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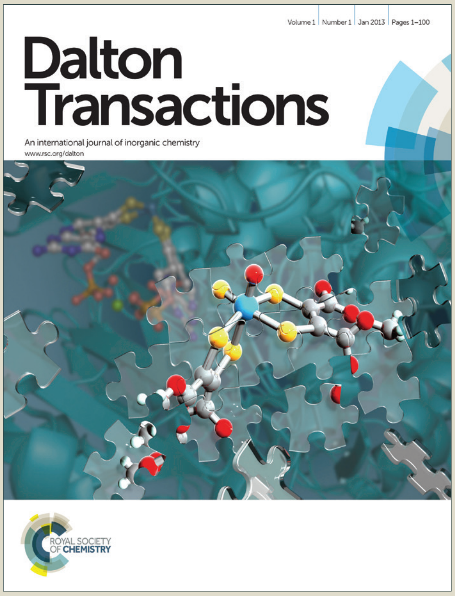

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Thermodynamics for Complex Formation between Palladium(II) and Oxalate

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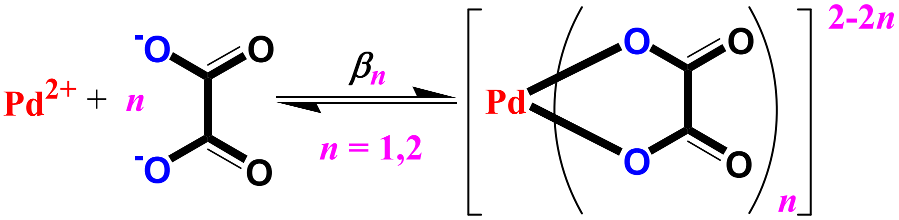
Overall stability constants and thermodynamic parameters for formation of palladium(II) oxalato complexes have been determined. The chelate effect is discussed.



KEY WORDS: palladium(II); oxalic acid; complex formation; thermodynamic parameters; Specific Ion interaction Theory (SIT); chelate effect.

Abstract

Complex formation between $[Pd(H_2O)_4]^{2+}$ and oxalate (ox = $C_2O_4^{2-}$) has been studied spectrophotometrically in aqueous solution at variable temperature, ionic strength and pH. Thermodynamic parameters at 298.2 K and 1.00 mol.dm^{-3} $HClO_4$ ionic medium for the complex formation

$$[Pd(H_2O)_4]^{2+} + H_2ox \rightleftharpoons [Pd(H_2O)_2(ox)] + 2H_3O^+$$

with equilibrium constant $K_{1,H}$ (in mol.dm^{-3}) are $\log_{10}K_{1,H} = 3.38 \pm 0.08$, $\Delta H_1^0 = -33 \pm 3$ kJ.mol^{-1}, and $\Delta S_1^0 = -48 \pm 11$ J.K^{-1}.mol^{-1}, as determined from spectrophotometric equilibrium titrations at 15.0, 20.0, 25.0 and 31.0 °C. Thermodynamic overall stability constants β_n^0 (in (mol.dm^{-3})^n, n=1,2) for $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$ at zero ionic strength and 298.2 K, defined as the equilibrium constants for the reaction

$$Pd^{2+} + n\ ox^{2-} \rightleftharpoons [Pd(ox)_n]^{2-2n}$$

(water molecules omitted) are $\log_{10}\beta_1^0 = 9.04 \pm 0.06$ and $\log_{10}\beta_2^0 = 13.1 \pm 0.3$, respectively, calculated by use of Specific Ion Interaction Theory from spectrophotometric titrations with initial hydrogen ion concentrations of 1.00, 0.100 and 0.0100 mol.dm^{-3} and ionic strengths of 1.00, 2.00 or 3.00 mol.dm^{-3}. The values derived together with literature data give overall stability constants for Pd(II) compounds such as [Pd(en)(ox)] and *cis*-$[Pd(NH_3)_2Cl_2]$, some of them analogs to Pt(II) complexes used in cancer treatment. The palladium oxalato complexes are significantly more stable than palladium(II) complexes with monodentate O-bonding ligands. A comparison between several different palladium complexes shows that different parameters contribute to the stability variations observed. These are discussed together with the so-called chelate effect.

Introduction

Palladium(II) chemistry in aqueous solution is of interest as a model for analogous platinum(II) systems, due to higher reactivity, well defined oxidation state and ease of preparation of the aqua ion.[1,2] Thermodynamic data for palladium(II) oxalato complexes are relevant *per se*, but also for the understanding of the *in vivo* reactivity of platinum(II) oxalato compounds used as cancerostatic drugs (*vide infra*),[3] and for the preparation of partially oxidized platinum(II)-oxalato systems as nanowires.[4,5]

Oxalic acid ($H_2C_2O_4$ or H_2ox) and other carboxylic acids are found in soils in comparatively high concentrations (10^{-4}-10^{-3} mol.dm^{-3}) as well as in surface waters.[6,7] Oxalic acid in natural waters is formed by microbial or chemical degradation of biomolecules originating from terrestrial and aquatic plant and animal residues.[7] It is also formed in Fenton-type reactions in the interior of waterlogged archaeological wood, causing artefact degradation.[8] Oxalates occur in nuclear waste depositories where it is a major product of radiolytic degradation of bitumen and ion exchange resins, employed for waste treatment.[9,10] Together with humic acids, oxalate is one of the most strongly binding naturally occurring organic ligands for metal ions.[11,12] Since the isotope ^{107}Pd is abundant among the long-lived fission products in spent nuclear fuel,[11,12] modelling of its chemical transformations and migration in natural waters requires reliable thermodynamic sequestering data, including those for oxalate complex formation.[9,10,13] Recently, the thermodynamic properties of oxalate complexation with some other radionuclides (*e.g.* U, Np) were studied.[13-15]

The reactivity of palladium(II) towards a number of mono- and dicarboxylic acids (formic, acetic, propionic, butyric, glycolic, DL-lactic, 2-methyllactic, methoxyacetic, malonic, succinic, oxydiacetic, L-malic, citric, chloroacetic) has been reported recently, taking thermodynamic as well as kinetic aspects into account.[16-20] The mechanism for the reaction between palladium(II) and maleic acid, resulting in formation of a palladium(II) olefin complex, has been studied in some detail.[18] Properties and crystal structures of $K_2[Pd(ox)_2]\cdot 4H_2O$ and $Na_2[Pd(ox)_2]\cdot 2H_2O$, which are isostructural with $K_2[Pt(ox)_2]\cdot 2H_2O$, have been reported,[21-23] as well as those for $[Pd(NH_3)_4][Pd(ox)_2]$.[24] The structural motif with oxalate acting as a bidentate chelating ligand is retained also in the mixed ternary species $K_2[Pt(ox)Cl_2]\cdot H_2O$ and in the platinum(IV) compound $Na_2[\textit{trans}\text{-}Pt(OH)_2(ox)_2]\cdot 6H_2O$.[25,26] Crystal structures of ternary complexes with vitamin-B_6 molecules $[Pd(ox)L_2]$ (L = pyridoxine, pyridoxal, pyridoxamine) have been reported.[27] Solid $M_2[Pd(ox)_2]\cdot xH_2O$ (M = K, Na) or aqueous solutions of Pd(II) and oxalic acid containing chloride decompose slowly to metallic palladium when exposed to sunlight or laser illumination.[21,22,28]

A qualitative study of complex formation between palladium(II) and oxalate using UV/VIS and FTIR spectroscopy at 25 °C and pH ≈ 6-7 as a function of the concentrations of chloride and oxalate has shown that palladium(II)-oxalato complexes are formed already at relatively low oxalato concentrations.[6,29] For $[Cl^-] > 1$ mol.kg^{-1}, only $[PdCl_4]^{2-}$ and one mono-oxalato complex were observed, whereas two oxalato complexes were found for lower chloride concentrations.[6,29] Only one quantitative study of palladium(II) oxalato complexes with calculated stability constants for the two complexes $[Pd(ox)_n]^{2-2n}$ ($n = 1,2$) has been found in the literature, determined at low ionic strength and low temperature, though.[29] These authors also demonstrated that the complexes formed in the presence of a 100-fold excess of oxalate are resistant to hydrolysis up to pH about 6.0.[29] Complex formation between palladium(II) and oxalate has been utilized for spectrophotometric or chelatometric determination of palladium(II) using the masking effect of oxalate.[29,30]

The present work extends our previous studies on reactions between palladium(II) and carboxylates.[16-20] The thermodynamics of palladium(II)-oxalate complex formation has been studied by spectrophotometric multi-wavelength measurements at variable temperatures, ionic strengths and pH.

Experimental

Chemicals

Stock solutions of palladium(II) perchlorate and perchloric acid were prepared and standardized as described earlier.[1,19,20] Analytical grade oxalic acid dihydrate from Merck (Germany) was used as received. Sodium perchlorate and perchloric acid were analytical grade from Fluka (Switzerland). Aqueous solutions were prepared using triply distilled water.

Equilibrium measurements

UV/VIS spectra were recorded by use of a single-beam diode-array spectrophotometer HP 8453 A (Hewlett Packard, USA). In the equilibrium measurements, ligand concentrations were varied between 0 and 0.05 mol.dm^{-3}, higher concentrations being limited by the solubility of oxalic acid under the experimental conditions used.[9] In order to follow the formation of the two stable complexes $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$, spectrophotometric titrations with initial hydrogen ion concentrations of 1.00, 0.100 or 0.0100 mol.dm^{-3} (adjusted with perchloric acid) and ionic strengths 1.00, 2.00 or 3.00 mol.dm^{-3} (adjusted with $NaClO_4$) were performed. A dilute solution of palladium(II) perchlorate ($\approx 4\times10^{-3}$ mol.dm^{-3}) with a preset hydrogen ion concentration and without added oxalate, was titrated under stirring and constant temperature with a solution of oxalic acid with the same ionic medium and hydrogen ion concentration. Since complex formation is fast,[31] samples of the equilibrated solutions were transferred as quickly as possible after mixing from the thermostated titration vessel to the spectrophotometer cell for absorbance recording, in order to eliminate side reactions, *e.g.* Pd(II) hydrolysis or photolytic decomposition of the palladium oxalato species formed. The palladium(II) perchlorate solutions in the slightly acidic $(Na,H)ClO_4$ medium were freshly prepared immediately before measurement in order to avoid slow formation of hydrolysis products.[32-37]

All experiments were carried out under reduced light in a dark laboratory and the titration vessel was wrapped with black paper to protect solutions from light. These precautions were undertaken since it is known that acidic palladium(II) solutions containing oxalate decompose slowly (during 24 h) when illuminated by day or artificial light, forming palladium black, probably due to reactions (A) and (B).[22,38]

$$[Pd(H_2O)_2(C_2O_4)] \rightarrow Pd + 2\ CO_2 + 2\ H_2O \qquad (A)$$

$$[Pd(C_2O_4)_2]^{2-} \rightarrow Pd + 2\ CO_2 + C_2O_4^{2-} \qquad (B)$$

Analogous reactions have been observed in the case of uranium(VI) oxalate.[13] Equilibrium data were collected at (25.0 ± 0.2) °C. Reaction enthalpy and entropy changes (ΔH^0, ΔS^0), were determined from additional titration data recorded at 15.0, 20.0 and 31.0 °C. Titrations were also performed at 2.00 and 3.00 mol.dm^{-3} ionic strength in order to extrapolate the calculated concentration stability constants of $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$ to zero ionic strength. Absorbance matrix data (number of solutions × number of wavelengths) were treated by use of the OPIUM program.[39] Experimental data are given in ESI, Figures S1-S3, and examples of data treatment are given in Fig. 1.

Figure 1

Results and discussion

Concentration stability constants

Complex equilibria were studied at hydrogen ion concentrations of 1.00, 0.100 and 0.0100 mol·dm^{-3} at 298.2 K. In 1.00 mol.dm^{-3} $HClO_4$, the complex $[Pd(H_2O)_2(ox)]$ is predominant. Formation of $[Pd(ox)_2]^{2-}$ only starts in less acidic medium (0.0100-0.100 mol.dm^{-3} $HClO_4$). Therefore, the stability constant for $[Pd(H_2O)_2(ox)]$ can be reliably calculated from measurements in 1.00 mol.dm^{-3} perchloric acid, without interference from the second complex formation step. The equilibrium constant for formation of $[Pd(H_2O)_2(ox)]$ according to reaction (C) is defined by eq. (1), where co-ordinated water molecules are omitted.

$$[Pd(H_2O)_4]^{2+} + H_2ox \underset{}{\overset{K_{1H}}{\rightleftharpoons}} [Pd(H_2O)_2(ox)] + 2\ H_3O^+ \qquad (C)$$

$$K_{1H} = [Pd(ox)][H^+]^2/([Pd^{2+}][H_2ox]) = K_{1H,cond}\,[H^+]^2 \qquad (1)$$

$$K_{1H,cond} = K_{1H}/[H^+]^2 = [Pd(ox)]/([Pd^{2+}][H_2ox]) \qquad (2)$$

The conditional equilibrium constant $K_{1H,cond}$ is obtained from the spectrophotometric equilibrium measurements, and K_{1H} from eq. (1).[40] If reaction (C) takes place, the value of K_{1H} should be the same for solutions with different pH, corrected for ionic strength effects (*vide infra*). This condition is fulfilled, as demonstrated below (SIT treatment of equilibrium constants). Noteworthy, $K_{1H,cond} = K_{1H}$ for $[H^+] = 1.00$ mol.dm^{-3}. In order to determine the uncertainty in K_{1H}, a duplicate experiment at 25.0 °C and 1.00 mol.dm^{-3} $HClO_4$ was performed. The two values obtained of $\log_{10}K_{1H}$ are 3.29 ± 0.01 and 3.38 ± 0.03, in good agreement. The final weighted average value is 3.34 ± 0.08, calculated by a numerical procedure described elsewhere.[9]

The stability constants β_1 and β_2 for the complexes $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$ formed according to reaction (D) were calculated by use of eq. (3), where $K_{p,1}$ and $K_{p,2}$ are the protonation constants for ox^{2-} and Hox^-, respectively (water molecules omitted):

$$Pd^{2+} + n\,H_2ox \overset{\beta_n}{\rightleftharpoons} [Pd(ox)_n]^{2-2n} + 2n\,H^+ \qquad (D)$$

$$\log_{10}\beta_n = \log_{10}K_{nH} + n\,(\log_{10}K_{p,1} + \log_{10}K_{p,2}) \qquad (3)$$

Due to the strong correlation between spectrophotometric parameters and stability constants for the complexes $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$, the following calculation strategy was applied. The stability constant β_1 for $[Pd(H_2O)_2(ox)]$ calculated from eq. (3) by use of titration data for 1.00 mol.dm^{-3} perchloric acid was fixed, and the stability constant β_2 for $[Pd(ox)_2]^{2-}$ was calculated separately from experimental data collected at perchloric acid concentrations of 0.100 and 0.0100 mol.dm^{-3}, where its formation is favoured (Fig. S4). In order to check the eventual influence of palladium(II) hydrolysis (*i.e.* formation of $[Pd(H_2O)_3OH]^+$) on the parameters calculated at these lower perchloric acid concentrations, the protolysis constant $\log_{10}K_h$ = -3.0 for $[Pd(H_2O)_4]^{2+}$ determined elsewhere,[35] was included in the calculation. No change of the calculated stability constant β_2 was observed, so it could be safely concluded that the hydrolysis of the palladium(II) tetra aqua ion is suppressed in the presence of oxalate in these solutions, as already postulated earlier.[29]

Calculated values of the equilibrium and stability constants for solutions of various ionic strengths are summarized in Table 1. Distribution diagrams for the palladium(II) oxalate system using the derived equilibrium constants are given in Fig. 2.

Table 1

Figure 2

UV-VIS spectra

Spectra for the two oxalato complexes formed, calculated by use of the equilibrium constants determined, are given in Fig. 3. As expected, the absorbance band of $[Pd(H_2O)_4]^{2+}$ at 380 nm is only shifted slightly towards higher wavelengths on complex formation with O-binding oxalate. The molar absorptivity of the two complexes at the isosbestic point at 390 nm is about 155 dm^{3}mol^{-1}cm^{-1}, which is of the same order of magnitude as the molar absorptivities of other palladium(II) carboxylato complexes[17,18] and palladium(II) complexes with other oxygen donor ligands, *e.g.* nitrate.[11] There is a large increase of absorbance of the charge-transfer bands in the UV, when the aqua ligands are replaced by oxalate, consistent with observations for other ligands with oxygen donor atoms, *e.g.* hydroxide,[35] sulfate[35] and nitrate[11], as well as for halide complexes.[41]

Figure 3

Stability constants at zero ionic strength

The thermodynamic equilibrium constant $K_{1H}{}^{0}$ for reaction (C), describing the formation of the palladium(II) mono-oxalato complex, is given by eq. (4), where a denotes activities and γ activity coefficients and where K_{1H} is defined by eq. (1).

$$K_{1H}{}^{0} = (a_{Pd(ox)}\, a_{H+}{}^{2}) / (a_{Pd2+}\ a_{H2ox}) = K_{1H}\ (\gamma_{Pd(ox)}\, \gamma_{H+}{}^{2}) / (\gamma_{Pd2+}\, \gamma_{H2ox}) \qquad (4)$$

Eq. (4) can be rearranged as follows:

$$\log_{10} K_{1H}{}^{0} = \log_{10} K_{1H} + \log_{10} \gamma_{Pd(ox)} + 2 \log_{10} \gamma_{H+} - \log_{10} \gamma_{Pd2+} - \log_{10} \gamma_{H2ox} \qquad (5)$$

According to the Specific Ion interaction Theory (SIT),[9,10] the activity coefficients of the species in a perchlorate medium are defined as

$$\log_{10} \gamma_{H+} = -\ (+1)^{2}\, D + \varepsilon(H^{+}, ClO_4^{-})m_{H+} \qquad (6)$$

$$\log_{10} \gamma_{Pd2+} = -\ (+2)^{2}\, D + \varepsilon(Pd^{2+}, ClO_4^{-})m_{ClO4^-} \qquad (7)$$

$$\log_{10} \gamma_{Pd(ox)} = \varepsilon(Pd(ox), HClO_4)m_{HClO4} \qquad (8)$$

where D denotes the Debye-Hückel term,[9.10,13,20] m the molality and ε the interaction coefficient. The activity coefficient for oxalic acid is defined arbitrarily[9,10] as

$$\log_{10} \gamma_{H2(ox)} = \varepsilon(H_2(ox), HClO_4)m_{HClO4} = \varepsilon(H_2(ox), NaClO_4)m_{NaClO4} \approx 0 \qquad (9)$$

Similarly, the activity coefficient for oxalate can be written as

$$\log_{10} \gamma_{ox2+} = -\ (-2)^{2}\, D + \varepsilon(ox^{2-}, M^{+})m_{M+} \qquad (10)$$

where M is H, Na or Li. Substitution of eqns. (6)-(9) into eq. (5) and rearrangement gives

$$\log_{10} K_{1H} + 2D = \log_{10} K_{1H}{}^{0} - (\varepsilon(Pd(ox), HClO_4) + 2\, \varepsilon(H^{+}, ClO_4^{-}) - \varepsilon(Pd^{2+}, ClO_4^{-}))\, m_{HClO4} \qquad (11a)$$

which is simplified to

$$\log_{10} K_{1H} + 2D = \log_{10} K_{1H}{}^{0} - \Delta\varepsilon_{K1H} \times m_{HClO4} \qquad (11b)$$

Assuming $m(HClO_4) \approx m(NaClO_4)$, gives eqns. (12) and (13) for the stability constants.

$$\log_{10} \beta_1 + 8D = \log_{10} \beta_1{}^{0} - \Delta\varepsilon_{\beta1} \times m_{MClO4} \qquad (12)$$

$$\log_{10} \beta_2 + 8D = \log_{10} \beta_2{}^{0} - \Delta\varepsilon_{\beta2} \times m_{MClO4} \qquad (13)$$

Here, the slopes are

$$\Delta\varepsilon_{\beta1} = (\varepsilon(Pd(ox), MClO_4) - \varepsilon(Pd^{2+}, ClO_4^{-}) - \varepsilon(ox^{2-}, M^{+}))\, m_{MClO4} \qquad (14)$$

$$\Delta\varepsilon_{\beta2} = (\varepsilon(Pd(ox)_2{}^{2-}, M^{+}) - \varepsilon(Pd^{2+}, ClO_4^{-}) - 2\varepsilon(ox^{2-}, M^{+}))\, m_{MClO4} \qquad (15)$$

By use of interaction coefficients from the literature, $\varepsilon(H^+,ClO_4^-)$ = 0.14 ± 0.02 kg.mol^{-1},[9,10] $\varepsilon(Pd^{2+},ClO_4^-)$ = 0.8 ± 0.2 kg.mol^{-1},[18,42,43] and $\varepsilon(ox^{2-}, Na^+)$ = -0.08 ± 0.01 kg.mol^{-1},[9] the following values for the interaction coefficients of the two palladium(II) complexes can be derived: $\varepsilon(Pd(ox),HClO_4)$ = $0.9_2 \pm 0.2_0$ kg.mol^{-1} and $\varepsilon(Pd(ox)_2^{2-},Na^+)$ = $1.3_0 \pm 0.2_5$ kg.mol^{-1}. The interaction coefficients increase in the order $Pd(H_2O)_4^{2+}$ < $[Pd(H_2O)_2(ox)]$ < $[Pd(ox)_2]^{2-}$ (0.8 < 0.92 < 1.3), opposite to what has been reported for oxalato complexes of uranium(VI) and nickel.[9,13] The recently determined value $\varepsilon(Pd^{2+},ClO_4^-)$ = 0.22 kg.mol^{-1}, [44] gives the following estimated values: $\varepsilon(Pd(ox),HClO_4)$ = 0.34 kg.mol^{-1} and $\varepsilon(Pd(ox)_2^{2-},Na^+)$ = 0.72 kg.mol^{-1}, in agreement with this order.

The measurements at different ionic strengths giving the logarithmic values of the equilibrium constants K_{1H}, β_1 and β_2 are summarized in Table 1. Figure 4 shows plots of these data according to eqns. (11b) and (13). The literature value[29] of K_{1H} obtained by ion exchange in 0.2 mol.dm^{-3} perchloric acid fits very well with the ionic strength dependence determined in the present study. In Figure 4, the bottom plot shows the left-hand side of eq. (11b) *vs*. the ionic strength m_{HClO4} in molal units, giving the $\log_{10} K_{1H}^0$ as the intercept. Similarly, the top plot shows the ionic strength dependence of $\log_{10} \beta_2$ according to eq. (13), giving $\log_{10} \beta_2^0$ as the intercept. These data for zero ionic strength are included in Table 1. The non-weighed least-squares fitting of the data in Figure 4 also gave the following values for the slopes: $\Delta\varepsilon_{K1H} = -0.39_7 \pm 0.02_7$ kg.mol^{-1} for $HClO_4$ medium, and $\Delta\varepsilon_{\beta 2} = -0.65_8 \pm 0.14_0$ kg.mol^{-1} for $(Na,H)ClO_4$ medium. Finally, using $\log_{10} K_{p,1} = 4.25$ and $\log_{10} K_{p,2} = 1.40$ for $I = 0$ mol.kg^{-1},[11] the value of $\log_{10} \beta_1^0 = 9.04 \pm 0.06$, was calculated from the value of K_{1H}^0 according to eqn. (3).

Together with literature data, the stability constants derived (Table 2) might help to estimate stability constants for other Pd(II) complexes, some of them analogs to Pt(II) complexes used in cancer treatment. For instance, the $\log_{10}$ of the stability constant for the mixed complex [Pd(en)(ox)] formed from its components will be (12.11+42.2)/2 = 27.2, using the values for $\log_{10} \beta_2$ of the oxalato and ethylenediammine complexes given in Table 2. Similarly, the $\log_{10}$ value for the stability constant of the *cis*-platin analogue $[Pd(NH_3)_2Cl_2]$ will be (11.5+32.8)/2 = 22.2.

Figure 4

Reaction enthalpies and -entropies

Thermodynamic parameters for the $[Pd(H_2O)_2(ox)]$ complex formation, reaction (C), were derived from the temperature dependence of the equilibrium constant K_{1H} in 1.00 mol.dm^{-3} perchloric acid medium, where formation of $[Pd(ox)_2]^{2-}$ can be neglected (*cf.* Fig. 2). The following values of $\log_{10} K_{1H}$ were determined: 3.52 ± 0.02 (15.0 ºC), 3.46 ± 0.02 (20.0 ºC), 3.29 ± 0.01 and 3.38 ± 0.03 (25.0 ºC) and 3.21 ± 0.01 (31.0 ºC). The enthalpy and entropy changes $\Delta H_1^0 = -33._3 \pm 3._2$ kJ.mol^{-1} and ΔS_1^0 = -

$47._8 \pm 10._8$ J.K^{-1}.mol^{-1} were calculated by fitting the van't Hoff eqn. (16) to these experimental data as shown in Figure 5.

$$-R \times \ln 10 \times \log_{10} K_{1\mathrm{H}} = \Delta H_1^0 / T - \Delta S_1^0 \qquad (16)$$

Since reaction (C) is isocoulombic and the approximation $\Delta C_\mathrm{p} \approx 0$ is roughly valid,[10] those values can be used for approximate extrapolation of the equilibrium constant also in a wider temperature interval. The thermodynamic parameters for the complex formation (D) were calculated from ΔH_1^0 and ΔS_1^0 by use of eqns. (17) and (18)[20] and $\Delta H^0_{\mathrm{H2ox}}$ = 1.44 kJ.mol^{-1} and $\Delta S^0_{\mathrm{H2ox}}$ = 85.6 J.K^{-1}.mol^{-1} reported elsewhere.[9]

$$\Delta H^0_{\mathrm{Pdox}} = \Delta H^0 + \Delta H^0_{\mathrm{H2ox}} \qquad (17)$$

$$\Delta S^0_{\mathrm{Pdox}} = \Delta S^0 + \Delta S^0_{\mathrm{H2ox}} \qquad (18)$$

The following values were derived: $\log_{10} \beta_{\mathrm{Pd(ox)}} = 7.56 \pm 0.08$, $\Delta H^0_{\mathrm{Pd(ox)}} = -31._9 \pm 3._2$ kJ.mol^{-1}, and $\Delta S^0_{\mathrm{Pd(ox)}} = 37._8 \pm 10._8$ J.K^{-1}.mol^{-1}. Comparing these values with data for the monodentate chloroacetate complex formation given in Table 2 shows that the stability constant and the enthalpy of formation of the oxalato complex are significantly larger than for the chloroacetato complex, which is most likely a consequence of a chelate effect (*vide infra*). Similarly, as expected, the entropy change for the reaction between Pd^{2+} and ox^{2-} resulting in a neutral complex and the release of two water molecules, is significantly more positive than the corresponding reaction between Pd^{2+} and monodentate chloroacetate, resulting in a positively charged complex and release of one water molecule only.

Figure 5

Formation of chelate complexes

The two palladium oxalato complexes with $\log_{10} \beta_1^0 = 9.04 \pm 0.06$ and $\log_{10} \beta_2^0 = 13.1 \pm 0.3$ are significantly more stable than some other oxalato complexes of divalent metal centres with higher co-ordination numbers such as nickel(II) ($\log_{10} \beta_1^0 = 5.19$, $\log_{10} \beta_2^0 = 7.64$) and uranium(VI) ($\log_{10} \beta_1^0 = 7.13$, $\log_{10} \beta_2^0 = 11.65$),[9] whereas the 4-co-ordinate mercury(II) complex [Hg(ox)] ($\log_{10} \beta_1 = 9.66$ at ionic strength 0.1 mol.dm^{-3})[45] is of similar stability. This difference observed between complexes with different co-ordination numbers might simply be due to the fact that metal ions with higher co-ordination numbers have more binding sites available for the second ligand and therefore smaller stability constant differences.

The ionic strength dependence of the stability constants of the oxalato complexes is strong. The data in Table 1 show that the ratio between consecutive stepwise stability constants ($\Delta\log_{10} K_{1\text{-}2} = 2 \log_{10} \beta_1 - \log_{10} \beta_2$) is about 5.0, 3.0, 2.3 and 1.9 for ionic strengths of 0, 1, 2, and 3 mol.dm^{-3}, respectively. The observed change is due to the fact that the $\log_{10}K_1$ values remain almost constant whereas the $\log^{10}K_2$ values increase with higher ionic strength. This might probably be a result of the formation of a charged complex, i.e. an electrostatic effect.

Table 2

The stabilization of palladium(II) chelates by complex formation can be illustrated by a comparison between the $\log_{10}\beta_1$ values for the ligands listed in Table 2. We arrive at the order chloroacetate < acetate ≈ chloride < bromide < iodide < oxalate < ammonia << ethylenediamine (3.15 < 4.34 ≈ 4.47 < 5.17 < 6.08 < 7.56 < 9.6 << 23.6). In the case of O-bonding oxalate and N-bonding ethylenediamine, their very large stabilities compared to complexes with monodentate ligands and the same donor atoms (O or N) obviously are an effect of the formation of strong chelate complexes, *i.e.* a chelate effect, whereas the trends observed for the rest of the ligands depend on the variation of ligand donor properties.

The thermodynamic parameters for the oxalato complexes show that the enthalpic contribution is about 70% of the total free energy change. For formation of $[PdBr]^+$ and $[PdCl_n]^{2-n}$ (n=1-4) complexes, on the other hand, a 50-60% enthalpic contribution is observed. The higher enthalpic contribution in the case of oxalate can also be seen as an effect of the formation of two Pd-O bonds, i.e. a chelate formation. Summarizing, the so-called “chelate effect” is only qualitative and composed of several different parameters.

Conclusions

Complex formation between palladium(II) and oxalate has been studied by means of spectrophotometric equilibrium measurements. The two oxalato complexes formed in aqueous solution were identified and their thermodynamic stability constants at zero ionic strength determined by extrapolation of experimental results recorded at 1.00, 2.00 and 3.00 $mol.dm^{-3}$ ionic strength. Enthalpies and entropies of formation were determined by measurement of the temperature dependence of the equilibrium constants determined at 15.0, 20.0, 25.0 and 31.0 ºC. The results can be utilized for chemical modelling in for instance materials-, environmental and bioinorganic chemistry.

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Figure Captions

Fig. 1 Equilibrium absorbance titration data at 298.2 K and 400 and 300 nm for $[Pd^{2+}]_{tot} \approx 4\times10^{-3}$ mol.dm^{-3}, I = 1.00 mol.dm^{-3} (Na,H)ClO$_4$. Closed symbols: $[H^+]_{initial}$ = 1.00 mol.dm^{-3}, open symbols: $[H^+]_{initial}$ = 0.0100 mol.dm^{-3}. Titrations indicate formation of a 1:1 complex.

Fig. 2 Calculated distribution diagrams for the palladium(II)-oxalato system under the experimental conditions employed: T = 298.2 K, I = 1.00 mol.dm^{-3} (Na,H)ClO$_4$), using the equilibrium constants given in Table 1 or taken from literature: pK_h for $[Pd(H_2O)_4]^{2+} \approx 3.0$,[35] log $K_{p,1}$ = 3.59 for ox^{2-} and log $K_{p,2}$ = 1.08 for Hox$^-$. Total concentration of $[Pd(H_2O)_4]^{2+}$is 4.00 mmol.dm^{-3}, A) $[H^+]_{tot}$ = 1.00 mol.dm^{-3} (black lines), $[H^+]_{tot}$ = 0.100 mol.dm^{-3} (blue lines), B) $[H_2ox]_{tot}$ = 10 mmol.dm^{-3}.

Fig. 3 Spectrum of $[Pd(H_2O)_4]^{2+}$ and calculated spectra of $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$.

Fig. 4 SIT plots according to eqns. (11b) and (13), showing the ionic strength dependencies of $\log_{10} K_{1H}$ for reaction (C), top plot, $Y = \log_{10} K_{1H} + 2D$, and for $\log_{10} \beta_2$ for the formation of $[Pd(ox)_2]^{2-}$ according to reaction (D), bottom plot, $Y = \log_{10} \beta_2 + 8D$, respectively The cross point is from the work of Nabivanets and Kalabina.[29]

Fig. 5 van't Hoff plot for the temperature dependence of the equilibrium constant K_1 for reaction (C) at ionic strength 1.00 mol.dm^{-3} HClO$_4$.

Table 1. Logarithmic values at 298.2 K as a function of ionic strength for the equilibrium constant K_{1H} of reaction (C), the stability constants β_1 and β_2 for formation of $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)]^{2-}$ according to reaction (D), and for the protonation constants $K_{p,1}$ and $K_{p,2}$ for ox^{2-} and Hox^-, respectively. The Table also includes the values extrapolated to zero ionic strength and values for $\log_{10} K_2$ defined as $\log_{10} \beta_2 - \log_{10} \beta_1$. The standard deviations of $\log_{10} \beta_1$ and $\log_{10} K_2$ are considered the same as $\log_{10} K_{1H}$ and $\log_{10} \beta_2$.

Ionic strength mol.dm^{-3}	**$\log_{10} K_{1H}$**	**$\log_{10} K_{p,1}$**	**$\log_{10} K_{p,2}$**	**$\log_{10} \beta_1$^{a,g}**	**$\log_{10} \beta_2$^{b,d}**	**$\log_{10} K_2$^{g}**
1.00	3.38 ± 0.03	3.354^a	0.863^a	7.60		
	3.29 ± 0.01	3.586^b	1.084^b	7.51		
	3.34 ± 0.08^e			7.56	12.11 ± 0.04	4.55
2.00	3.83 ± 0.02	3.157^a	0.665^a	7.65		
		3.617^b	1.104^b		12.96 ± 0.04	5.31
3.00	4.16 ± 0.02	3.001^a	0.478^a	7.64		
		3.772^b	1.212^b		13.40 ± 0.04	5.76
0.20	3.18 ± 0.10^{ac}	3.690	1.104	7.97		
0.2-0.3^c					11.52 ± 0.20^h	3.55
→ 0	3.39 ± 0.06	4.25^f	1.40^f	9.04	13.1 ± 0.3	4.06

a) Ionic medium $HClO_4$ using approximation $\varepsilon(ox^{2-}, H^+) \approx \varepsilon(ox^{2-}, Li^+)$,

b) Ionic medium $(Na, H)ClO_4$.

c) From Nabivanets and Kalabina[29] at 18 °C.

d) Calculated with fixed values of log β_1 and protonation constants for $NaClO_4$,

e) Average value from two values, the uncertainty calculated as proposed elsewhere.[9]

f) From Hummel.[9]

g) Tentative estimated value.

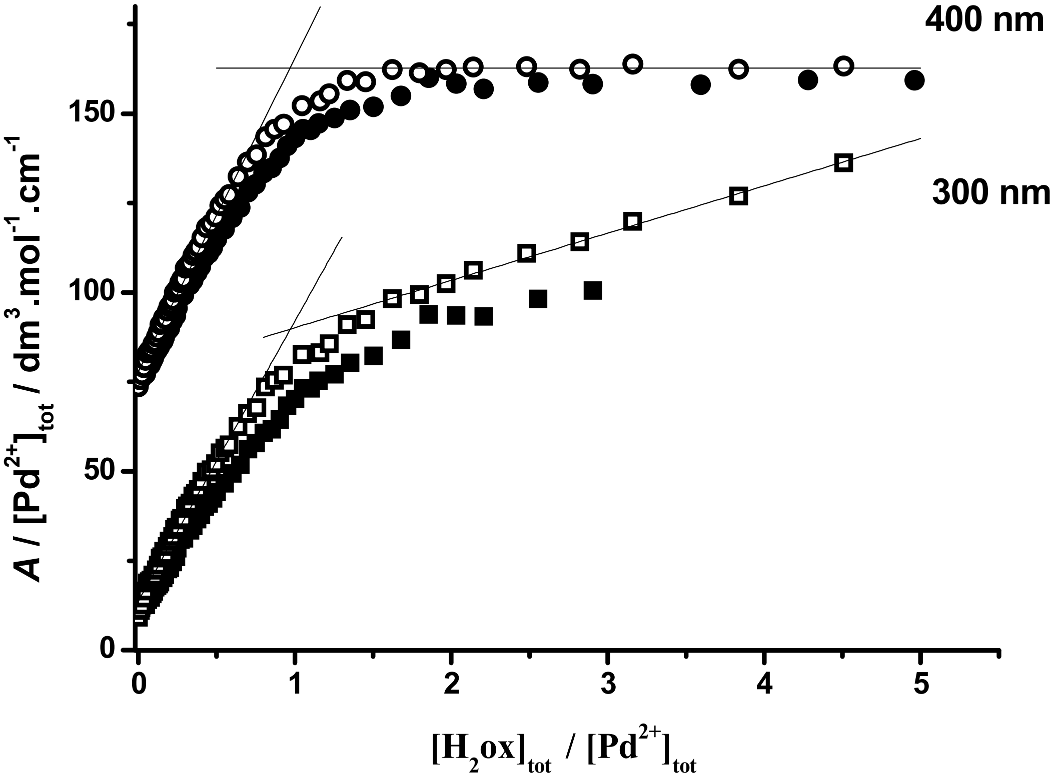
h) Not used for calculations because of varying ionic strength.

Table 2. Thermodynamic parameters of palladium(II) complexes at 25 °C and 1.0 mol.dm^{-3} ionic strength (Na, H)ClO$_4$.

Ligand	Thermodynamic parameters		Reference
Hydroxide	$\log_{10} \beta_1 = 10.8$		35, 43
Chloroacetate	$\log_{10} \beta_1 = 3.15$ $\Delta H^0_{PdL} = -12.5$ kJ.mol^{-1}, $\Delta S^0_{PdL} = 18.4$ J.K^{-1}.mol^{-1}		19, 20
Acetate	$\log_{10} \beta_1 = 4.34$, $\log_{10} \beta_2 = 9.30$	$\Delta\log_{10} K_{1\text{-}2} \approx -0.6$ [a]	6, 16
Oxalate	$\log_{10} \beta_1 = 7.56$, $\log_{10} \beta_2 = 12.11$ $\Delta H^0_{PdL} = -31.9$ kJ.mol^{-1}, $\Delta S^0_{PdL} = 37.8$ J.K^{-1}.mol^{-1}	$\Delta\log_{10} K_{1\text{-}2} \approx 3.0$ [a]	This work
Chloride	$\log_{10} \beta_1 = 4.47$, $\log_{10} \beta_2 = 7.76$ $\log_{10} \beta_3 = 10.17$, $\log_{10} \beta_4 = 11.54$ $\Delta H^0_{PdL} = -12.7$ kJ.mol^{-1}, $\Delta S^0_{PdL} = 43.1$ J.K^{-1}.mol^{-1} $\Delta H^0_{PdL2} = -23.5$ kJ.mol^{-1}, $\Delta S^0_{PdL2} = 69.8$ J.K^{-1}.mol^{-1} $\Delta H^0_{PdL3} = -34.2$ kJ.mol^{-1}, $\Delta S^0_{PdL3} = 79.8$ J.K^{-1}.mol^{-1} $\Delta H^0_{PdL4} = -48.5$ kJ.mol^{-1}, $\Delta S^0_{PdL4} = 58.1$ J.K^{-1}.mol^{-1}	$\Delta\log_{10} K_{1\text{-}2} \approx 1.2$ [a] $\Delta\log_{10} K_{2\text{-}4} \approx 4.0$ [b]	1, 47, 51
Bromide	$\log_{10} \beta_1 = 5.17$, $\log_{10} \beta_2 = 9.42$ $\log_{10} \beta_3 = 12.72$, $\log_{10} \beta_4 = 14.94$ $\Delta H^0_{PdL} = -21.3$ kJ.mol^{-1}, $\Delta S^0_{PdL} = 27.2$ J.K^{-1}.mol^{-1}	$\Delta\log_{10} K_{1\text{-}2} \approx 0.9$ [a] $\Delta\log_{10} K_{2\text{-}4} \approx 3.9$ [b]	1, 47, 48
Iodide	$\log_{10} \beta_1 = 6.08$, $\log_{10} \beta_2 \approx 22$ $\log_{10} \beta_3 = 25.8$, $\log_{10} \beta_4 = 28.3$	$\Delta\log_{10} K_{1\text{-}2} \approx -9.8$ [a] $\Delta\log_{10} K_{2\text{-}4} \approx 15.7$ [b]	47, 48
Ammonia	$\log_{10} \beta_1 = 9.6$, $\log_{10} \beta_2 = 18.5$ $\log_{10} \beta_3 = 26.0$, $\log_{10} \beta_4 = 32.8$	$\Delta\log_{10} K_{1\text{-}2} \approx 0.7$ [a] $\Delta\log_{10} K_{2\text{-}4} \approx 4.2$ [b]	49
Ethylenediamine	$\log_{10} \beta_1 = 23.6$, $\log_{10} \beta_2 = 42.2$	$\Delta\log_{10} K_{1\text{-}2} \approx 5.0$ [ab]	50

a) $2 \log_{10} \beta_1 - \log_{10} \beta_2$

b) $2 \log_{10} \beta_2 - \log_{10} \beta_4$



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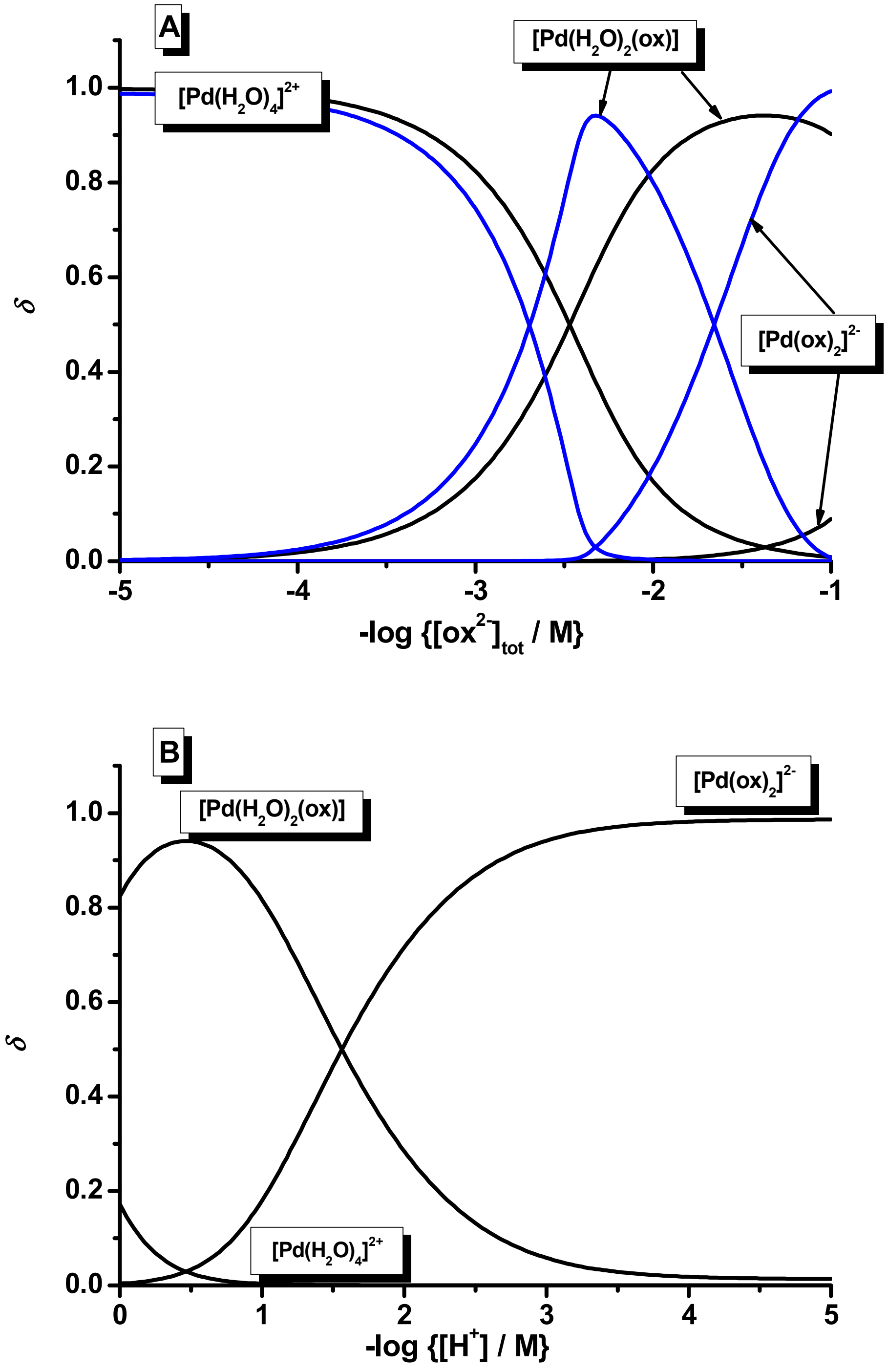

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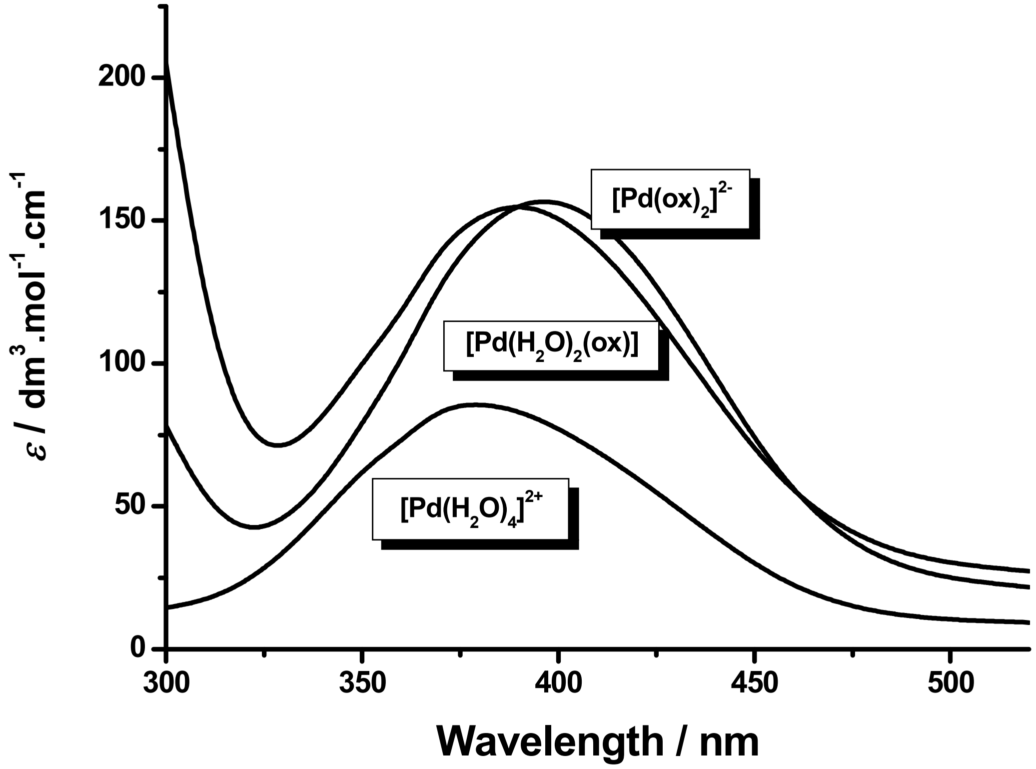

Fig. 3 Spectrum of $[Pd(H_2O)_4]^{2+}$ and calculated spectra of $[Pd(H_2O)_2(ox)]$ and $[Pd(ox)_2]^{2-}$.

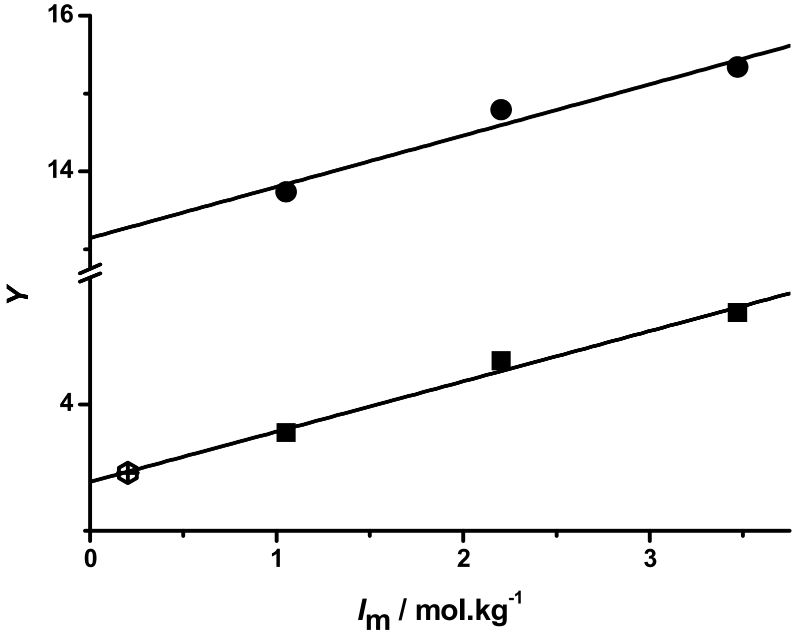

Fig. 4 SIT plots of data from Table 1 according to eqns. (11b) and (13), showing the ionic strength dependencies of $\log_{10} K_{1H}$ for reaction (C), top plot, $Y = \log_{10} K_{1H} + 2D$, and for $\log_{10} \beta_2$ for formation of $[Pd(ox)_2]^{2-}$ according to reaction (D), bottom plot, $Y = \log_{10} \beta_2 + 8D$, respectively. The cross point is from the work of Nabivanets and Kalabina.[29]

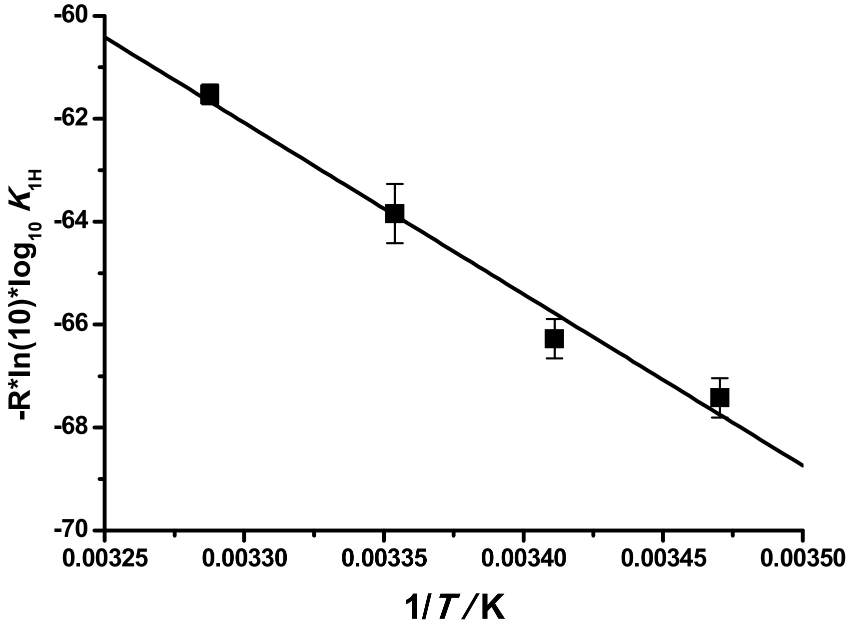

Fig. 5 van't Hoff plot for the temperature dependence of the equilibrium constant K_{1H} for reaction (C) at ionic strength 1.00 mol.dm^{-3} $HClO_4$.

Thermodynamics for Complex Formation between Palladium(II) and Oxalate

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Graphical Abstract

Overall stability constants and thermodynamic parameters for formation of palladium(II) oxalato complexes have been determined. The chelate effect is discussed.