

Self-Assembly of Palladium(II) and Platinum(II) Complexes of 2-Hydroxypyrimidine to Novel Metallacalix[4]arenes. Receptor Properties through Multiple H-Bonding Interactions

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Reaction of $[\text{enM}(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (en = ethylenediamine, M = Pd^{II}, Pt^{II}) with 2-hydroxypyrimidine (Hpymo) in water results in self-assembly to cyclic complexes of type $[\text{enM}(\text{pymo-}N^1, N^3)]_4(\text{NO}_3)_4$ (**1**, M = Pd^{II}; **2**, M = Pt^{II}) which are structurally analogous to calix[4]arenes. The tetranuclear cations in compounds **1** and **2** adopt, in the solid state, a 1,3-alternate orientation of the pymo residues. Attempts to coordinate either soft (Pd^{II}, Pt^{II}), borderline (Cu^{II}, Zn^{II}), or hard (La^{III}, Be^{II}, Na^I) metal ions to the oxo surface of the metallacalix[4]arene lower rim were fruitless. In fact, X-ray studies performed on $\{[\text{enPt}(\text{pymo-}N^1, N^3)]_4(\text{ClO}_4)_4\}_2 \cdot [\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot 9\text{H}_2\text{O}$ (**4**) showed that multiple H-bonding interactions between the water coordination sphere of the copper center and the oxo surface of two tetranuclear cations take place instead of a direct interaction between the heterometal and the oxo surface of the metallacalix[4]arene. Encapsulation of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is also responsible for the stabilization of the pinched-cone conformation of the tetranuclear cations in **4**. pH* dependent ¹H NMR spectra of compounds **1** and **2** indicate a very low basicity of the O-donor group of the pymo residues, revealing no protonation of this position down to pH* 0. Moreover, recrystallization of **2** from strongly acidic aqueous solution (~1 M HClO₄) affords the adduct $\{[\text{enPt}(\text{pymo-}N^1, N^3)]_4(\text{ClO}_4)_4\}_2 \cdot [\text{H}_2\text{O}_8](\text{ClO}_4)_4$ (**6**). Analogously to **4**, the cationic $[\text{H}_2\text{O}_8]^{4+}$ species is sandwiched between two tetranuclear cations as a result of multiple H-bonding interactions with the oxo surface of two metallacalix[4]arenes. Again a pinched-cone orientation of the pymo residues is realized.

Introduction

There is presently considerable interest in molecules capable of acting as selective hosts for other molecules. The majority of such compounds has been prepared by applying elaborate organic synthetic procedures to generate the appropriate structures for encapsulation of target guests.¹ More recently, this approach has also been extended to systems containing metal ions in addition to organic ligands.^{2–5} In fact, formal heteroatom substitution procedures lead to a close analogy between purely organic host systems (crown ether, cryptand, calix[*n*]arene, molecular box) and the metalla analogues.^{1a} The use of these modified frames widens the range of possible applications of such molecules given the stereochemical, spectroscopic, magnetic, and optical properties introduced by the metal entities.

We have recently described the metallacalix[4]arene $[\text{enPt}(\text{uracilate})]_4(\text{NO}_3)_4$, which behaves as a versatile host. It can either act as an efficient ligand for metal ions,⁴ employing the exocyclic uracil O-donor groups, or selectively encapsulate organic anions.⁵ The later process is the result of a combination

of positive charge of the compound and the existence of an apolar cavity of appropriate size formed by four heteroaromatic uracil rings. This compound differs from related organic calixarenes⁶ in its affinity for anions in water. Only appropriately substituted organic calixarenes exhibit anion affinity.⁷

In continuation of our previous work on the synthesis and host–guest chemistry of metallacalix[3]arenes⁸ and metallacalix[4]arenes,^{4,5} we report here on several complexes derived from

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enPd^{II} and enPt^{II} entities and the 2-hydroxypyrimidine (Hpymo) ligand. In this study, we readily generate structures of a defined geometry in a self-assembly process by taking advantage of metal fragments with 90° bond angles and a simple and symmetric heterocyclic ligand with a 120° angle. Although of cationic nature, these metallacalix[4]arenes behave, via multiple H-bonding interactions, as acceptors for other cations.

Experimental Section

Materials. enPtCl₂⁹ and enPdCl₂¹⁰ were prepared from K₂PtCl₄ and K₂PdCl₄, respectively. 2-Hydroxypyrimidine hydrochloride (Hpymo·HCl) was purchased from Aldrich and converted to the corresponding HNO₃ adduct by anion exchange. Sodium *p*-toluenesulfonate was purchased from Merck, and sodium 3-(trimethylsilyl)propanesulfonate, sodium propanesulfonate, sodium ethanesulfonate, and sodium methanesulfonate were purchased from Aldrich. **CAUTION!** Perchlorate salts are potentially explosive and should be handled in small quantities only.

Preparation of [enPd(pymo)]₄(NO₃)₄ (1). enPdCl₂ (1 mmol) was added to a solution of AgNO₃ (2 mmol in 25 mL of H₂O), and the suspension was stirred in the dark at 70 °C for 40 min. Subsequent filtration of AgCl, addition of Hpymo·HNO₃ (1 mmol in 10 mL of H₂O) and addition of NaOH to pH 7.5 led to the formation of a pale yellow solution. Heating for 48 h at 60 °C caused an acidification of the solution (pH 5) and the formation of a single product as deduced from ¹H NMR. Subsequent concentration of the mother liquor to 10 mL led, after 2 weeks, to the formation of yellow crystals of **1**. Yield: 210 mg (61%). Anal. Calcd for Pd₄C₂₄H₄₄N₂₀O₁₆: C, 22.27; H, 3.43; N, 21.64. Found: C, 22.0; H, 3.5; N, 21.5. ¹H NMR (D₂O, pH* 7): δ 2.77 (s, 4H, CH₂), 6.49 (t, *J* = 5.7 Hz, 1H, H5), 8.25 (d, *J* = 5.7 Hz, 2H, H4, H6).

Preparation of [enPt(pymo)]₄(NO₃)₄ (2). enPtCl₂ (2 mmol) was added to a solution of AgNO₃ (4 mmol in 50 mL of H₂O), and the suspension was stirred at 80 °C in the dark for 2 h. Subsequent filtration of AgCl led to a pale yellow solution, which, after addition of Hpymo·HNO₃ (2 mmol in 20 mL of H₂O), gave rise to the formation of a white foggy solution (pH 2.0). After the pH was raised to 5.0 (NaOH), the reaction mixture was heated at 80 °C for 4 days. After 10 days at room temperature, 200 mg (25%) of **2** was recovered. Crystals suitable for X-ray analysis were obtained upon recrystallization from 1 M HNO₃. Anal. Calcd for Pt₄C₂₄H₄₄N₂₀O₁₆: C, 17.48; H, 2.69; N, 16.99. Found: C, 17.2; H, 2.7; N, 16.8. ¹H NMR (D₂O, pH* 7): δ 2.71 (s, 4H, CH₂), 6.45 (t, *J* = 5.7 Hz, 1H, H5), 8.35 (d, *J* = 5.7 Hz, 2H, H4, H6). ¹⁹⁵Pt NMR (D₂O, pH* 7.0) δ -2738 (s, 1Pt).

Preparation of [enPt(pymo)]₄(NO₃)₄·2NaNO₃·4H₂O (3). Compound **3** was isolated in low yield as colorless crystals from a small portion of the mother liquor of **2**, 2 weeks after the precipitation of **2**. Yield: 50 mg (7%). Anal. Calcd for Na₂Pt₄C₂₄H₅₂N₂₂O₂₆: C, 15.28; H, 2.56; N, 16.33. Found: C, 15.8; H, 2.7; N, 16.8. ¹H NMR (D₂O, pH* 7): δ 2.71 (s, 4H, CH₂), 6.45 (t, *J* = 5.7 Hz, 1H, H5), 8.35 (d, *J* = 5.7 Hz, 2H, H4, H6).

Preparation of {[enPt(pymo-N¹,N³)]₄(ClO₄)₄}₂·[Cu(H₂O)₆](ClO₄)₂·9H₂O (4). To a solution of **2** (0.05 mmol in 5 mL of H₂O) was added CuClO₄·6H₂O (500 mg). After 1 day colorless crystals of **4** were recovered. Yield: 45 mg (45%). Anal. Calcd for Cu₁Pt₈C₄₈H₁₀₀N₃₂O₅₄·Cl₁₀ (anhydrous compound): C, 14.53; H, 2.54; N, 11.29. Found: C, 14.7; H, 2.7; N, 11.2. ¹H NMR (D₂O, pH* 7): δ 2.71 (s, 4H, CH₂), 6.45 (t, *J* = 5.7 Hz, 1H, H5), 8.35 (d, *J* = 5.7 Hz, 2H, H4, H6).

Preparation of [enPt(pymo)]₄(ClO₄)₄·NaClO₄·4H₂O (5). Following a procedure similar to that described for **4** but using NaClO₄·H₂O instead of CuClO₄·6H₂O, a colorless crystalline material was recovered after 1 week. Yield: 55 mg (55%). Anal. Calcd for NaPt₄C₂₄H₅₂N₁₆O₂₈·Cl₅: C, 14.46; H, 2.63; N, 11.24. Found: C, 14.4; H, 2.6; N, 11.7. ¹H NMR (D₂O, pH* 7): δ 2.71 (s, 4H, CH₂), 6.45 (t, *J* = 5.7 Hz, 1H, H5), 8.35 (d, *J* = 5.7 Hz, 2H, H4, H6).

Preparation of {[enPt(pymo-N¹,N³)]₄(ClO₄)₄}₂·[H₂O]₈(ClO₄)₄ (6). A solution of **2** (0.04 mmol in 3.3 mL of H₂O) was treated with 5 M HClO₄ (1 mL). The colorless solution gave, after 1 week, colorless needles of **6**. Yield: 40 mg (50%). Anal. Calcd for Pt₈C₄₈H₁₀₈N₃₂O₆₈·Cl₁₂: C, 13.73; H, 2.59; N, 10.67. Found: C, 13.7; H, 2.6; N, 10.9. ¹H NMR (D₂O, pH* 2.2): δ 2.71 (s, 4H, CH₂), 6.45 (t, *J* = 5.7 Hz, 1H, H5), 8.35 (d, *J* = 5.7 Hz, 2H, H4, H6).

Instruments. IR spectra (KBr pellets) were recorded on a Bruker IFS 113v FT spectrometer. ¹H NMR and ¹⁹⁵Pt NMR spectra were recorded on a Bruker AC 200 FT NMR spectrometer using D₂O as solvent. pH* denotes uncorrected pH value. NMe₄⁺ (3.18 ppm relative to TMS) was used as internal standard for the ¹H NMR spectra and K₂PtCl₆ as external reference for the ¹⁹⁵Pt NMR spectra.

Solution Studies. pH dependent ¹H NMR spectra were recorded in an attempt to determine the acidity constants of the compounds described in this study following the method described previously by us.¹¹ The interaction of various sulfonate anions with the metallacalix[4]arenes described in this paper was studied by ¹H NMR spectroscopy following the method earlier described by us.⁵

X-ray Crystallography. Intensity data for **1**, **2**, and **4** were collected on an Enraf-Nonius KappaCCD¹² (Mo Kα, λ = 0.71069 Å, graphite monochromator) with sample-to-detector distances of 35.7, 32.7, and 29.7 mm, respectively. They covered the whole sphere of reciprocal space by measurement of 1216 (**1**) and 360 (**2**, **4**) frames rotating about ω in steps of 1° with scan times of 15, 50, and 200 s per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames, respectively, and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.¹³ The scaling and the global refinement of crystal parameters were performed by SCALEPACK.¹³ Reflections, which were partly measured on previous and following frames, are used to scale the frames on each other. Merging of redundant reflections in part eliminates absorption effects and also considers crystal decay if present.

The structures were solved by standard Patterson methods¹⁴ and refined by full-matrix least squares based on *F*² using the SHELXTL-PLUS¹⁵ and SHELXL-93 programs.¹⁶ The scattering factors for the atoms were those given in the SHELXTL-PLUS program. Transmission factors were calculated with SHELXL-97.¹⁷ Hydrogen atoms were placed at calculated positions and refined with a common isotropic temperature factor. All non hydrogen atoms have been refined anisotropically with the following exceptions in **4** because of the poor reflections-to-parameter ratio: the nitrogen ring atoms, the oxygen atoms of two perchlorate anions, the disordered oxygens of another perchlorate, and all atoms of the two half-occupied anions as well as all water molecules, a part of them also only half-occupied.

Crystal data and data collection parameters are summarized in Table 1.

Results and Discussion

Synthesis and Solution Studies of 1 and 2. The reaction of [enM(H₂O)₂](NO₃)₂ (M = Pd^{II}, Pt^{II}) with 2-hydroxypyrimidine (Hpymo) in water affords, in a single step, the cyclic compounds [enM(pymo-N¹,N³)]₄(NO₃)₄ (**1**, M = Pd^{II}; **2**, M = Pt^{II}) which are structurally analogous to calix[4]arenes. From ¹H NMR spectroscopy, it can be deduced that the reaction is quantitative in the case of Pd^{II} and ca. 70% for Pt^{II}. ¹H NMR spectra of compounds **1** and **2** are diagnostic of a N1, N3 bridging

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Table 1. Crystallographic Data for **1**, **2**, and **4**

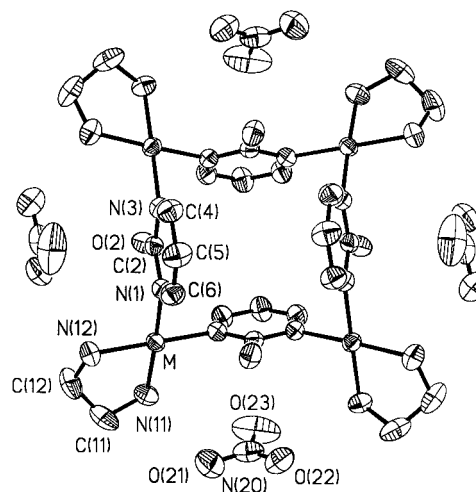
	1	2	4
empirical formula	C ₆ H ₁₁ O ₄ N ₅ Pd	C ₆ H ₁₁ O ₄ N ₅ Pt	C ₂₄ H ₅₉ O _{31.5} N ₁₆ Cl ₅ Cu _{0.5} Pt ₄
fw (g mol ⁻¹)	323.60	412.29	2065.25
temp (K)	293(2)	153(2)	293(2)
λ (Å)	0.71069	0.71069	0.71069
space group	I $\bar{4}$	I $\bar{4}$	P2 ₁ /n
a (Å)	16.063(2)	16.053(2)	16.693(3)
b (Å)	16.063(2)	16.053(2)	15.203(3)
c (Å)	8.649(2)	8.556(2)	23.483(5)
β (deg)			99.50(3)
V (Å ³)	2231.6(6)	2204.9(6)	5878(2)
Z	8	8	4
μ(Mo Kα) (mm ⁻¹)	1.672	12.74	9.99
ρ _{calc} (g cm ⁻³)	1.926	2.484	2.334
T _{min} , T _{max}	0.37, 0.49	0.14, 0.36	0.16, 0.69
R1 ^a	0.023	0.030	0.046
wR2 ^b	0.057	0.048	0.097
max Fourier diff (e Å ⁻³)	1.17	0.66	1.35

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

coordination mode of pymo, with retention of the original equivalence of H4 and H6 protons in pymo. Replacement of the acidic protons at N1 and N3 in H₂pymo⁺ by two metal entities in compounds **1** and **2** is responsible for significant high-field shifts of the aromatic protons of pymo, namely, H4, H6 (-0.47 ppm) and H5 (-0.56 ppm) for **1** and H4, H6 (-0.57 ppm) and H5 (-0.60 ppm) for **2**. The presence of only one set of signals for each resonance of the pyrimidine ring indicates fast rotation (on the NMR time scale) of the pyrimidine rings about the Pt-N1 and Pt-N3 bonds. This behavior should lead to rapid conformational changes in solution (see below), unlike in the case of the uracil metallacalix[4]arene [enPt(uracilate)]₄(NO₃)₄, where rotation about Pt-N1 and Pt-N3 bonds is hindered and consequently slow due to the presence of two exocyclic carbonyl groups. The poor solubility of **2** in common organic solvents does not permit this assumption to be proven by variable temperature NMR spectroscopy, however. The ¹⁹⁵Pt NMR spectrum of **2** in D₂O shows a single sharp signal at -2740 ppm, which is in agreement with a PtN₄ environment and with the equivalence of the four Pt^{II} centers in **2**.

Structures of Compounds 1 and 2. Compounds **1** and **2** are composed of tetranuclear cyclic [enM(pymo-N¹,N³)]₄⁴⁺ (**1**, M = Pd^{II}; **2**, M = Pt^{II}) cations and nitrate anions. A perspective view of the molecular structure of compounds **1** and **2** is depicted in Figure 1. A selection of structural parameters for compounds **1** and **2** is listed in Table 2. The X-ray analysis shows that metal binding occurs as expected at both the N1 and N3 donor atoms of the pymo residues, leading to the desired metallacalix[4]arene. The four metal centers show a square planar geometry, in which bonding distances and angles are in the usual range. The geometry of the pyrimidine ligand is similar to that found in compounds with the pymo exhibiting the same N1, N3 bridging coordination mode.^{11,18} The tetranuclear cations display a 1,3-alternate arrangement of the pymo residues, similar to that found in [enPt(uracilate)]₄(NO₃)₄.⁴ The dimensions of the box defined as the mean separation between the metal centers are ~5.9 Å for the sides and ~8.3 Å for the diagonals for compounds **1** and **2**.

One of the major interests in metallacalixarenes is their possible use as hosts for guest molecules. Actually, we have recently proven that metallacalix[4]arene [enPt(uracilate)]₄⁴⁺ in its cone conformation and metallacalix[3]arene [(enPt)(2,2'-

**Figure 1.** View of the molecular structure of the isomorphous complexes **1** and **2** (M = Pd^{II} or Pt^{II}). Ellipsoids are drawn at the 50% probability level.**Table 2.** Selected Bond Distances (Å), Angles (deg), and H-Bonding Distances (Å) in **1**, **2**, and **4**

	1	2	4
M-N1	2.032(2) ^a	2.015(7) ^a	2.03(1)
M-N3	2.020(2)	2.039(7)	2.05(1)
M-N11	2.033(2)	2.033(7)	2.04(1)
M-N12	2.032(2)	2.026(7)	2.04(1)
N1-M-N3	89.89(9) ^a	90.1(3) ^a	90.4(5)
N11-M-N12	84.25(9)	83.7(3)	82.7(5)
Cu1-O11A			1.98(1)
Cu1-O12A			1.97(1)
Cu1-O13A			2.42(1)
O11A...O2D			2.76(1)
O11A...O2C			2.59(1)
O12A...O2A			2.60(1) ^b
O12A...O2B			2.67(1) ^b
O13A...O2A			2.84(1)
O13A...O2D			3.10(1)

$$^a -y, x, -z + 2. \quad ^b x + 1/2, -y + 3/2, z + 1/2.$$

bipyrazine)(enM)]₃¹²⁺ (M = Pd^{II}, Pt^{II})⁸ act as hosts for anions. The ability of **1** and **2** to include anions in their cavities has been studied by means of ¹H NMR spectroscopy applying a series of sulfonate anions. The tetranuclear cations in compounds **1** and **2**, despite their high positive charge, are unable to include anions. The 1,3-alternate conformation exhibited by the cations in the solid state makes them poor candidates as hosts, however. The opening of the cavity as defined by the mean separation between the C5 atoms of two opposite pymo residues (~4.3 Å) is simply too small to permit inclusion of guest molecules. In solution, compounds **1** and **2** are conformationally flexible, probably adopting other conformations (see below). Nevertheless, none of them (among them the pinched-cone conformation adopted by **4** and **6**) seem to be appropriate for anion inclusion.

In the crystal, the tetranuclear cations in **1** and **2** are stacked along the crystallographic z axis, thereby producing long channels (Figure 2). Repeating units are 8.649(2) and 8.556(2) Å apart for **1** and **2**, respectively. This feature is similar to the one found in [enPt(uracilate)]₄(NO₃)₄.^{4a,b} Nitrate anions interact with the tetranuclear cations via H bonding involving NH₂ of en ligands.

Coordination Chemistry of the Metallacalixarenes. Organic calix[4]arenes act as efficient ligands for metal ions through their basic oxo surface.^{19,20} Likewise, metallacalix[4]arene [enPt(uracilate)]₄(NO₃)₄ behaves as a very efficient ligand

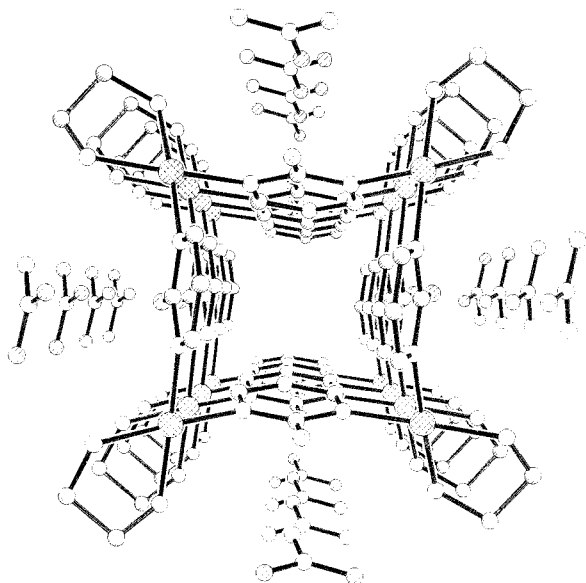


Figure 2. Packing of tetranuclear cations and nitrate anions in **1** and **2** along the *z* axis.

toward diverse metal ions.^{4c,d,5} Compounds **1** and **2** were initially thought to be also good candidates for binding additional metal ions. However, our attempts to coordinate different metal ions to their oxo surface were fruitless. In contrast to [enPt(uracilate)]₄(NO₃)₄ there is no evidence from ¹H NMR studies (D₂O) of binding of either soft (Pd^{II}, Pt^{II}), borderline (Zn^{II}), or hard (Na^I, Be^{II}, La^{III}) metal ions. This result is not surprising if the acidic character of the O-donor groups in **1** and **2**, as deduced from pH* dependent ¹H NMR studies, is taken into account (see below). Nevertheless, three adducts (compounds **3**–**5**) which contain Na^I and Cu^{II} metal ions were isolated. One of these, {[enPt(pymo)]₄(ClO₄)₄}₂·[Cu(H₂O)₆](ClO₄)₂ (**4**), was successfully characterized by X-ray analysis. It reveals that there is no Cu^{II} coordination to the oxo surface of the metallacalix[4]arene. We presume that a similar situation is realized in **3** and **5**.

Structure of Compound 4. Selected bond distances and angles for **4** are given in Table 2. The structure solution revealed the composition of the material as [Cu(H₂O)₆]²⁺ and [enPt(pymo)]₄⁴⁺ cations in a 1:2 ratio, ClO₄⁻ counterions, and lattice water molecules. In **4** the basic structure of the metallacalix[4]arene is retained. The Pt centers are coordinated to both N1 and N3 donor atoms of pymo residues. However, in contrast to the solid-state structures of **1** and **2**, a pinched-cone arrangement of the pymo residues is now found (Figure 3). This arrangement is similar to the one displayed by uracil nucleobases in {Ag₄[enPt(uracil)]₄}(NO₃)₈.^{4b} {Zn[enPt(uracilate)]₄}SO₄⁵ presents, however, a regular cone conformation and behaves as an anion receptor. The cavity of **4** is not well structured since two pymo residues are too close (C5–C5 separation of 3.63(3) Å) while the other two pymo residues are 10.45(3) Å apart. So it is to be concluded that the pinched-cone conformation is not suitable for inclusion of a guest molecule. Nevertheless, a [Cu(H₂O)₆]²⁺ cation is sandwiched between the oxo surface of two [enPt-

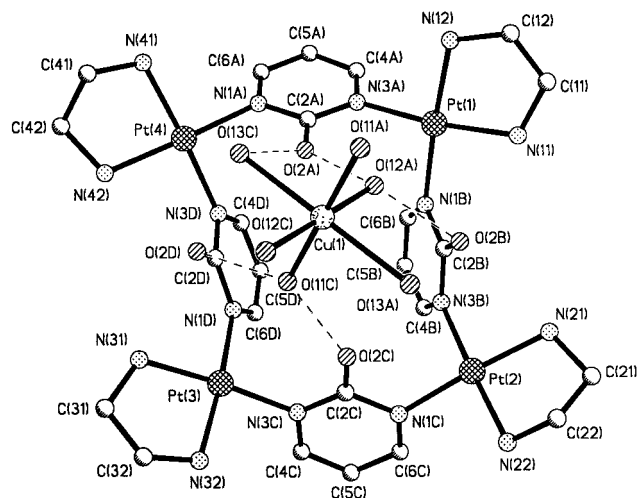


Figure 3. Perspective view of the interaction between [Cu(H₂O)₆]²⁺ and a tetranuclear [enPt(pymo-*N*¹,*N*³)]₄⁴⁺ cation in **4**.

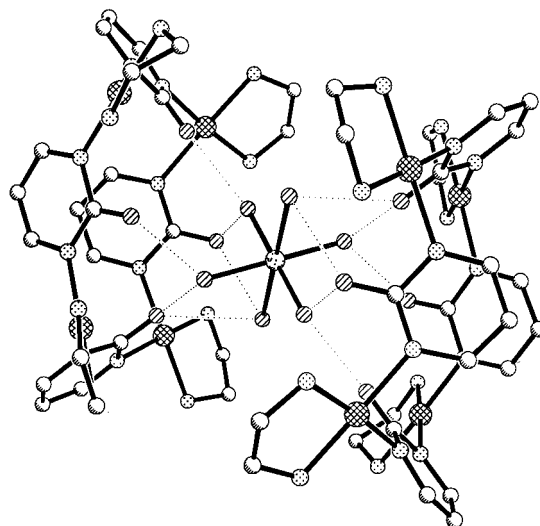


Figure 4. View of a [Cu(H₂O)₆]²⁺ cation sandwiched between the oxo surfaces of two metallacalix[4]arenes in **4**.

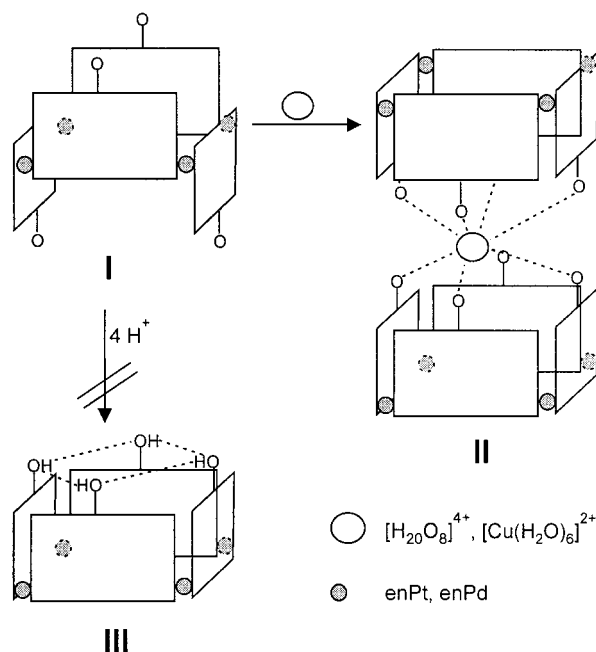
(pymo)]₄⁴⁺ cations (Figure 4). The heterometal is not directly bound to the oxygen atoms of the metallacalix[4]arene as in Cu₄[enPt(uracilate)]₈X₄ (X = Cl, (SO₄)_{0.5}),^{4d} but it interacts strongly through H bonding between the water molecules coordinated to the copper center and the oxo surface of the metallacalix[4]arenes (see Table 2), thereby stabilizing the pinched-cone conformation found in **4**. The fact that the H bonding interactions of the [Cu(H₂O)₆]²⁺ guest are responsible for the switch from 1,3-alternate (structure **I** of Scheme 1) to pinched-cone conformation (structure **II** of Scheme 1) of the tetranuclear cation is a direct proof of the low energy barrier between both conformers. In this context we note that we have recently discussed the role played by H bonding in the stabilization of a specific conformation in Pt complexes of model nucleobases which present a high degree of rotational freedom.²¹ In the present case, interaction of [Cu(H₂O)₆]²⁺ with [enPt(pymo)]₄⁴⁺ is responsible for the stabilization of the pinched-cone conformation within a large variety of possibilities. The ¹H NMR spectrum of **4** in D₂O is identical with that of **2** with

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Scheme 1



virtually no paramagnetic broadening due to the presence of Cu^{II} . We conclude that the structure of **4** is not retained in solution and that rapid conversion between 1,3-alternate, pinched-cone, and other possible conformers of **2** takes place.

There are no unusual packing features in **4**. The $[\text{Pt}_4\text{CuPt}_4]^{10+}$ units do not interact directly but are rather separated by counterions and water molecules. There are multiple H-bonding interactions between anions, diamine ligands, and water molecules, none of which are unusual, however.

Acid–Base Properties of the Metallacalixarenes. We had anticipated that protonation of the O-donor groups of the metallacalix[4]arenes **1** and **2** might lead to a situation similar to that found in the classic organic calix[4]arenes, in which the incorporation of four protons is responsible for the stabilization of the cone conformation through formation of a cyclic H-bonding pattern (structure **III** of Scheme 1).⁶ pH^* dependent ^1H NMR studies provide no evidence for protonation of the exocyclic O-donor groups down to $\text{pH}^* 0$ in **2**, however, which is in agreement with the very low basicity of the cation. In the case of **1** acidification does not lead to shifts of the pymo signals. However, an additional set of signals for H5 (6.77 ppm) and H4, H6 (8.85 ppm) grows in at $\text{pH}^* < 2$ and increases in intensity when the pH^* is lowered. This process may be ascribed to an equilibrium of $\mathbf{1} + 4\text{H}^+ \rightleftharpoons 4[\text{enPd}(\text{Hpymo}-N^1)(\text{H}_2\text{O})]^{2+}$ or related species. The extent of the hydrolysis at $\text{pH}^* 0$ is ca. 20–30%. Taking into account the relatively labile nature of Pd^{II} species, the low tendency of **1** to hydrolyze may be considered an indication of a pronounced thermodynamic stability of the cyclic complexes. Crystallization of **2** from strongly acidic solution (1 N HClO_4) produced crystals of a compound for which the elemental analysis suggested a composition $\text{H}_2[\text{enPt}(\text{pymo})_4(\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ (**6**). Titration of the product with NaOH confirms the presence of two strongly acidic protons per formula unit. Attempts were also made to crystallographically character-

ize this compound. Small crystals of **6** were isolated and examined by X-ray crystallography. The structure determination is not of high precision due to poor crystal quality and high disorder of anions and, therefore, will not be reported in detail. However, the composition of the compound is clearly confirmed. The structure presents a number of similarities to that found in **4**. Coordination of the Pt^{II} atoms is not altered and takes place at N1 and N3 donor atoms of pymo residues, giving rise to a metallacalix[4]arene with a pinched-cone conformation (Scheme 1). As in **4**, the pinched-cone conformation appears to be stabilized by multiple H-bonding interactions between the oxo-surface of two $[\text{enPt}(\text{pymo})_4]^{4+}$ cations and a protonated water cluster $[\text{H}_{20}\text{O}_8]^{4+}$, which is found in the middle of two metallacalix[4]arenes (structure **II** of Scheme 1). In contrast to the classical organic calix[4]arenes,²² there is no direct H-bonding interaction between two O-donor groups in the oxo surface (structure **III** of Scheme 1). The large O2–O2 separation of ~ 3.8 Å found in the pinched-cone arrangement may be responsible for the lack of direct interaction, which is mediated by the insertion of hemiprotonated water molecules between two O-donor groups of the cyclic cation. Of particular interest is the protonated $[\text{H}_{20}\text{O}_8]^{4+}$ water cluster. In the literature there is only one case of a crystallographically characterized $(\text{H}_2\text{O})_8$ cluster that possesses a cubelike structure.²³ In addition, there are several reports which theoretically predict the stability of octameric water clusters.²⁴

As with **4**, the ^1H NMR spectrum of **6** registered immediately after its dissolution in D_2O is identical with that of **2**. This fact suggests either that the pinched-cone conformation is only stable in the solid state as a consequence of the H-bonding scheme or, more probably, that the energy barrier between the two conformers is small.

Conclusions. By making use of a combination of 120° and 90° bond angles provided by the Hpymo ligand and enM ($\text{M} = \text{Pd}^{\text{II}}, \text{Pt}^{\text{II}}$) metal entities, respectively, the direct synthesis of metallacalix[4]arenes by a self-assembly process is possible. These compounds are analogous to classic organic calix[4]arenes in both their structure and conformational dynamics. Despite the positive charge of these metallacalix[4]arenes, interactions with positively charged species are possible. Multiple H-bonding interactions between metallacalix[4]arenes and guest molecules are the driving force in the molecular recognition process.

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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