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FULL PAPER

Synthesis and crystal structures of palladium(II) complexes of 1,11-bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione

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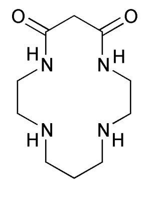
The two palladium(II) complexes, $[PdL^2][ClO_4]_2 \cdot H_2O$ **1** and $[Pd(H_{-2}L^2)] \cdot H_2O$ **2** with 1,11-bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione, L^2, were prepared and characterized by X-ray crystallography and UV-visible spectroscopy. In **1** the palladium centre is co-ordinated by the tertiary amines of the macrocycle and the two pyridylmethyl nitrogens, forming a square-planar geometry in which two amide nitrogen groups remain protonated and do not take part in co-ordination. Moreover, there is a weak interaction between palladium and H(–N(8)) [$d(Pd^{II} \cdots H) = 2.90$ Å]. In contrast, **2** isolated under basic conditions has a square-planar geometry but the palladium ion is co-ordinated by two deprotonated amides and the two tertiary amines of the macrocycle. In solution the reversible interconversion between complexes **1** and **2** easily occurs through pH-dependent deprotonation of the amide group.

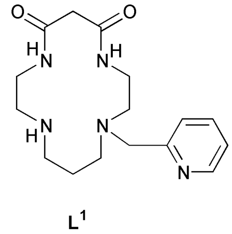
Introduction

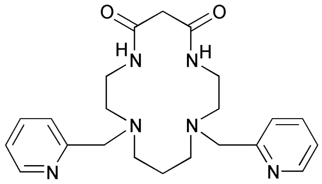
The co-ordination chemistry of transition metals in a +II oxidation state ($M^{II} = Cu^{II}$, Ni^{II} or Pt^{II}) with macrocyclic tetraamines (N_4) has extensively been studied.[1,2] Especially, the 14-membered tetraamine macrocycles incorporate metal ions into their N_4 cavities to form kinetically and thermodynamically stable complexes.[3] The 1,4,8,11-tetraazacyclotetradecane-5,7-dione ligand (dioxocyclam = L^0) possesses two amide and two secondary amine groups.[4] With divalent transition metal ions M^{II}, L^0 acts as a quadridentate ligand to form doubly deprotonated $[M^{II}(H_{-2}L^0)]$ complexes.[5] Several metal complexes with *C*-functionalized dioxocyclam were prepared and shown to be powerful reactants for catalysis of alkene oxidation,[6] oxygen uptake,[7] and carriers for the membrane transport of Cu^{II}.[8] These *C*-functionalized ligands stabilize higher oxidation states of transiton metals[9,10] than the parent one L^0. Conversely only a few examples of *N*-functionalized dioxocyclam derivatives have been reported compared to the large number of publications related to L^0.[11]

For example, Bu and Kimura *et al.* prepared 1-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione L^1, and 1,11-bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione, L^2 (where one or two pyridylmethyl groups are attached to the secondary amine functions of dioxocyclam, L^0) and studied their complexation reaction with Cu^{II}.[11]

Our recent investigations have focussed on the preparation of various metal complexes of Group 10 (*i.e.* Ni^{II}, Pd^{II} or Pt^{II}) with L^2 and on their characterization in the solution and solid states. Although palladium(II) complexes of amines have been investigated, thermodynamic data for co-ordination of Pd^{II} with polyamine ligands in aqueous solution are rare due to the very high stabilities of the complexes which make determination of the binding constants more difficult.[12]


dioxocyclam; L^0


L^1


L^2

Herein we describe the synthesis of two palladium(II) complexes, $[PdL^2][ClO_4]_2 \cdot H_2O$ **1** and $[Pd(H_{-2}L^2)] \cdot H_2O$ **2**, where $H_{-2}L^2$ represents the doubly deprotonated form of L^2 and their structural properties both in solid state and in solution.

Results and discussion

The ligand, L^2, was synthezised according to a literature method.[11b] The palladium(II) complexes, $[PdL^2][ClO_4]_2 \cdot H_2O$ **1**

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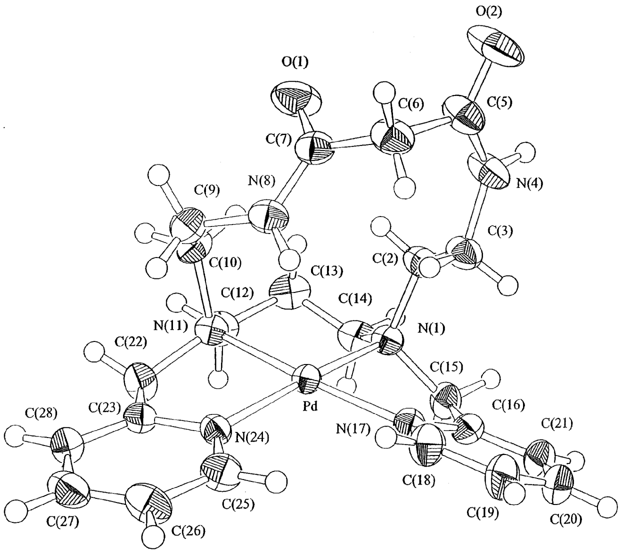
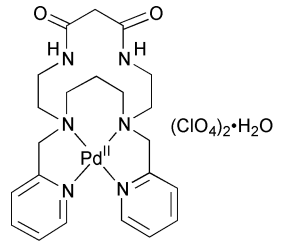
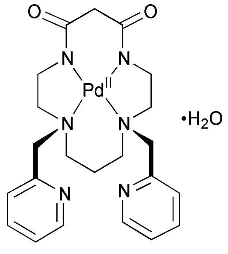


Fig. 1 ORTEP drawing for the cation of complex **1**.



$[Pd^{II}L^2](ClO_4)_2{\cdot}H_2O$, **1**



$[Pd^{II}(H_{-2}L^2)]{\cdot}H_2O$, **2**

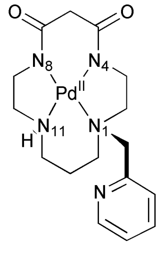
and $[Pd(H_{-2}$**L**$^2)]{\cdot}H_2O$ **2**, were synthesized as follows. Complex **1** was prepared by treating **L**^{2} with an equimolar amount of $Na_2[PdCl_4]$ in water, followed by addition of 2.1 equivalents of $NaClO_4$ at room temperature. **1** was then obtained by filtration and crystallization from water–acetonitrile. Complex **2** was formed by slow evaporation at room temperature of the previous filtrate adjusted to pH 10.

The infrared spectrum of complex **1** shows the presence of the protonated amides and perchlorate ions with intense bands observed at 1664 ($\nu_{C=O}$) and 1100 cm^{-1} (ν_{Cl-O}), respectively. Moreover, the appearance of the C=N stretching of the pyridine ring at a higher wavenumber (1614 *vs.* 1589 cm^{-1} for the "free" ligand) indicates co-ordination of the two pyridylmethyl nitrogen atoms to the central metal.[13] In contrast, the infrared spectrum of complex **2** shows a carbonyl stretching band ($\nu_{C=O}$) at 1573 cm^{-1} lower by *ca.* 68–89 cm^{-1} than that of the "free" ligand (1641 and 1662 cm^{-1}) and the disappearance of perchlorate ion vibration. These data indicate the deprotonation of two amide groups.

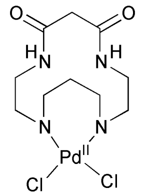
The ORTEP[14] drawing of the cation of complex **1** is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. Complex **1** exhibits a square-planar structure in which the two pyridylmethyl nitrogens (N(17) and N(24)) and the two nitrogens of tertiary amines (N(1) and N(11)) co-ordinate Pd^{II} whereas the two amido nitrogens (N(4) and N(8)) remain protonated and do not co-ordinate. The Pd–N$_{tertiary}$ (2.072(4) and 2.072(4) Å) and Pd–N$_{py}$ bond lengths (2.077(4) and 2.078(3) Å) are comparable with those given for other square-planar palladium(II) complexes, namely [2,6-bis(1-methylethyl)-*N*-(2-pyridylmethylene)phenylamine]dichloropalladium(II), **6**[15] and $[Pd(H_{-2}$**L**$^1)]$, **3** complexes.[16] The C(5)–N(4) (1.355(6) Å) and C(7)–N(8) (1.359(6) Å) bond lengths are close to those observed for Pt^{II}–**L**^{0}, $[Pt$**L**$^0Cl_2]$, **4** (1.31(1) and 1.33(1) Å)[17] and Cu^{II}–**L**^{2}, $[Cu$**L**$^2]^{2+}$, **5** (1.343(11) Å),[11b] complexes. The Pd^{II} is displaced by 0.062 Å above the 4N mean basal plane formed by N(1), N(11), N(17), and N(24) towards the apical direction. The torsion angles N(8)–C(9)–C(10)–N(11) and N(1)–C(2)–C(3)–N(4) are different (*i.e.* 78.8(5) and −176.2(4) °), indicating that the two ethylene moieties possess a *syn* and an *anti* configuration, respectively. The two pyridylmethyl groups are twisted to each other due to steric repulsion between the hydrogen atoms of both pyridine groups and the dihedral angle is equal to 25.6(2)°.

Table 1 Selected bond distances (Å) and angles (°) for complex **1**

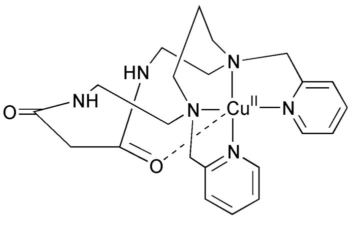
Pd–N(1)	2.072(4)	Pd–N(11)	2.072(4)
Pd–N(17)	2.077(4)	Pd–N(24)	2.078(3)
C(3)–N(4)	1.455(5)	C(5)–N(4)	1.355(6)
C(5)–O(2)	1.238(6)	C(5)–C(6)	1.506(7)
C(6)–C(7)	1.513(7)	C(7)–N(8)	1.359(6)
C(7)–O(1)	1.215(6)	N(8)–C(9)	1.453(6)
C(9)–C(10)	1.524(7)		
N(1)–Pd–N(11)	95.9(1)	N(1)–Pd–N(17)	80.8(1)
N(1)–Pd–N(24)	174.5(1)	N(11)–Pd–N(17)	176.2(1)
N(11)–Pd–N(24)	82.4(1)	N(17)–Pd–N(24)	101.1(1)



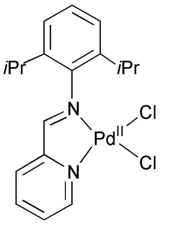
$[Pd^{II}(H_{-2}L^1)]^0$, **3**



$[Pd^{II}L^0Cl_2]^0$, **4**



$[Cu^{II}L^2]^{2+}$, **5**



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The ORTEP drawing of complex **2** is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The neutral complex has a square-planar structure and the Pd^{II} is bound to the two tertiary nitrogen and the two deprotonated amido nitrogen atoms. The bond lengths of Pd–N$_{amide}$ (1.979(1) and 1.985(1) Å) and Pd–N$_{tertiary}$ (2.077(1) and 2.081(1) Å) are similar (within < 0.01 Å) to those measured for the Pd^{II}–**L**^{1} complex, **3**, which exhibits Pd–N$_{amide}$ of 1.970(5) and 1.975(5) Å and a Pd–N$_{tertiary}$ of 2.070(4) Å.[16] The palladium atom lies in the

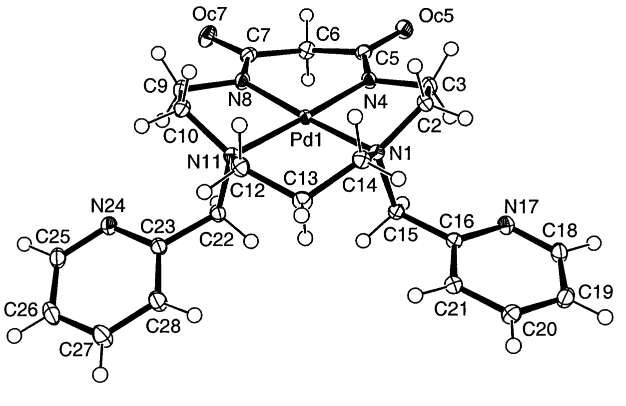


Fig. 2 ORTEP drawing for complex **2**.

Table 2 Selected bond distances (Å) and angles (°) for complex **2**

Pd–N(1)	2.0772(12)	Pd–N(4)	1.9848(13)
Pd–N(8)	1.9788(12)	Pd–N(11)	2.0813(13)
N(4)–C(5)	1.3242(19)	O(C5)–C(5)	1.2625(19)
N(8)–C(7)	1.3259(19)	O(C7)–C(7)	1.2547(18)
N(1)–Pd–N(4)	83.84(5)	N(4)–Pd–N(8)	94.08(5)
N(8)–Pd–N(11)	83.17(5)	N(1)–Pd–N(11)	98.90(5)
N(4)–C(5)–O(C5)	123.80(14)	N(8)–C(7)–O(C7)	123.11(15)

4N mean basal plane (it is only displaced by 0.022(2) Å from the four nitrogen mean plane, which leads to a r.m.s.d. value of 0.020 Å). In contrast to complex **1**, the two pyridylmethyl groups of **2** do not co-ordinate and a *cis* configuration is obtained as shown in Fig. 2. The dihedral angle between their respective mean planes is 23.4°, whereas the angles between the 4N mean plane of the macrocycle and the pyridine mean planes are 8.6 (almost parallel) and 19.5°. The six-membered chelate rings Pd–N(1)–C(14)–C(13)–C(12)–N(11) and Pd–N(4)–C(5)–C(6)–C(7)–N(8) exhibit chair and boat conformations, respectively, as supported by ring puckering analysis[18] ($Q = 0.566(2)$ Å, $\theta = 19.0(1)°$, $\varphi = 165.6(5)°$ and $Q = 0.262(1)$ Å, $\theta = 94.2(2)°$, and $\varphi = 353.6(3)°$, for chair and boat conformations). Thus, the C(13) and Pd$^{\text{II}}$ are respectively located 0.741(2) and 0.665(2) Å below and above the N(1)–C(12)–C(14)–N(11) mean plane (r.m.s.d. = 0.025 Å) and both C(6) and Pd atoms are located 0.248(2) and 0.193(2) Å, respectively, below the N(4)–C(5)–C(7)–N(8) mean plane (r.m.s.d. value = 0.015 Å). Both five-membered chelate rings, Pd–N(1)–C(2)–C(3)–N(4) and Pd–N(8)–C(9)–C(10)–N(11), exhibit a half-chair conformation (puckering parameters $Q = 0.459(1)$ Å, $\varphi = 232.4(2)°$ and $Q = 0.453(1)$ Å, $\varphi = 126.8(2)°$, respectively).

Concerning the molecular structure of complexes **1** and **2**, the main difference arises from the co-ordination scheme of the metal, involving the pyridylmethyl groups in the case of **1** only. This feature is related to the deprotonated amide nitrogens, N(4) and N(8), in **2**. In this case the pyridylmethyl groups are non-coordinating due to a more stable complexation of the metal when co-ordinated by the amide and amine nitrogens inside of the macrocycle cavity. Particularly, it is noteworthy that the position of the H(–N(8)) atom is roughly along the apical direction from the 4N mean basal plane in complex **1** (the four $\alpha(\text{H} \cdots \text{Pd}^{\text{II}} \cdots \text{N})$ angles are 110.1, 89.1, 90.3 and 75.2°). Although the distance $d(\text{Pd}^{\text{II}} \cdots \text{H})$ of 2.90 Å is longer than the sum of the ionic and van der Walls radii of Pd$^{\text{II}}$ and H (0.78 and 1.2 Å, respectively),[19] the particular position of H(–N(8)) and the displacement of Pd$^{\text{II}}$ (0.062 Å) above the 4N mean plane towards the apical direction seems to indicate a long-distance interaction between these atoms. A similar observation was made earlier by Kimura *et al.*[20] for a cyclam–nickel(II) complex ($d(\text{Ni}^{\text{II}} \cdots \text{H})$ 2.41 Å), where the ^{1}H NMR spectrum in D_2O exhibited a sharp one-proton resonance at δ *ca.* 12 ($J_{\text{HH}} = 7.8$ Hz) corresponding to the interacting proton. This experimental procedure could not be reproduced here due to the low solubility of complex **2** in solution.

In order to investigate the complexation behaviour of complex **1** in solution, a preliminary spectrophotometric pH-titration measurement was carried out in aqueous solution at 25 °C and I (ionic strength) = 0.10 M (NaCl). At pH 3.13 the UV spectrum of **1** exhibits absorption maxima at 260, 265, and 275 nm and a shoulder at 320 nm. As the pH is increased up to 9.97 the absorbances at 275 and 320 nm decrease, then new bands at 255, 260, and 265 nm appear along with two isosbestic points at 245 and 270 nm between pH 3.13 and 9.97 (Fig. 3a). Above pH 7 the absorption spectrum is identical with that of complex **2**.

The absorption changes at 255, 260, 275, and 320 nm as a function of pH between pH 3.13 and 9.97 for complex **1** show one inflection point at pH 5.5 (Fig. 3b). These results suggest that the reversible deprotonation of the two amide groups (pK_a = 5.5 ± 0.2) yields the doubly deprotonated complex **2** as shown in Scheme 1.

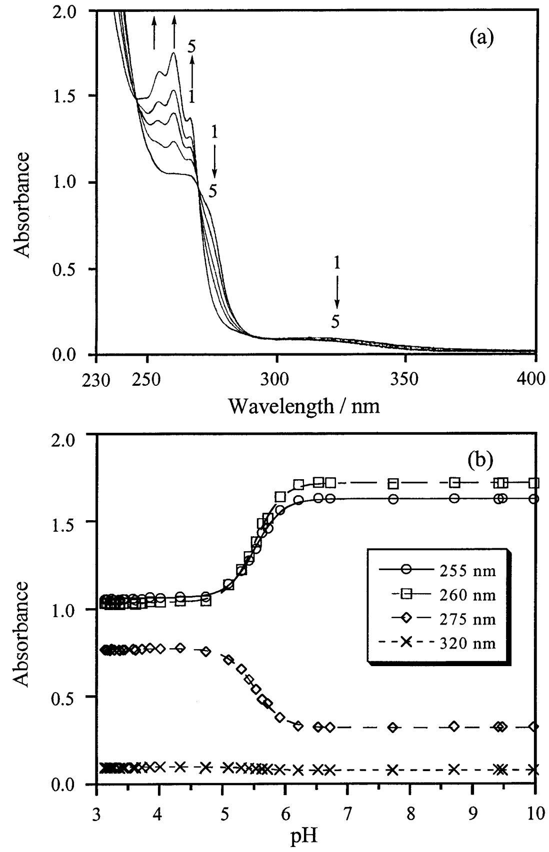
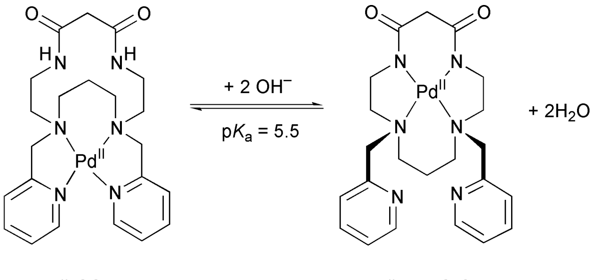


Fig. 3 (a) Absorption spectra of complex **1** ($[\text{Pd}]_t = 0.2$ mM) in aqueous solution at 25 °C and I = 0. 10 M (NaCl) for different pH values (3.13 (1); 5.29 (2); 5.53 (3); 5.71 (4); 9.97 (5)). (b) Spectrophotometric titration of **1** showing the absorbance changes at 255, 260, 275, and 320 nm for different pH values from 3.13 to 9.97. The solid lines are calculated from eqn. (1) with $K_{\text{PdH}_{-2}\text{L}^2} = (1 \pm 0.3) \times 10^{17}$.



Scheme 1

The complexation constant, $K_{\text{PdH}_{-2}\text{L}^2} = [\text{Pd}(\text{H}_{-2}\text{L}^2)][\text{H}_2\text{O}]^2/[\text{PdL}^2][\text{OH}^-]^2$, according to the mechanism given in Scheme 1 is expressed by eqn. (1), where A_{obs}, $[\text{Pd}]_\text{T}$, $[\text{H}^+]$, and K_w represent

$$A_{\text{obs}} = [\text{Pd}]_\text{T}(\varepsilon_1[\text{H}^+]^2 + \varepsilon_2 K_{\text{PdH}_{-2}\text{L}^2} K_\text{w}^2)/(K_{\text{PdH}_{-2}\text{L}^2} K_\text{w}^2 + [\text{H}^+]^2) \quad (1)$$

the apparent absorbance, total palladium complex concentration, proton concentration, and water dissociation constant, respectively. ε_1 and ε_2 are the molar absorptivities for complexes **1** and **2**, respectively, at a given wavelength, calculated from the absorbances measured at pH 4.01 and 8.71. The fitting of the pH–absorbance profiles according to eqn. (1) gave a value of $(1 \pm 0.3) \times 10^{17}$ for $K_{\text{PdH}_{-2}\text{L}^2}$.

Conclusion

Two palladium(II) complexes, $[PdL^2][ClO_4]_2\cdot H_2O$ **1** and $[Pd(H_{-2}L^2)]\cdot H_2O$ **2**, have been isolated from aqueous solutions at pH 7 and 10 and characterized by X-ray crystallography. Both complexes have square-planar structures but the nature of the donor group is different. Two pyridylmethyl nitrogen atoms and two tertiary amines co-ordinate the Pd^{II} in **1**, where the two amide groups are not co-ordinated. On the other hand, for **2**, the two deprotonated amide nitrogen atoms and the two tertiary amines co-ordinate the Pd atom while the two pyridylmethyl nitrogen atoms are not involved in co-ordination. In solution, the reversible interconversion between complexes **1** and **2** easily occurs through a pH-dependent deprotonation of the amide group.

Experimental

Materials

Commercially available solvents and chemicals were used without further purification.

Physical measurements

The UV-visible spectra absorption measurements were performed on a Shimadzu UV-2200 spectrophotometer, using 1 cm quartz cells. IR spectra (KBr pellets) were obtained on a JEOL GIR-6500 spectrophotometer.

Syntheses

Ligand. 1,11-Bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione, L^2, was prepared according to a published procedure.[11b]

$[PdL^2][ClO_4]_2\cdot H_2O$ 1. To a solution of L^2 (106 mg, 0.26 mmol) in 5 cm^3 of water (pH 6) was added dropwise a solution of $Na_2[PdCl_4]$ (76 mg, 0.26 mmol) in 3 cm^3 of water (pH 6). The reaction mixture was stirred for 3 h at room temperature and evaporated to give an oily product, which was redissolved in 2 cm^3 of water. To this solution, a solution of $NaClO_4$ (67 mg, 0.55 mmol) in 2 cm^3 of water was added. The precipitated yellow crystals were collected by filtration and recrystallized from water–acetonitrile. Yield 100 mg (53%) (Found: C, 35.97; H, 4.14; N, 11.17. $C_{22}H_{32}Cl_2N_6O_{11}Pd$ requires C, 36.01; H, 4.40; N, 11.45%).

$[Pd(H_{-2}L^2)]\cdot H_2O$ 2. The filtrate from the complex **1** synthesis was adjusted to pH 10 with a 0.1 M NaOH aqueous solution and filtered. This filtrate was allowed to stand for 3 days and the resulting colourless crystals were collected by filtration. Yield 23 mg (17%) (Found: C, 49.40; H, 5.66; N, 15.62. $C_{22}H_{30}N_6O_3Pd$ requires C, 49.58; H, 5.67; N, 15.77%).

Spectrophotometric titration

The complexation constant of the palladium(II) complex, $K_{PdH_{-2}L^2} = [Pd(H_{-2}L^2)][H_2O]^2/[PdL^2][OH^-]^2$, was determined by spectrophotometric titration in the wavelength range 230–400 nm in aqueous solution at $I = 0.1$ M (NaCl) and 25 °C, where at least three independent titrations were always performed. The concentration of complex **1** was 2×10^{-3} M (total volume: 10 cm^3) and each solution tested covered the pH range between 3.13 and 9.97 adjusted with 0.1 M HCl or 0.1 M NaOH. The molar absorptivities of **1** and **2**, ε_1 and ε_2 (M^{-1} cm^{-1}), were as follows: **1** at pH 4.01; 255 (5330), 260 (5200), 275 (3870), and 320 nm (490); **2** at pH 8.71; 255 (8130), 260 (8590), 275 (1600), and 320 nm (390). The complexation constant, $K_{Pd^{II}H_{-2}L^2}$, was obtained by fitting the experimental data according to eqn. (1) using a non-linear least-squares curve fitting program.[21]

Crystallography

Crystal data for complex **1**: $C_{22}H_{32}Cl_2N_6O_{11}Pd$, $M = 733.83$, monoclinic, space group $P2_1/n$ (no. 14) $a = 13.984(5)$, $b = 11.090(7)$, $c = 18.636(5)$ Å, $\beta = 106.44(2)°$, $U = 2772(1)$ $Å^3$, $T = 293$ K, $Z = 4$, μ(Mo-Kα) = 9.33 cm^{-1}, 6975 reflections measured, 6706 unique ($R_{int} = 0.052$) which were used in all calculations. One of the two perchlorate ions was found to be disordered between two positions, showing occupancy factors of 0.67 and 0.33. The final $wR(F)$ was 0.048 (all data). Crystal data for **2**: $C_{22}H_{30}N_6O_3Pd$, $M = 532.92$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.7739(1)$, $b = 13.1341(2)$, $c = 16.7446(2)$ Å, $\beta = 90.9842(7)°$, $U = 2149.21(5)$ $Å^3$, $T = 110 \pm 2$ K, $Z = 4$, μ(Mo-Kα) = 9.02 cm^{-1}, 28126 reflections measured, 9284 unique ($R_{int} = 0.037$) which were used in all calculations. The final $wR(F^2)$ was 0.0776 (all data).

CCDC reference numbers 155103–155105.

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