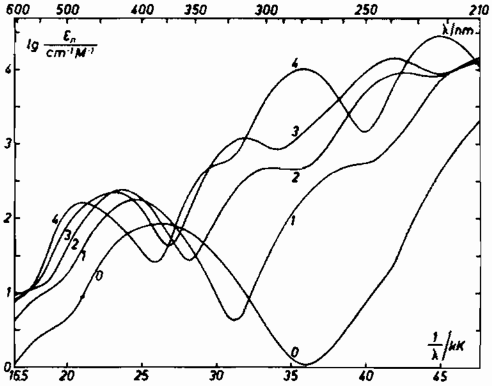

Figure 7. Spectra of the complexes $PdCl_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4.

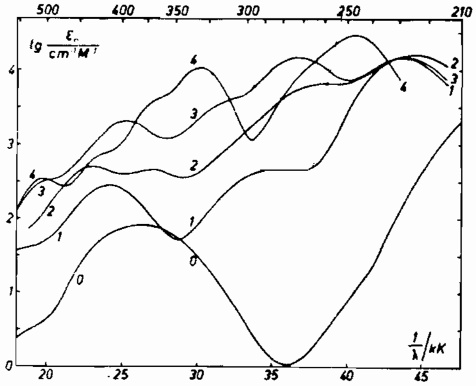

Figure 8. Spectra of the complexes $PdBr_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4.

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gular ($\delta_- = 2.2$, $\delta_+ = 2.0$ kK) According to Gray,[32] this band originates from two transitions, close in energy. When the chloride ligands are replaced by the less efficient electron donor water, the bands are displaced towards higher energies, and the first complex band splits into one shoulder and one peak. For $PdCl_3H_2O^-$, the shoulder appears at about 37 and the peak at 41.8 kK. The second band has its maximum at about 49 kK. For $PdCl_2(H_2O)_2$, the shoulder has moved to about 42.5 and the first peak to about 49kK. The second band has moved to so short wavelenghts that it can no longer be observed. For $PdCl(H_2O)_3^+$, the shoulder has developed into a peak at 47.2 kK. The charge transfer bands have lower energies than the corresponding bands for the platinum(II) chloro aqua complexes,[33] since Pd^{2+} is a better electron acceptor than Pt^{2+}.

In the region between these charge transfer bands and the *d-d* bands, shoulder can be observed at 29.8, 31.8, 33.5 and 38 kK for the complexes $PdCl_4^{2-}$ to $PdCl(H_2O)_3^+$. A corresponding shoulder for $Pd(H_2O)_4^{2+}$ should be expected at about 45 kK. (The weak shoulder with ε about 5 cm^{-1} M^{-1} observed for $Pd(H_2O)_4^{2+}$ at 40.5 kK seems to be too weak even for a *d-d* band). For $PdCl_3H_2O^-$ the shoulder has developed into a peak. The shoulder of $PdCl_4^{2-}$ has previously been attributed to the last spin-allowed *d-d* transition, like the corresponding shoulder for $PtCl_4^{2-}$ at 38kK.[31] Since the shoulder lies so close to the intense band at 35.8 kK, its observed ε of about 500 cm^{-1} M^{-1} is not too high for a *d-d* band. However, this shoulder is displaced about 5 kK between $PdCl_2(H_2O)_2$ and $PdCl(H_2O)_3^+$, and the distance to a corresponding shoulder for $Pd(H_2O)_4^{2+}$ should be at least 7 kK. According to Jørgensen[34] these large displacements probably indicate that the whole series of shoulders are not *d-d* bands, but weak charge transfer bands, corresponding to a transition $\delta_{2g}(\pi) \rightarrow d(x^2-y^2)b_{1g}$. The increased intensity for $PdCl_3H_2O^-$ is also in accordance with this assignment.

The *d–d* spectra of the chloro aqua complexes consist of one small and one broad band (Figure 9). The small peak, due to a spin-forbidden *d–d* transition, has an ε of about 8 to 10 cm^{-1} M^{-1} and appears at 16.5, 17.1, 17.5, 18.0 and 18.8 kK for the complexes $PdCl_4^{2-}$ to $Pd(H_2O)_4^{2+}$. The broad band lies at 21.1, 23.5, 23.7, 24.6, and 26.3 kK and has ε-values of 161, 227, 242, 175 ,and 82.8 cm^{-1} M^{-1}. It is probably composed of two or three closely spaced absorption bands.[31] The complexity of this band is indicated by its irregular shape for $PdCl_4^{2-}$, $PdCl_3H_2O^-$, and $Pd(H_2O)_4^{2+}$, and by its large half-widths. The Gaussion analysis indicated in Figure 9 might be ambiguous for this reason.

The charge transfer bonds of the bromo complexes appear at lower energies than those of the chloro complexes, since bromide is a more efficient electron donor than chloride. Three charge transfer bands are observed (Figure 8). For $PdBr_4^{2-}$, a shoulder appears at 27.3 kK, a peak at 30.2 and a second, higher peak at 40.5 kK. In addition, the second peak has a shoulder at about 36kK, probably a splitting, due to relativistic effects.[35] For $PdBr_3H_2O^-$, the first shoulder lies at 31.5 kK, and the peaks at 36.7 and 43.8 kK. For $PdBr_2(H_2O)_2$ only the shoulder at 37.5 and the peak at 44.5 kK are observable. For $PdBr(H_2O)_3^+$ the shoulder has moved to 43.7 kK and has developed into a peak.

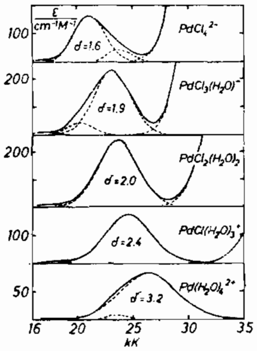

Figure 9. *d-d*-spectra of the palladium(II) chloro aqua complexes.

The charge transfer bands of the chloro complexes are displaced 5 to 7 kK and those of the bromo complexes 4 to 8 kK for each substitution of halide by water. Therefore, the first charge transfer band of $Pd(H_2O)_4^{2+}$ might be expected at about 52 kK, *i.e.* at a somewhat lower energy than that proposed by Jørgensen and Rasmussen[20] (~57 kK).

The charge transfer bands of the bromo complexes appear at such low energies that they partly conceal the weaker bands, especially those of $PdBr_4^{2-}$, $PdBr_3H_2O^-$ and $PdBr_2(H_2O)_2$. Shouders, corresponding to the series observed for the chloro aqua complexes, appear for $PdBr_2(H_2O)_2$ at 32.5 and for $PdBr(H_2O)_3^+$ at 35 kK. These should also be weak charge transfer bands.

Bands, probably due to spin-allowed *d-d* transitions, appear for $PdBr_4^{2-}$ at 19.7 and 23.5 kK, for $PdBr_3(H_2O)^-$ at 20.3 and 25.2, and for $PdBr_2(H_2O)_2$ at 22.9 and 27.2. For $PdBr(H_2O)_3^+$ only one broad band ($\delta = 2.2$ kK), probably due to at least two transitions, is observed at 24.2 kK. A weak, spin-forbidden *d-d* band with an ε of about 30 cm^{-1} M^{-1} appears for $PdBr(H_2O)_3^+$ at about 18.0 kK.

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