

Studies on the Complexation Between Generation-4.5 Methyl Ester-Terminated Poly(amidoamine) Dendrimer and Pd²⁺ Ions in Methanol

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ABSTRACT: Poly(amidoamine) (PAMAM) dendrimers have attracted attention because of their well-defined molecule structures and chemical versatility, which also complicate the mechanism of interactions between metal ions and PAMAM dendrimers. To further understand the complexation of dendrimers with metal ions, the interactions between Pd²⁺ ions and G4.5-COOCH₃ PAMAM dendrimers were investigated by UV-vis and FTIR spectrophotometric method. The results show that the addition of K₂PdCl₄ results in covalent attachment of the PdCl₃⁻ alcoholysis product of this complex to tertiary amines within the dendrimers under the appropriate conditions. This process was

also supported by X-ray photoelectron spectroscopy data of the new complex which indicated a 1 : 3 Pd/Cl ratio. The maximum loading of 80 Pd²⁺ ions within the G4.5-COOCH₃ dendrimers and the best pH value of 8.3 for complexation system are also obtained. Details regarding the Pd species present in solution of different chemical environments are reported. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2854–2858, 2009

Key words: poly(amidoamine); (PAMAM); dendrimers; Pd²⁺ ions; complexation; spectrophotometric method; template method

INTRODUCTION

Recently, dendrimers templating synthesis of metallic nanoparticles has been developed because of their unique structures, properties, and their abilities to complex with a great variety of metal ions or compounds.^{1–3} With these unique properties, dendritic macromolecules have attracted much attention as advanced materials for a variety of applications, such as nanoreactors for synthesis of nanoparticles, light harvesting devices, and especially as metal complexing agents.^{4–6} Many of these applications have made use of the interactions between dendrimers and metal ions, with the metal ions present as either structural or nonstructural moieties.

One useful property of dendrimers is their three-dimensional branched nature, which provides cavities to complex many metal ions. Dendrimers may act as hosts for metal nanoparticles with coordination occurring potentially at the periphery, interior, or both. Thus, they may serve as useful polyfunctional ligands and metal ion sequestering agents. Research concerning about the binding of various metal ions and

poly(amidoamine) (PAMAM) dendrimers has been reported, such as Cu²⁺,⁷ Cr³⁺,⁸ Cd²⁺,⁹ Ti⁴⁺,¹⁰ Ag⁺,¹¹ Au⁺,¹² Pt²⁺,¹³ and so on. Crooks and coworkers¹⁴ have suggested that in aqueous phase, Pd²⁺ ions binds to the interior tertiary amines of amine- and hydroxyl-terminated dendrimers. Different from them, methyl ester-terminated PAMAM dendrimers were employed as hosts, which were easier to be synthesized and purified than hydroxyl-terminated PAMAM dendrimers. Furthermore, methanol was used as solvent instead of water, which would be significant in context of application in organic phase. In this article, easily interpreted UV-vis and FTIR spectrophotometric technique were main methods to study the interactions between Pd²⁺ ions and dendrimers.

EXPERIMENTAL

Materials

Potassium chloropalladite (K₂PdCl₄, ≥99.5%) was purchased from Shanghai July Chemical Co., Ltd. of China. High purity nitric acid (HNO₃), sodium hydroxide (NaOH), and absolute methanol (CH₃OH) were purchased from Beijing Chemical Company of China. These materials above were used as received without further purification. Methyl ester-terminated G4.5 PAMAM dendrimer having an ethylenediamine core were synthesized by ourselves according

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to Ref. 15. Dialysis sacks having a molecule weight cutoff of 3500 were purchased from Beijing Jingkehongda Company of China.

Synthesis of complexation of Pd²⁺/G4.5 PAMAM

In a typical preparation of G4.5-COOCH₃ dendrimers containing nominally 20 Pd²⁺ ions (Pd²⁺₂₀/G4.5), 10 mL of a 10⁻⁵ mol L⁻¹ methanol solution of G4.5 dendrimers was dissolved in 9.8 mL of methanol, followed by slow addition of 0.2 mL of an aqueous 0.01 mol L⁻¹ K₂PdCl₄ solution with stirring. The color of the solution was light yellow, whereas the color of K₂PdCl₄ solution was yellow, which indicated the interaction between Pd²⁺ ions and G4.5 PAMAM. The solution above was dialyzed in 1 L absolute methanol before further use.

Characterization

UV-vis absorption spectra were recorded on a HITACHI U-3010 UV-vis spectrophotometer with the optical path length of 1.0 cm, absolute methanol used as a reference, and the scan speed of 1 nm/s. FTIR data were acquired using a THERMO NICOLET 8700 FTIR spectroscopy. The freeze-dried sample was mixed with KBr powder, and the mixture was pressed in a pellet die under a pressure of about 6000–10,000 psi to obtain a transparent disk. The stretching vibrational of C–H at ~2900 cm⁻¹ was used as the internal standards to normalize the series of spectra. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Surface Science X-Probe spectrometer equipped with an Al K α monochromatized X-ray source with a penetration depth of 3–10 nm. A submonolayer of freeze-dried sample was deposited on small pieces of aluminum foil for XPS sample. Analysis of the data were executed using the multippeak data reduction software.

RESULTS AND DISCUSSION

Comparison of complexation in different solvents

In our experiment, methanol with a low-boiling point was employed as solvent instead of water.¹⁴ Moreover, the sort of solvent used would influence the process of interactions between Pd²⁺ ions and dendrimers because of the differences in their physical properties, such as dielectric constant, coordination, and polarity.

To simplify the research on the complexes between Pd²⁺ ions and PAMAM dendrimers, it is indispensable to choose the proper concentration of dendrimers, because at higher concentration conglomeration occurs among the dendrimers. Therefore, a dendrimers con-

centration of 5 × 10⁻⁶ mol L⁻¹ was employed for all subsequent experiments.

Figure 1 shows UV-vis spectra of G4.5 PAMAM, K₂PdCl₄, and complex of Pd²⁺₄₀/G4.5 PAMAM in dilute aqueous and methanol solutions, respectively. The aqueous Pd²⁺ salt has two strong ligand-to-metal charge-transfer (LMCT) bands at 207 and 235 nm (curve 3) corresponding to literature values for the hydrolysis product PdCl₃(H₂O)⁻.¹⁴ By comparison, the corresponding maximum absorption wavelength of Pd salt methanol solution shifts to 217 and 240 nm (curve 4), which indicates the formation of alcoholysis product (Fig. 1, inserted a).¹⁶ The red shift could be explained as the higher splitting energy (Δ) that CH₃OH ligand causes between the orbitals of central metal ions. In addition, this higher splitting energy also leads to much lighter color of Pd salt in methanol solution (yellow) than in aqueous solution (dark yellow).

After the addition of the Pd²⁺ salt solution to the G4.5 PAMAM dendrimers, a single strong band is observed at $\lambda_{\text{max}} = 224$ (aqueous solution, curve 5) and $\lambda_{\text{max}} = 228$ (methanol solution, curve 6) respectively. These peaks correspond to a LMCT band associated with complexation of the complex Pd anion to interior tertiary amines of the G4.5 PAMAM dendrimers. This can be deduced by the Spectrochemical Series¹⁷ which lists that the ligand containing N atoms has the ability to provide a stronger ligand field, and in the G4.5 PAMAM molecule the complexing ability of different ligands rank in this order: -NR₂ > -CONH- > -COOCH₃. Complexation likely occurs via displacement of CH₃OH ligand from PdCl₃(CH₃OH)⁻, followed by covalent reaction with the interior tertiary amines of the dendrimer (Fig. 1,

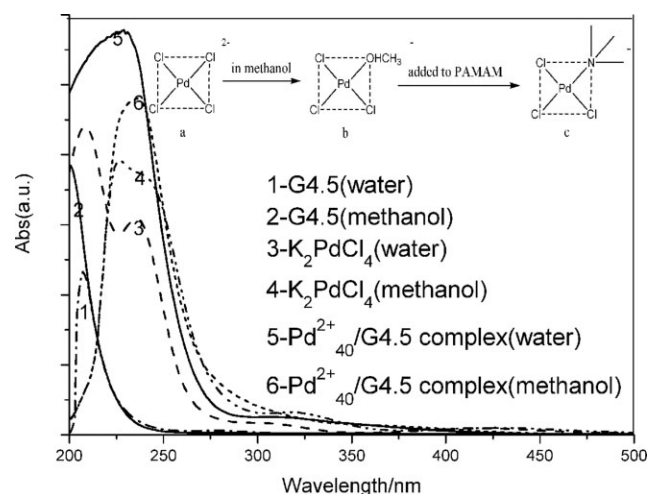


Figure 1 UV-vis absorbance spectra of G4.5 PAMAM, K₂PdCl₄, complex of Pd²⁺₄₀/G4.5 in deionized water and absolute methanol. Inserted figure shows series of Pd²⁺ complexes (N represents the N-ligand of dendrimer).

inserted b). This inference is supported by XPS data indicating a 1 : 3 Pd/Cl ratio after dialysis of the new complex solution (Fig. 2). These series of complex Pd anion and their changes can be described as inserted figure in Figure 1.

These conclusions can also be supported by the FTIR spectra for the complex of Pd²⁺/G4.5 PAMAM system (Fig. 3). In the case of G4.5 PAMAM dendrimers alone (curve a), the amide I ($\nu_{C=O}$), amide II (δ_{NH}), and amide III (ν_{C-N}) bands are observed at 1648, 1542, and 1330 cm⁻¹, respectively. The methyl ester band also appears at 1200 and 1733 cm⁻¹. To further compare the Pd species before and after complexing, the spectrum of physical mixture of G4.5 PAMAM dendrimer and K₂PdCl₄ is offered (curve b). The two spectra above are much similar, indicating that there is no interaction between Pd²⁺ and dendrimers in their physical mixture. Enough time after mixing dendrimers and Pd salt together in solution, the amide I band (curve c) shifted to 1661 cm⁻¹ and became weaker. The amide II band shifted to 1554 cm⁻¹ and became stronger. It is clear from both UV-vis and FTIR data that Pd²⁺ ions has migrated into the dendrimers and complexed with the interior amide groups.¹³

Maximum loading number of Pd ions per dendrimer

The spectrophotometric traces upon titration of the solution of the methyl ester-terminated PAMAM dendrimers with a K₂PdCl₄ solution are used to study the maximum loading number of Pd²⁺ ions per PAMAM dendrimer. The process is as follows. To fiercely stirred PAMAM methanol solution, K₂PdCl₄ solution is quantitatively added. After each addition when the

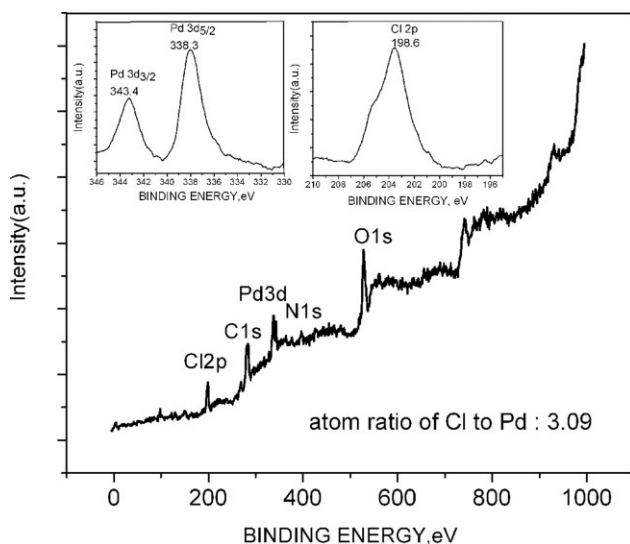


Figure 2 XPS spectra of complex of Pd²⁺₄₀/G4.5 PAMAM. Insert: Pd 3d and Cl 2p.

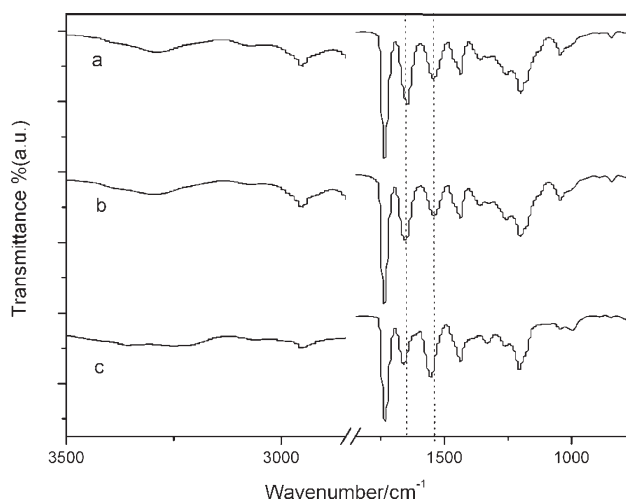


Figure 3 FTIR spectra of (a) G4.5 PAMAM, (b) physical mixture of G4.5 PAMAM and K₂PdCl₄, and (c) complex of Pd²⁺₄₀/G4.5 PAMAM.

system comes to balance, the spectroscopic data of Pd²⁺/PAMAM at different molar ratio are recorded.

As Figure 4 shows, four aspects of these spectra should be noticed: First, the maximum absorption wavelength of Pd-N LMCT band has a red shift (from 208 to 228 nm, as shown by the two broken lines) with the increase of the molar ratio of Pd²⁺/PAMAM (5–80). Second, plots obtained at the maximum wavelength for complex solutions are linear up to Pd²⁺/G4.5 PAMAM ratios of around 80 (as shown in an inserted figure of Fig. 4). Third, as the molar ratio of Pd²⁺/PAMAM increases from 100 to 150, the absorbance of Pd-N LMCT band gradually decreases, together with increasing amount of slight yellow precipitate formed. Fourth, after the absorbance of Pd-N LMCT band reaches minimum point when the molar

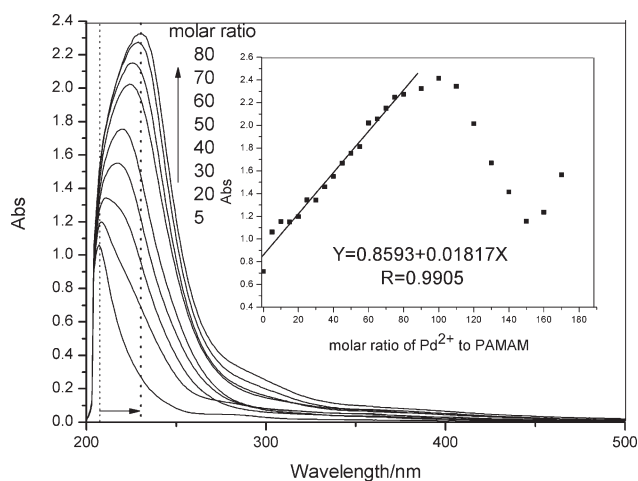


Figure 4 UV-vis absorbance spectra of complex of Pd²⁺/G4.5 PAMAM with different molar ratios. Inserted figure shows the photometric titration curve of Pd²⁺/G4.5 PAMAM.

ratio of Pd²⁺/PAMAM is 150, the peak value of UV-vis spectra of clear liquid begin to increase again with Pd²⁺/PAMAM ratio.

The first phenomenon occurs because the ligand field stabilization energy of N-ligand is larger than that of O-ligand according to ligand field theory. This phenomenon also suggests that there are different relative amount of complexing patterns changes with the increase of the molar ratio of Pd²⁺/PAMAM. The second observation indicates that when the molar ratio of Pd²⁺/PAMAM is less than 80, the complex Pd ions are exclusively converted to single specie, namely the complex with the interior amide groups of dendrimers. The third phenomenon is presumably explained as crosslinking of the dendrimers by extra free Pd ions. It also indicates that dendrimer molecule has been "saturated" when precipitate appears at $n(\text{Pd}^{2+})/n(\text{PAMAM}) = 100$. The fourth observation shows that almost all the dendrimers are agglomerated out of the solution when the molar ratio of Pd²⁺/PAMAM is 150, and the peak values begin to increase resulting from the free Pd²⁺ ions.

To confirm the interaction between Pd²⁺ and dendrimer at larger molar ratio, FTIR spectra for Pd²⁺/G4.5 PAMAM or participate at different molar ratios were measured (as shown in Fig. 5). Different from the complex at smaller molar ratio, the FTIR spectra of precipitate shows a broad strong band at 3466 cm⁻¹ which can be explained as crosslinking of the dendrimers caused by extra free Pd²⁺ ions. The absorption band at 1554 cm⁻¹ (curve a) became stronger and showed a slight blue shift (curves b, c, and d). Simultaneously, the band at 1403 cm⁻¹ (curves b, c, and d) which is the characteristic peak resulting from the symmetric stretching of carboxylate (COO⁻) newly forms, which indicates that this kind of crosslinking

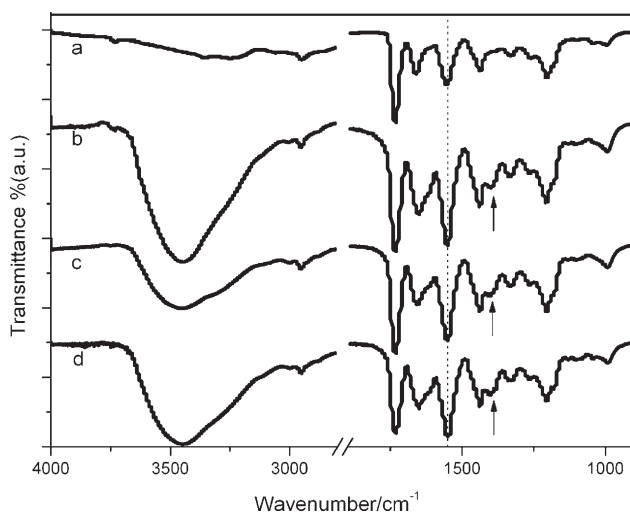


Figure 5 FTIR spectra of Pd²⁺/G4.5 PAMAM of different molar ratio (curves a, b, c, and d are the spectra of the molar ratio of 40, 70, 80, and 90, respectively).

TABLE I
Relationship Between N Functional Groups and the Number of Complexed Pd²⁺

Generation of dendrimers	Number of the outmost NR ₃	Number of NR ₃	Theo. value ^a	Theo. value ^b	Exp. value
4.5	64	126	64	126	≈80

^a Only the outmost NR₃ involved.

^b All the NR₃ involved.

probably arises from the formation of some palladium carboxylate. Noticeably, such agglomeration is not observed for Gn-OH PAMAM dendrimers,¹⁴ which emphasizes the poorer affinity of Pd²⁺ ions for hydroxyl groups than methyl ester groups.

In summary, all the results suggest a maximum loading of around 80 Pd²⁺ ions per G4.5 PAMAM dendrimer, which also suggests the ability of G4.5 PAMAM dendrimers to complex large amount of metal ions. The relationship between the number of tertiary amine N and the number of Pd²⁺ complexed is shown in Table I. The data indicates that not only the outmost but also the interior tertiary amines are involved in complexing which arises from the expansion of dendrimer molecule in its good solvent methanol. However, because of the blocking-effect, experimental value is much smaller than the theoretical value.

The influence of pH value of solution on the complexation system

After G4.5 PAMAM dendrimers react with diluent nitric acid or solution of NaOH to attain a certain pH value, K₂PdCl₄ solution is added to study the effect of pH on the complexation between Pd²⁺ ions and dendrimers. Figure 6 shows the relation between the pH

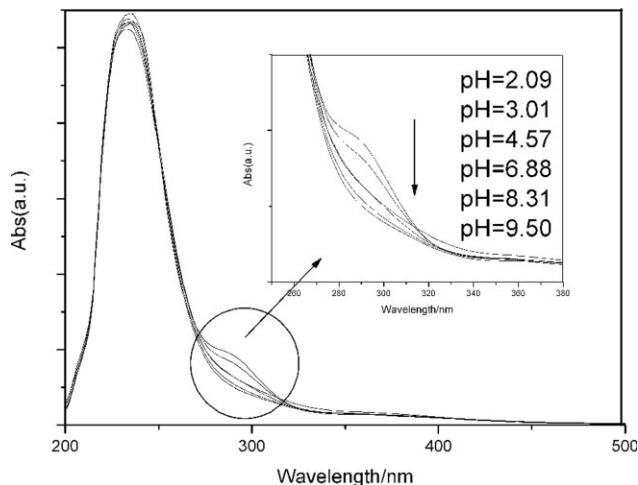


Figure 6 UV-vis absorbance spectra of complexes of Pd²⁺₂₀/G4.5 PAMAM prepared in different pH values.

value and absorption spectra of the complex solution at the molar ratio of Pd^{2+} and G4.5 PAMAM of 20. Clearly, the maximum adsorption wavelength of Pd-N LMCT band has a red shift with the increase of pH value, and the absorbance of the Pd-N LMCT band and degree of λ_{max} red shift reaches maximum at $\text{pH} = 8.3$. This observations suggest that the complexation of Pd^{2+} /G4.5 PAMAM is more stable at $\text{pH} = 8.3$ than under other conditions. Furthermore, the absorbance of the Pd-Cl co-LMCT bands at 290 nm hit rock bottom at $\text{pH} = 8.3$, which shows that the process of Cl-N ligand is carried sufficiently at $\text{pH} = 8.3$.

At low pH values, the concentration of H^+ is high, which causes dendrimers protonated, thus preventing the Pd^{2+} ions from complexing with the dendrimers. At high pH values, the OH^- ions with increasing concentration have certain ability to coordinate with Pd^{2+} , thus the formation of Pd^{2+} /G4.5 PAMAM complex would also be adversely influenced. In summary, alkaline environment is optimal for complexation system.

The influence of Cl^- ions on the complexation system

As the ligands of series of complex Pd anion, Cl^- ions would influence the alcoholysis product of K_2PdCl_4 and the complexation process of Pd^{2+} ions and G4.5 PAMAM.

When extra Cl^- ions are added to K_2PdCl_4 solutions, a newly formed band at 279 nm corresponding to Pd-Cl co-LMCT band indicates the forming of PdCl_4^{2-} (as shown in Fig. 7). After that, dendrimers are added to the solution above. It shows that all UV-vis spectra of complexation system with different con-

tent of Cl^- ions (containing the condition of no addition of extra Cl^- ions) coincide entirely with each other. These phenomena suggest that extra Cl^- ions would change the alcoholysis product of K_2PdCl_4 , but not the product of the complexation of Pd^{2+} and dendrimers, and the complex of Pd^{2+} and G4.5 PAMAM is exclusively $\text{PdCl}_3(\text{N})^-$. These processes are shown as inserted figure in Figure 7.

CONCLUSIONS

The interactions between Pd^{2+} ions and G4.5- COOCH_3 PAMAM dendrimers were investigated by UV-vis and FTIR spectrophotometric method. The addition of K_2PdCl_4 results in covalent attachment of the PdCl_3^- alcoholysis product of this complex to tertiary amines within the dendrimers. The maximum loading of around 80 Pd^{2+} ions within the G4.5- COOCH_3 dendrimer is obtained in our experiment. Furthermore, pH value and extra added Cl^- influence on the formation and stability of Pd^{2+} /G4.5 PAMAM complexation. As effective Pd^{2+} ions trapping agents, PAMAM dendrimers can be used to recycle noble metal ions, or act as templates for preparing Pd nanoclusters.

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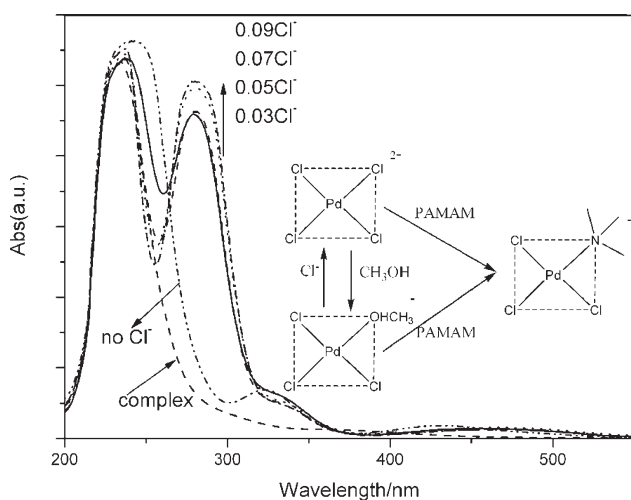


Figure 7 K_2PdCl_4 and Pd^{2+}_{40} /G4.5 PAMAM complexation system with different content of Cl^- ions (mol L^{-1}) added. Inserted figure shows series of Pd^{2+} complexes (N represents the N-ligand of dendrimer).