The Influence of Nitrate and Other Anions on the Absorption Spectra of Palladium(II)

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Whereas (at negative pH) *p*-toluenesulfonate and perchlorate only produce marginal "salt effects" on the spectrum of palladium(II) aqua ions, nitrate shows a definite change of the band positions and intensities indicating the first complex to have $K_1 = (1.2 \pm 0.4) \text{ M}^{-1}$ though it is likely that bis- and perhaps higher complexes also occur. Sulfate complexes, and general treatments of data about weak complexes (and their first-order band shift), as well as the stereochemistry of Pd(II) and its behaviour compared to copper(II), are also discussed.

dielectric constant. Strong aqueous solutions of lithium or calcium nitrate, or to a somewhat larger extent nitric acid, modify the visible spectrum of the aqua ion measurably, and about three times more than comparable concentrations of perchlorates. It is a fundamental difficulty that such "salt effects" always can be interpreted¹ as formation of a weak complex with the formation constant $K_1 = [\text{MX}]/[\text{M}][\text{X}]$ and the molar extinction coefficient ϵ_1 (as function of the wave-length).

I. INTRODUCTION

Though unidentate nitrate complexes such as $\text{Co}(\text{NH}_3)_5(\text{ONO}_2)^{+2}$ and $\text{Co}(\text{NH}_3)_3(\text{ONO}_2)_3$ were prepared by S. M. Jørgensen, and a large number of crystal structures are known to involve bidentate nitrate, such as anhydrous $\text{Co}(\text{O}_2\text{NO})_3$ isoelectronic with $\text{Co}(\text{O}_2\text{CO})_3^{-3}$, icosahedral $\text{Ce}(\text{O}_2\text{NO})_6^{-3}$, hexagonal-bipyramidal $\text{UO}_2(\text{O}_2\text{NO})_3^{-}$, ... most solution chemists consider nitrate almost as non-complexing as perchlorate. This may very well be a specific property of aqueous solutions, since the spectacular intensification of visible bands of cobalt(II) and nickel(II) nitrate in approximately anhydrous ethanol¹ was shown by Katzin^{2,3} to be dependent on the presence of one nitrate ligand besides nearly all the other ligands being ethanol. This observation cannot be explained simply as an order of affinity $\text{H}_2\text{O} > \text{NO}_3^- > \text{C}_2\text{H}_5\text{OH}$ since a huge excess of nitrate^{1,3} does not modify perceptibly the aqua ion spectrum in 80 vol. % alcohol (5 M H_2O) nor in mixtures containing 50 % CCl_4 having a far lower

$$\epsilon_1 = \epsilon_0 + (\epsilon_s/K_1) \quad (1)$$

where the salt effect is linear ($\epsilon = \epsilon_0 + \epsilon_s C_x$) and the amount of complex so small that the total and free concentrations C_x and $[\text{X}]$ cannot be distinguished within experimental uncertainty. Such a result is indeterminate insofar as the ratio (ϵ_s/K_1) cannot be separated in its two terms unless the mass-action law remains approximately valid in concentration units, and K_1 is sufficiently large that $[\text{X}]$ can be made larger than $(1/K_1)$ (at which point $\bar{n} = 1/2$). It is an additional difficulty that perchlorate and nitrate "salt effects" have ϵ_s positive and actually roughly proportional to ϵ_0 (the bands are not shifted much) whereas robust complexes dissolved in mixtures of two solvents do not normally obey eqn. (1) but show a smooth shift of the band positions^{4,5} without an isosbestic point (as when ϵ_s changes its sign) or being expressed as a linear combination of two spectra ϵ_0 and ϵ_1 .

Table 1. Absorption spectra of 0.01 M palladium(II) solutions (when marked with an asterisk, 0.001 M only). Hts is *p*-toluenesulfonic acid.

No.	Composition	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	ϵ_{490}	ϵ_{520}
1	2 M Hts	382	86	6.6	4.3
2	1 M Hts	380	85	6.3	4.2
3	1 M Hts + 1 M HClO ₄	381	83	6.5	4.2
4	1 M Hts + 1 M NaClO ₄	381	84	6.7	4.4
5	1 M Hts + 2 M NaClO ₄	383	85	6.8	4.3
6	1 M Hts + 0.5 M H ₂ SO ₄	390	106	9.5	5.7
7	0.5 M H ₂ SO ₄	392	120	12.1	7.2
8	0.5 M H ₂ SO ₄ + 0.25 M Na ₂ SO ₄	395	141	14.7	8.6
9	0.5 M H ₂ SO ₄ + 0.5 M Na ₂ SO ₄	396	145	15.5	8.8
10	0.5 M H ₂ SO ₄ + 1 M NaClO ₄	392	118	11.8	6.7
11	0.5 M H ₂ SO ₄ + 1 M NaNO ₃	396	127	14.4	9.2
12	1 M Hts + 1 M NaNO ₃	395	111	14.1	10.4
13	1 M Hts + 1 M HNO ₃	396	114	19.3	11.2
14	1 M Hts + 0.1 M HNO ₃	382	91	8.4	5.6
15*	1 M Hts + 0.01 M HNO ₃	381	83	—	—
16	0.5 M Hts + 0.1 M HNO ₃	381	90	7.5	5.0
17	5 M HNO ₃	414	143	42.3	23.5
18	1 M HNO ₃ + 4 M NaNO ₃	408	134	34.2	18.8
19	1.1 M HNO ₃ + 2 M NaNO ₃	404	129	27.0	15.0
20	1.1 M HNO ₃	395	116	17.2	9.8
21	1.1 M HNO ₃ + 4 M NaClO ₄	402	116	22.4	12.3
22	1.1 M HNO ₃ + 1 M NaClO ₄	395	115	18.0	10.0
23	0.6 M HNO ₃ + 1.5 M NaClO ₄	392	104	13.3	7.7
24*	0.5 M HNO ₃ + 1.5 M NaClO ₄	390	101	—	—
25	0.35 M HNO ₃ + 1.75 M NaClO ₄	388	95	10.4	6.1
26*	0.25 M HNO ₃ + 1.75 M NaClO ₄	386	95	—	—
27	0.1 M HNO ₃ + 1 M HClO ₄ + 1 M NaClO ₄	382	87	7.4	4.5

II. THE PALLADIUM(II) AQUA ION

It is a condition for studying this yellow species⁶ to have pH below 0.5 in order to avoid slow irreversible hydrolysis to dark brown products. Since a positively charged ion cannot be studied without the presence of anions, the first step is to assure that two solutions in different strong acids, say perchloric and *p*-toluenesulfonic, have the same spectrum. The latter acid has the advantage³ not to esterify alcohols at a detectable rate. In the following, CH₃C₆H₄SO₃⁻ is called ts⁻. From a critical point of view,⁷ coincidence of two such spectra does not prove the exclusive presence of the aqua ion, because it may have (though rather unlikely) exactly the same ϵ values as one of the anion complexes (or both). Fig. 1 and Table 1 show that the spectra are indeed very similar at pH=0, whereas sulfuric acid shows a small, and nitric acid a marked shift toward longer wave-lengths. Such a shift and intensification in nitrate solutions has been mentioned in a qualitative

Fig. 1. Absorption spectra of the solutions Nos. 2, 20 and 17 (compositions given in Table 1) and the mono-nitrato complex extrapolated according to eqn. (6).

way⁸ though many results in literature are hampered by the brown hydrolysis products occurring when precipitated palladium hydroxide (oxide?) is dissolved in acidic solutions.

Palladium(II) has exceedingly large formation constants with "conventional" ligands. Thus, $\log \beta_4 = 12$ for the chloro and 32.8 for the ammonia⁶ complexes. It might be argued that in such a situation, nitrate may very well have the much smaller $K_1 = 1$. However, NO_3^- is not normally considered a "soft" ligand in Pearson's sense^{7,9} and it would not be expected to compete more successfully with water as a ligand than, say, with Co(II). Arguments of "ligand field stabilization" applicable to octahedral complexes¹⁰ are not as relevant in quadratic complexes. Actually, the absorption spectra are closely similar⁷ to copper(II) having roughly half the wave-numbers of Pd(II) with the same ligands, but higher wave-numbers than Ni(II), expressing a certain "tetragonality ratio". It is an experimental fact⁶ that most Pd(II) ammine complexes show only one, almost symmetrical absorption band. Seen from the point of the *angular overlap model*^{11,12} this suggests almost identical one-electron energies of all four filled $4d$ -like orbitals, showing transitions to the strongly anti-bonding empty ($x^2 - y^2$). One would have expected the filled ($3z^2 - r^2$) to be one-third as anti-bonding. This experiment discrepancy (first noted¹³ in PtCl_4^{2-}) is most readily explained by a mixture of $4d$ and $5s$ characters. More direct experimental evidence has recently been obtained¹⁴ for such $3d-4s$ mixing in the yellow nickel(II) complex of the strained cyclic aliphatic diamine "daco" where the three almost coinciding transitions (at 22370, 23480 and 24540 cm^{-1}) can be distinguished, using polarized light. Like in the Cu(II) aqua ion,⁷ the Pd(II) aqua ion⁶ shows a perceptible shoulder at 410 nm (*cf.* Fig. 1) and it has even been suggested¹² that it might be tetragonal-pyramidal $\text{Pd}(\text{OH}_2)_5^{+2}$ with a loosely bound fifth water molecule destabilizing ($3z^2 - r^2$). Another argument is the marginal increase^{6,15} of ϵ from 200 to 210 for $\text{Pd}(\text{NH}_3)_4^{+2}$ going from dilute solution to 1 M NaClO_4 . This may either be a salt effect as discussed above, or due to a five-coordinate $\text{Pd}(\text{NH}_3)_4(\text{OCIO}_3)^+$. Many such observations are known, but not fully understood. For instance Harry C. Jones found in 1909 that moderate nitrate concentrations (above 0.5 M) modify the narrow absorption bands of trivalent lanthanides, and the spectroscopic effects¹⁶ of such nitrate complexation can be quite spectacular. This forms a striking

contrast with chloro complexes, where spectral changes indicating direct $\text{Ln}-\text{Cl}$ contacts only occur well above 5 M HCl, though classical physico-chemical techniques (measuring activities) suggest outer-sphere complexes with K_1 close to 1. Anyhow, it is beyond doubt that Pd(II) phenanthroline¹⁷ with two (three in the case of OH^-) residual coordination positions shows a considerable affinity for nitrate, and Schurter¹⁸ prepared complexes of php^- , the deprotonated 2-phenylpyridine (becoming isoelectronic with bidentate 2,2'-dipyridyl) containing either nitrate or even solid $\text{Pd}(\text{php})(\text{OCIO}_3)(\text{OH}_2)$. A recent review¹⁹ of platinum group nitrate complexes notes that low electronegativity of the other ligands enhances the affinity to nitrate, based on preparative methods. A characteristic of the (usually single) Pd(II) absorption band^{6,7} is the unusually large ϵ . It must be noted that multidentate organic ligands^{20,21} readily can enhance ϵ to the region 500 to 1500 again showing a certain similarity with Cu(II). The less pronounced intensification (ϵ increasing 60 %) by one nitrate ligand is reminiscent of the hypersensitive pseudoquadrupolar transitions.¹⁶

It is worthwhile to start the discussion with a few remarks about the sulfate complexes. It is seen from Table 1 that 0.25 M Na_2SO_4 added to 0.5 M H_2SO_4 almost doubles the effect of the acid alone. This seems to indicate a weak complex of SO_4^{2-} of which the free concentration is decreased by protonation ($\text{p}K_2$ around 1) as seen from the effect of 1 M Hts. The question of sulfate complexes is important to us, because the preparation of anhydrous and hydrated modifications of PdSO_4 described by Kane in 1842 serves^{6,17} to make solutions of the aqua ion (say 0.01 M) of which the spectra do not change perceptibly if treated by stoichiometric amounts of $\text{Ba}(\text{ClO}_4)_2$ or $\text{Ba}(\text{ts})_2$ and the BaSO_4 is carefully filtered off. Actually, eleven of our solutions were made in parallel experiments either using the sulfate or with the alternative of making 1.5 M Pd(II) from the metal in concentrated nitric acid. However, it is necessary to boil such a solution for several hours in order to avoid subsequent persistent formation of NO_2 presumably due to intermediate nitrosyl or nitrito complexes.

III. NITRIC ACID AND NITRATE SOLUTIONS AND BAND SHIFTS OF WEAK COMPLEXES

Spectral data for 27 solutions are given in Table 1, Nos. 1–13 made from 0.01 M PdSO_4 and 14–27 from a stock solution of Pd(II) in 5 M HNO_3 to a final palladium concentration 0.01 M (except 15, 24 and 26 marked with an asterisk, 0.001 M). Five solutions of 0.001 M Pd(II) , but otherwise having the compositions of Nos. 17, 18, 29, 21 and 22, were shown to have the same spectra, with ϵ_{max} not differing more than 1 or 2 %, and λ_{max} within 1 nm. As one would expect, no evidence for oligomeric complexes occurs, and the differences in 24* and 26* are due to differing nitrate concentration originating from the stock solution.

There is a smooth shift of the spectra (in contrast to the marginal salt effects in presence of high concentrations of ts^- and ClO_4^-) as a function of increasing total nitrate concentration C_x . However, a comparison of 17 with 18 shows that 5 M nitric acid, rather than being partly undissociated, actually exhibits an activity higher than 5 M sodium nitrate. It is noted in solution 10 that 1 M NaClO_4 rather counteracts the formation of sulfate complexes slightly, whereas the spectrum 11 may be due to mixed nitrate-sulfate coordination. Also solution 21 with 4 M NaClO_4 may contain nitrate-perchlorate complexes.

One might imagine that the shift of ϵ_{max} would be a quadratically unstable function of small $\bar{n}$ values in the case of an aqua ion (ϵ_0) in equilibrium with a mono-complex (ϵ_1) showing an apparent

$$\epsilon = (1 - \bar{n}) \epsilon_0 + \bar{n} \epsilon_1 \quad (2)$$

However, this is not true, as seen from the simple model of ϵ_0 varying as an inverted parabola close to the maximum ϵ_0^0 at λ_0 (we are here adapting the description by Claus Schäffer of absorption bands as Gaussian error-curves with the wavelength λ as variable) and ϵ_1 increasing linearly for λ slightly above λ_0 :

$$\begin{aligned} \epsilon_0 &= \epsilon_0^0 - \frac{1}{2} \epsilon'' (\lambda - \lambda_0)^2 \\ \epsilon_1 &= \epsilon_1^0 + \epsilon' (\lambda - \lambda_0) \end{aligned}$$

The differential quotient of ϵ in eqn. (2) is then

$$(\bar{n} - 1) \epsilon'' (\lambda - \lambda_0) + \bar{n} \epsilon' \quad (4)$$

which is zero for the maximum at

$$(\lambda - \lambda_0) = \frac{\bar{n} \epsilon'}{(1 - \bar{n}) \epsilon''} \quad (5)$$

The aqua ion spectrum seen in Fig. 1 has $\epsilon'' = 0.04 \text{ nm}^{-2}$. If ϵ' has the plausible value 1 nm^{-1} , eqn. (5) indicates a shift of λ_{max} to the extent 25 nm times the quantity $\bar{n}/(1 - \bar{n})$ which is equal to the product $K_1 C_x$. If the solutions in Table 1 having total nitrate concentrations C_x between 0.25 and 0.6 M are considered, λ_{max} is seen to shift (20 nm) C_x . Taken at its face value, this argument gives $K_1 = (20/25) = 0.8$. However, the extrapolated spectrum of the mono-nitrato complex discussed below (and given as a dashed line in Fig. 1) suggests $\epsilon' = 0.8 \text{ nm}^{-1}$ which has the corollary $K_1 = 1$. Obviously, this method can only produce the order of magnitude of K_1 but it should be emphasized that the shift of λ_{max} has no direct relation to the actual maximum of ϵ_1 at λ_1 since small shifts are determined by the ratio (ϵ'/ϵ'').

If higher complexes are not formed, or if (K_2/K_1) is reasonably small, it is possible to exploit a set of spectra like ours without having the opportunity of evaluating the depletion of $[\text{X}] = C_x - \bar{n} C_M$. The most practical technique is to study ϵ as a function ($1/C_x$). We know the asymptotic ϵ_0 from the aqua ion, and the mass-action law for one complex then gives

$$\epsilon = \epsilon_1 + \frac{\bar{n}}{K_1 C_x} (\epsilon_0 - \epsilon_1) \quad (6)$$

Thus, the spectra for ($1/C_x$) = 1.67, 0.91 and 0.33 M^{-1} allow an extrapolation to 0 M^{-1} giving $\epsilon_1 = 137$ at 410 nm and $\epsilon_1 = 133$ at 420 nm. In both cases, $\epsilon = (\epsilon_0 + \epsilon_1)/2$ indicating $\bar{n} = \frac{1}{2}$ (= 102 and 95, respectively) occurs for ($1/C_x$) = 1.4 M^{-1} corresponding to $K_1 = 1.4$.

However, there is no doubt that higher complexes are formed. The maximum for ϵ_1 derived from eqn. (6) every 10 nm in the interval 360 to 420 nm occurs at 404 ± 2 nm, 10 nm below the observed maximum in 5 M HNO_3 . If one had the extreme situation of four complexes, up to $\text{Pd}(\text{NO}_3)_4^{-2}$, formed statistically, K_1 in eqn. (6) would be the average K_{av} and the real $K_1 = 4K_{\text{av}}$. However, this is entirely improbable in view of the pronounced⁶ characteristic coordination number $N_0 = 2$ for Pd(II) . If $K_1 = 2K_{\text{av}}$ and $K_2 = \frac{1}{2}K_{\text{av}}$ the spectra ϵ_1 and ϵ_2 can be determined in a way

compatible with our data, ϵ_2 having its maximum close to 422 nm. It is not possible without circumspection^{6,7} to apply Tsuchida's rule of average environment to quadratic complexes, though the spectrochemical position of nitrate then at first seems almost as low as of chloride.

Table 1 indicates the ϵ values at 490 and at 520 nm. We measured the spectra of 0.01 M Pd(II) in 4 cm cells in the region below 650 nm in the hope of finding an interval with $\epsilon_2 \gg \epsilon_1 > \epsilon_0$ which might have helped to characterize the bis-complex, much like CoCl_4^{2-} and CuCl_4^{2-} in the visible.²² However, this did not succeed, insofar ϵ at several λ varies with the same proportionality factor. This unexpected regularity is connected with the spin-forbidden transitions to excited triplet states in the 500–550 nm region. If these absorption band tails are treated according to eqn. (6), K_1 is close to 1.0. However, this value may be influenced by the bis-complex having $\epsilon_2 > 2\epsilon_1$ with resulting admixture of the smaller K_2 during the extrapolation.

IV. CONCLUSION

In aqueous solution, at pH close to zero, palladium(II) forms a mono-nitrate complex with

$$K_1 = (1.2 \pm 0.4) \text{ l/mol}$$

There is little hope of ameliorating the uncertainty, because of variable activity coefficients. As discussed in the text, several of the techniques for evaluating the spectra tend to weight the contribution from a bis-complex at higher nitrate concentration. On the other hand, *p*-toluenesulfonate and perchlorate at 1 to 2 M only induce marginal "salt effects" which is surprising, since one might expect the stereochemistry of the aqua ion to be rather flexible. It is noteworthy that Pd(II) both forms an ethylenediamine complex⁶ of which K_1 is so large that it cannot be determined in solvents remaining essentially aqueous solutions with a few M ions, and a nitrate complex where K_1 is so small that it is difficult to determine in a meaningful way, much like the first chloro complex²² of copper(II).

V. EXPERIMENTAL

The spectra were measured in 1 cm (or 4 cm) cells on a Unicam SP8-100 spectrophotometer. Palladium sulfate was prepared⁶ and found by grav-

imetric analysis (Pd as dimethylglyoximate, SO_4 as barium sulfate) to be almost anhydrous and stoichiometric: Pd 51.5 %, SO_4 46.5 % and 2 % of water. The solutions were made from Merck *p.a.* 65 % concentrated nitric acid, *p.a.* 96 % sulfuric acid, 70 % perchloric acid, sodium perchlorate monohydrate, sodium nitrate and sodium sulfate and from Fluka *p.a.* *p*-toluenesulfonic acid monohydrate (known to contain H_3O^+ ts^-).

A solution of palladium nitrate was made by boiling 5.4 g of palladium powder (Métaux Précieux, Neuchatel) in 34.6 ml of conc. nitric acid, to complete dissolution, followed by prolonged heating for 3 h to destroy an unidentified source of NO_2 , and finally diluted to 100 ml with water.

A solution of $\text{Ba}(\text{ts})_2$ was obtained by dissolving Merck *p.a.* barium carbonate in 1 M Hts. All the solutions were tested with a drop of silver nitrate solution under conditions⁶ particularly sensitive to the presence of Cl^- (or Br^-) forming strongly coloured complexes with palladium.

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