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Cyclic Trimer versus *Head–Tail* Dimer in Metal–Nucleobase Complexes: Importance of Relative Orientation (*Syn*, *Anti*) of the Metal Entities and Relevance as a Metallaazacrown Compound

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The formation and crystal structure analysis of a cyclic trinuclear Pd complex with bridging 1-methylcytosinato model nucleobases is reported: $[\{(tmeda)Pd(1\text{-}MeC^{-}\text{-}N3,N4)\}_3](ClO_4)_3 \cdot 5.5H_2O$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine; 1-MeC$^-$ = 1-methylcytosine deprotonated at exocyclic amino group) is obtained, among others, from the hydroxo-bridged dinuclear species $[\{(tmeda)Pd(OH)\}_2](ClO_4)_2$, which likewise has been characterized by X-ray crystallography, and 1-MeC (1-MeC = neutral 1-methylcytosine) in aqueous solution. The usual *head–tail* dimer (HT1) appears not to be formed presumably because of the steric bulk of the tmeda ligand, which prevents a close approach of two tmeda ligands. There is also no evidence for formation of an alternative *head–tail* dimer structure (HT2) which, in principle, would not lead to any steric clash of ligands, but would require an orientation of the metal at N(4) that is almost perpendicular to the nucleobase plane. In the Pd_3 compound, the bridging metals are approximately in an *anti* arrangement, thereby leading to Pd···Pd separations within the Pd_3 triangle close to 5.2 Å. This arrangement is reflected in the ^{1}H NMR spectrum by a strongly deshielded H5 resonance of the nucleobase, occurring at 6.56 ppm (D_2O). The overall structure of the Pd_3 is that of a double cone, with ClO_4^- counterions approaching the cavities from either side. The trinuclear structure is also maintained in Me_2SO-d_6. In this solvent, Pd_3 acts as a fluoride anion receptor, with F^- binding to the N(4)H protons, as evident from large downfield shifts of these protons. The compound is compared with cyclic adeninato complexes of hexacoordinated metal ions, and a conceptional analogy with [12]metallacrown-3 species is outlined.

Introduction

Self-assembly processes of mononuclear metal complexes to cyclic oligomers are a phenomenon of topical interest.[1] Factors determining ring size of oligomers appear to be a combination of different features which include thermodynamics (ring strain, entropic effects),[2] physicochemical conditions of sample preparation (temperature,[2,3] pressure,[4] concentration,[2,5,6] crystal packing forces,[7] solvent,[5] anions), and inherent molecular properties of the building blocks (e.g., coordination geometry of metal, steric bulk of ligands).[8,9] These aspects have been intensely discussed in terms of equilibria between trimers and tetramers,[5,7,8] tetramers and pentamers,[10] and tetramers and hexamers,[3] as well as more complex equilibria.[11,12] In contrast, equilibria between the smallest cyclic species, the dimer and the second largest cycle, the trimer, have received much less attention.

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This applies also to pyrimidine model nucleobase compounds derived from *cis*-L_2M^{II} ($L = NH_3$, PR_3, or L_2 = diamine; M= Pt, Pd), a class of compounds we[13] and others[14−17] have been particularly interested in. In the large majority of cases with N(1) blocked uracil, thymine, and cytosine nucleobases (as well as of structurally related ligands[18]), dinuclear compounds have been described.[19] There is only a single example, from the group of Longato, on a cyclic trinuclear complex, derived from *cis*-$(PMe_3)_2Pt^{II}$ and 1-methylcytosine (1-MeC).[17]

Here we report on our findings of how steric bulk of the amine ligand L_2 in *cis*-[L_2Pd^{II} (1-MeC-*N3*)(H_2O)]$^{2+}$ (with L_2 = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) appears to prevent formation of the dinuclear *head*−*tail* complex and instead leads to a cyclic, trinuclear one. In the trimer, the Pd ions are mutually *anti*, whereas for a stable *head*−*tail* dimer a *syn* arrangement is required. In a formal sense, the trinuclear complex can be considered a [12]metallaazacrown-3 ([12] mac-3) compound, hence an inorganic analogue of 1, 5, 9-triazacyclododecane.

With this work we continue our studies on cyclic metal complexes of N-heterocyclic ligands,[3,20] including of pyrimidine nucleobases.[19a]

Experimental Section

Preparation. The title compound [{(tmeda)Pd(1-MeC$^-$)}$_3$]-(ClO_4)$_3$·5.5H_2O was prepared from (tmeda)$PdCl_2$[21] and 1-methylcytosine (1-MeC)[22] as follows.

[{(tmeda)Pd(*μ*-OH)}$_2$](ClO$_4$)$_2$. Addition of $AgNO_3$ (340 mg, 2 mmol) to a suspension of *cis*-[(tmeda)$PdCl_2$] (294 mg, 1 mmol) in 20 mL of water resulted in the immediate precipitation of AgCl. The mixture was stirred at room temperature in the dark for 2 h and then filtered from AgCl. A1-equiv amount of aqueous NaOH (0.5 M) and excess $NaClO_4$ were added to the filtrate, which was stirred for 1 h. The resulting solution was subsequently concentrated in vacuo to a volume of 5 mL. Yellow crystals were obtained upon cooling the solution in ice water. The yield was 224 mg, 66%. Anal. Calcd (%) for $C_{12}H_{34}N_4O_{10}Cl_2Pd_2$: C, 21.25; H, 5.05; N, 8.26. Found: C, 20.90; H, 5.00; N, 8.20. ^{1}H NMR (200 MHz, D_2O): δ (ppm) 2.58 (s, 12H, CH_3), 2.72 (s, 4H, CH_2). IR (cm^{-1}): 3438 vs, 3334 s, 2923 w, 1464 vs, 1408 w, 1385 w, 1285 m, 1107 vs, 1065 vs, 956 m, 931 w, 811 m, 773 w, 624 s, 513 m, 489 w, 456 w.

[{(tmeda)Pd(1-MeC$^-$)}$_3$](ClO$_4$)$_3$·5.5H$_2$O. A solution of [(tmeda)-Pd(*μ*-OH)]$_2$(ClO_4)$_2$ (134 mg; 0.2 mmol) and 1-methylcytosine (50 mg; 0.4 mmol) in 10 mL of H_2O was stirred at room temperature for 48 h and then warmed to 80 °C for 3 days. The solution was centrifuged from some black powder (presumably Pd) and then evaporated under vacuum. Crystals suitable for X-ray crystallography were obtained upon slow cooling of a saturated (at 80 °C) aqueous solution of the complex. The yield was 150 mg, 79%. Anal. Calcd (%) for $C_{33}H_{79}N_{15}O_{20.5}Cl_3Pd_3$: C, 27.53; H, 5.53; N, 14.59. Found: C, 27.45; H, 5.30; N, 14.65. ^{1}H NMR (400 MHz, D_2O, pD 3.5): δ (ppm) 7.17 (d, ^3J = 7.6 Hz, 3H, H6), 6.51 (d, ^3J = 7.6, 3H, H5), 5.20 (s, 3H, N(4)H; slow isotopic exchange; cf. text), 3.21 (s, 9H, CH_3), 2.72 (m, 12H, CH_2), 2.62 (m, 36H, CH_3). IR (cm^{-1}): 3788 vw, 3659 w, 3434 s, 3229 m,2924 w, 1651 vs, 1537 vs, 1493 s, 1467 m, 1383 s, 1341 s, 1270 s, 1089 vs, 1016 w, 957 w, 810 m, 770 m, 697 w, 625 m, 572 w, 476 w.

[(tmeda)Pd(1-MeC-*N*3)$_2$](NO$_3$)$_2$·2H$_2$O. $AgNO_3$ (340 mg, 2 mmol) was added to a suspension of *cis*-[(tmeda)$PdCl_2$] (294 mg, 1 mmol) in 20 mL of water, and the mixture was stirred at room temperature in the dark for 2 h and then filtered from AgCl. 1-MeC (250 mg, 2 mmol) was added to the filtrate and stirred for 1 h. The resulting solution was subsequently concentrated in vacuo to a volume of 5 mL. Yellow crystals were obtained after 2 days. The yield was 417 mg, 71%. Anal. Calcd (%) for $C_{16}H_{34}N_{10}O_{10}Pd$: C, 30.36; H, 5.41; N, 22.13. Found: C, 30.40; H, 5.25; N, 22.35. ^{1}H NMR (200 MHz, D_2O, pD 7): δ (ppm) 7.63 (d, ^3J = 7.2 Hz, 2H, H6), 6.02 (d, 2H, H5), 3.44 (s, 6H, CH_3), 2.96 (m, 4H, CH_2), 2.64 (m, 12H, CH_3). IR (cm^{-1}): 3243 vs, 3085 vs, 1666 vs, 1544 s, 1506 s, 1465 m, 1383 vs, 1064 w, 1041 m, 958 s, 787 vs, 643 vs

Spectroscopy and other Measurements. ^{1}H NMR spectra were recorded on a Varian Mercury 200 instrument in D_2O using sodium 3-(trimethylsilyl)propanesulfonate (TSP) as internal reference and in Me_2SO-d_6 using the solvent peak at 2.50 ppm as a reference. F$^-$ binding to the Pd_3 compound was studied by ^{1}H NMR spectroscopy following addition of aliquots of [NMe_4]F dissolved in Me_2SO-d_6 to solutions of Pd_3 in the same solvent. Relative amounts of Pd_3 and of F$^-$ were determined on the basis of integrated intensities of aromatic protons of 1-MeC$^-$ in Pd_3 and [NMe_4]$^+$. The downfield shifts of the N(4)H, as well as one of the tmeda-CH_3 resonances, were followed. The presence of water in the mixture (primarily from water of crystallization of Pd_3 and the strongly hygroscopic fluoride salt) prevented a quantitative determination of the association constant of Pd_3 with F$^-$ (see Results and Discussion). IR spectra (KBr pellets) were recorded on an IFS 28 FT spectra. Elemental analysis measurements were performed with a Carlo Erba model 1106 Strumentazione element-analyzer.

X-ray Crystallography. A single crystal was selected for compound [(tmeda)Pd(*μ*-OH)]$_2$(ClO_4)$_2$, while several crystals of [{(tmeda)Pd(1-MeC$^-$)}$_3$](ClO_4)$_3$·5.5H_2O were tested for their suitability. X-ray intensity data were collected at room temperature for [(tmeda)Pd(*μ*-OH)]$_2$(ClO_4)$_2$ and at 120 K for [{(tmeda)Pd(1-MeC$^-$)}$_3$](ClO_4)$_3$·5.5H_2O on an Enraf-Nonius-KappaCCD diffrac-

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Table 1. Crystallographic Data

	[(tmeda)Pd-(μ-OH)]$_2$(ClO$_4$)$_2$	[{(tmeda)Pd-(1-MeC$^-$)}$_3$](ClO$_4$)$_3$·5.5H$_2$O
formula	$C_{12}H_{34}N_4O_{10}Cl_2Pd_2$	$C_{33}H_{79}Cl_3N_{15}O_{20.5}Pd_3$
fw	678.13	1426.56
space group	$P2_1/c$	$P\bar{1}$
a (Å)	5.9929(12)	12.621(3)
b (Å)	9.6322(19)	13.074(3)
c (Å)	21.324(5)	19.722(4)
α (deg)	90	78.22(3)
β (deg)	105.48(3)	86.87(3)
γ (deg)	90	65.56(3)
V (Å^3)	1186.3(5)	2898.6(14)
Z	2	2
D_{calcd} (Mg/m^3)	1.899	1.635
μ (mm^{-1})	1.794	1.138
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0448, 0.0734	0.0636, 0.1266
R indices (all data)	0.0990, 0.0872	0.1461, 0.1510

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

tometer[23] using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). None of the crystals showed evidence of crystal decay during data collection. For data reduction and cell refinement, the programs DENZO and SCALEPACK[24] were used. Corrections for incident and diffracted beam absorption effects were applied using SADABS.[25] The structures were solved by conventional direct methods and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 using the SHELXTL 5.1 program.[26]

In [(tmeda)Pd(μ-OH)]$_2$(ClO$_4$)$_2$, a rotationally disordered perchlorate anion is present. For [{(tmeda)Pd(1-MeC$^-$)}$_3$](ClO$_4$)$_3$·5.5H$_2$O, one of the ClO$_4^-$ (Cl(5A/ 5B)) is poorly defined, and only four positions were found for the oxygen atoms that could not be resolved over the eight positions due to the disorder. Therefore, some Cl−O distances deviate from the average literature values. No rational disorder scheme has been found which yielded better results. Of the ClO$_4^-$ anions, the Cl(5A) is disordered over four positions (25% for each, cf. Supporting Information) around a center of inversion, making two positions each symmetry related. The Fourier-difference syntheses revealed the presence of 5.5 water molecules, several of which were disordered. The hydrogen atom on O(1) in [(tmeda)Pd(μ-OH)]$_2$(ClO$_4$)$_2$ was located in a difference Fourier map and refined isotropically while the other hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. Except for the disordered atoms and C(6C), all non-hydrogen atoms in the structures were refined anisotropically. Crystallographic data and details of refinement are reported in Table 1.

Results and Discussion

***μ*-OH Starting Compound.** [(tmeda)Pd(OH)(H$_2$O)]$^+$, prepared in solution from the diaqua species upon addition of 1 equiv of NaOH, was isolated as a bis-μ-hydroxo bridged dimer, [(tmeda)Pd(OH)$_2$Pd(tmeda)]$^{2+}$, and crystallized as its ClO$_4^-$ salt. Two different views of the cation are shown in Figure 1. Selected interatomic distances and angles are listed in Table 2. The cation is closely analogous to similar bis-μ-hydroxo bridged dimers of Pd^{II} [27] and Pt^{II}.[28] The four angles about the Pd centers and their immediate donor atoms deviate markedly (by 7−9° in either direction) from the ideal 90° angle in square-planar metal complexes, resulting in slight tetrahedral distortions about the metals (e.g.: N(1A)−Pd(1)−O(1A), 174.12(3)°; N(2A)−Pd(1)−O(1), 175.10(2)°). Similarly, the central Pd(1)−O(1)−Pd(1A)−O(1A) unit is not a square but rather a parallelogram, with the two halves of N$_2$PdO$_2$ slightly bent and forming an angle of 6.6°. We note that there are other examples of bis(μ-hydroxo) dimers of Pt^{II} which display strongly bent butterfly structures with hinge angles of up to 43°.[29]

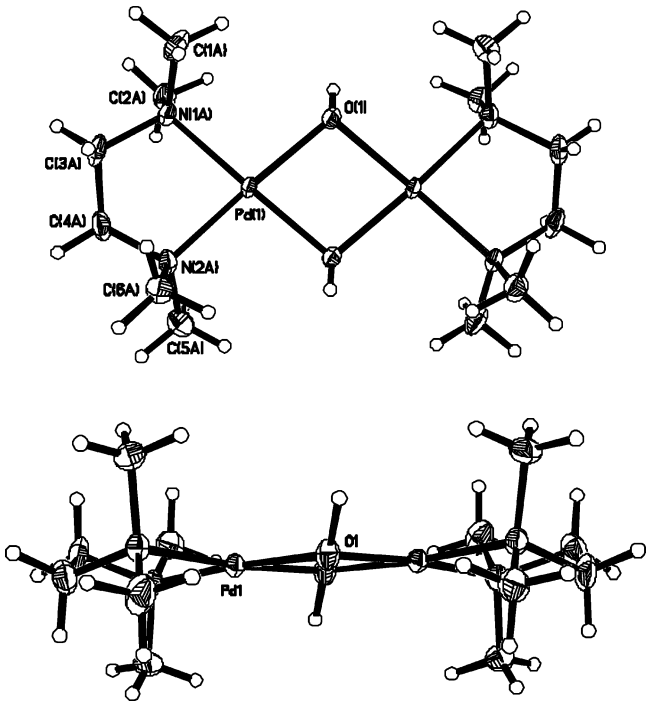

Figure 1. Top and side views of [(tmeda)Pd(OH)$_2$Pd(tmeda)]$^{2+}$ cation with atom numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(tmeda)Pd(μ-OH)]$_2$(ClO$_4$)$_2$[a]

Pd1−O1	2.029(4)	N1A−C1A	1.473(8)
Pd1−N1A	2.049(4)	N1A−C2A	1.489(8)
Pd1−N2A	2.052(5)	N1A−C3A	1.498(9)
Pd1−O1A	2.040(4)	N2A−C4A	1.481(9)
O1−Pd1−N1A	97.59(2)	Pd1−N2A−C4A	105.8(4)
O1−Pd1−N2A	175.10(2)	Pd1−N2A−C5A	112.9(4)
O1−Pd1−O1A	80.38(2)	Pd1−N2A−C6A	108.9(4)
N1A−Pd1−N2A	85.62(2)	Pd1−N1A−C3A	106.7(3)
O1A−Pd1−N1A	174.12(3)	Pd1−N1A−C2A	108.1(7)
O1A−Pd1−N2A	96.78(2)	Pd1−N1A−C1A	114.1(3)
Pd1−O1−Pd1A	99.62(1)		

[a] Symmetry transformations used to generate equivalent atoms: $2 - x$, $-2 - y$, $-z$.

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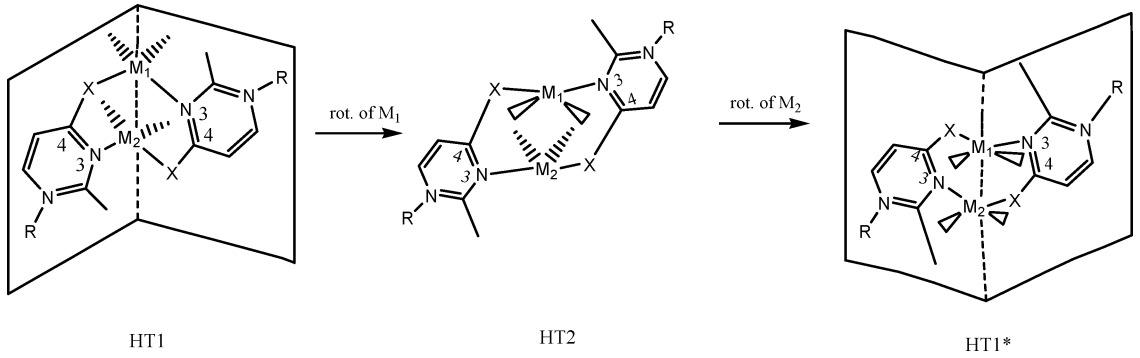

Figure 2. Inter-relationship between two enatiomers (HT1, HT1*) of head−tail dimers and hypothetical second head−tail dimer HT2. Rotation of M planes by 180° leads to the different forms. Note that HT1 and HT1* are V-shaped, with the two metals *syn*, and relatively short M···M distances. (3 ±0.2 Å with pyrimidine bases). In contrast, in HT2 the two nucleobases are essentially parallel, the mutual orientation of the metals is halfway between *syn* and *anti*, and the M···M distance is long (≥5 Å with pyrimidine bases).

The OH ligands in the here-described Pd dimer are involved in hydrogen bonding with oxygen atoms of the perchlorate anions (O(1)···O(14A)), 2.88(1) Å; Pd(1)−O(1)···O(14A), 117.4(3)°).

Oligomerization of Pyrimidine Nucleobase Complexes of *cis*-L_2M^{II} (M = Pt, Pd). The 1:1 complexes of type *cis*-$L_2M^{II}(Nb)(H_2O)$ (M = Pt or Pd, Nb = nucleobase; charge of complex omitted) have a tendency to undergo condensation reactions with formation of oligomeric species. Similarly, reaction of dinuclear *cis*-$[L_2M(OH)_2ML_2]^{2+}$ with 2 equiv of nucleobase can lead to formation of oligomeric nucleobase complexes. These processes can be accompanied by nucleobase deprotonation. With N1-blocked pyrimidine bases, cyclic dimers[13−16] and in one case a cyclic trimer[17] have been structurally characterized. There is a good chance that larger oligomers with cyclic or open structures exist.[30] In general, the two bases in a cyclic dimer adopt a *head−tail* arrangement, in agreement with expectations from its way of formation from monomeric *cis*-$L_2M(Nb)(H_2O)$. Occasionally, this arrangement is also reached via isomerization of a corresponding *head−head* dimer.[31] Without exception and irrespective of the mutual orientation of the two bases (*head−tail* or *head−head*), in all dinuclear X-ray structurally characterized complexes derived from *cis*-L_2M^{II}, the two metals are mutually *syn* and both metal ions are essentially coplanar with the two nucleobases. This is depicted for the head−tail dimer HT1 in Figure 2. As a consequence, the metal coordination planes are more or less parallel or slightly tilted, with the d_{z^2} orbitals pointing toward each other. M···M contacts are relatively short (ca. 3.0 ± 0.2 Å), depending on the bulk of the L ligands, the tilt angle of the metal coordination planes, and the torsion angle about the M···M vectors. Although inter-related in a number of cases,[32] a universal relationship between these parameters appears not to exist.[33] In the case of M^{II} = Pt and with small L ligands such as NH_3, the short approach of the Pt centers facilitates metal oxidations and metal−metal bond formation.

It is obvious that increasing steric bulk of the L ligands leads to a lengthening of the intramolecular metal−metal distance, but it is presently unknown to which extent the M···M distance can be stretched with the *head−tail* structure HT1 still retained. From model building, it becomes evident that an elongation of the metal−metal distance causes the metal ions bonded to the exocyclic X group (N(4)H in case of cytosine; O(4) or O(2) in case of uracil and thymine) to move out of the nucleobase plane. After a rotation of one of the two metal planes by 180°, the metal at the exocyclic group of the base is almost at right angle to the base plane. Structural features of this second, hypothetical *head−tail* dimer (HT2) can be described as follows: The cation has no longer the characteristic V-shape of HT1, but rather the two bases are oriented approximately parallel like steps of a stair with no overlap (Figure 2). Unlike in HT1, the L_2 ligands of both metal entities point in different directions in HT2, thus avoiding any steric interference. Finally, the M···M distance is long (estimated ≥5 Å). It is unclear if HT2 can exist with pyrimidine nucleobases as a bridging ligand. The sp^2 hybridization of the exocyclic X groups and the spatial orientation of the lone electron pair(s) seem to make such an arrangement not very favorable. Irrespective of the question of existence of HT2 as a stable entity, it is worth noting that successive rotation of both metal planes leads again to a *head−tail* dimer HT1*, although its chirality is opposite to that of HT1. This discussion on metal plane rotation has anticipated that no bond breakage takes place during this process. It is obvious that opening of a single M−nucleobase bond would facilitate this rearrangement process greatly and likewise would speed up the interconversion of the two *head−tail* enantiomers.

Our attempt to obtain an HT2 form of $[\{(tmeda)Pd(1\text{-}MeC^-)\}_2]^{2+}$ under the assumption that steric bulk of the tmeda ligands might favor HT2 over HT1 was clearly not successful. Rather, the cyclic trimer $[\{(tmeda)Pd(1\text{-}MeC^-)\}_3]^{3+}(Pd_3)$ was detected in solution and eventually isolated. In this trimer, like in HT1 and in contrast to HT2, the metal ions are again close to coplanar with the nucleobase planes, albeit the metals adopt mutual *anti* orientations. The

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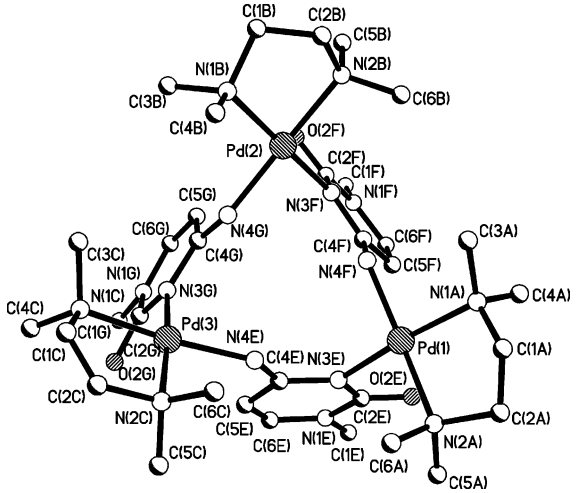

Figure 3. Perspective view of trinuclear cation $[\{(tmeda)Pd(1\text{-}MeC^{-}\text{-}N3,N4)\}_3]^{3+}$ and atom numbering scheme. The view is down the pseudo-3-fold axis of the double cone.

Table 3. Selected Distances (Å) and Angles (deg) for $[\{(tmeda)Pd(1\text{-}MeC^{-})\}_3](ClO_4)_3\cdot 5.5H_2O$

Pd1−N1A	2.076(8)	Pd2−N3F	2.056(7)
Pd1−N2A	2.086(6)	Pd2−N4G	2.018(6)
Pd1−N3E	2.065(6)	Pd3−N1C	2.077(8)
Pd1−N4F	2.015(6)	Pd3−N2C	2.083(6)
Pd2−N1B	2.064(8)	Pd3−N3G	2.045(6)
Pd2−N2B	2.072(6)	Pd3−N4E	2.019(7)
Pd1···Pd2	5.166(3)	Pd1···Pd3	5.175(2)
Pd2···Pd3	5.169(1)		
N1A−Pd1−N2A	85.3(3)	N2B−Pd2−N3F	94.7(3)
N1A−Pd1−N3E	171.6(3)	N2B−Pd2−N4G	171.8(3)
N1A−Pd1−N4F	91.9(3)	N3F−Pd2−N4G	89.7(3)
N2A−Pd1−N3E	93.7(3)	N1C−Pd3−N2C	84.9(3)
N2A−Pd1−N4F	171.4(3)	N1C−Pd3−N3G	93.9(3)
N3E−Pd1−N4F	90.2(2)	N1C−Pd3−N4E	169.9(3)
N1B−Pd2−N2B	85.7(3)	N2C−Pd3−N3G	173.9(3)
N1B−Pd2−N3F	174.8(3)	N2C−Pd3−N4E	91.9(3)
N1B−Pd2−N4G	90.7(3)	N3G−Pd3−N4E	90.3(3)
Pd1−N1A−C1A	106.7(5)	Pd2−N2B−C2B	103.3(6)
Pd1−N1A−C3A	117.2(6)	Pd2−N2B−C5B	114.4(6)
Pd1−N1A−C4A	103.7(6)	Pd2−N2B−C6B	110.8(5)
Pd1−N2A−C5A	117.7(5)	Pd3−N1C−C3C	110.9(7)
Pd1−N2A−C6A	106.1(5)	Pd3−N1C−C4C	115.3(6)
Pd1−N2A−C2A	105.9(5)	Pd3−N1C−C1C	105.2(6)
Pd2−N1B−C3B	109.9(6)	Pd3−N2C−C6C	113.5(6)
Pd2−N1B−C4B	114.1(6)	Pd3−N2C−C2C	104.9(7)
Pd2−N1B−C1B	106.4(6)	Pd3−N2C−C5C	110.3(6)

relationship between HT1, the hypothetical HT2, and the cyclic trimer Pd_3 thus can be reduced to their differences in relative orientations of the two metals at N(3) and the exocyclic groups X: The metals are *syn* in the case of HT1, *anti* in the case of Pd_3, and intermediate in the hypothetical HT2.

X-ray Crystal Structure of Trimer. A view of the cation of the cyclic trimer $[\{(tmeda)Pd(1\text{-}MeC^{-}\text{-}N3,N4)\}_3](ClO_4)_3\cdot 5.5H_2O$ is provided in Figure 3, and pertinent structural data are listed in Table 3. The cyclic trimer cation is chiral, but only one of the two enantiomers present in the crystal is shown.

The anionic 1-methylcytosine nucleobases act as bridging ligands, binding the Pd^{II} centers via N(3) and the deprotonated N(4) position. Relative orientations of two adjacent metal ions with regard to the bridging nucleobase are *anti*.

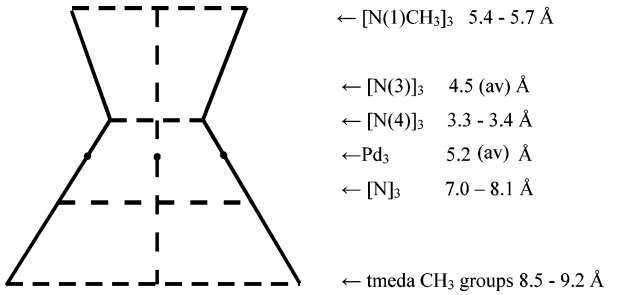

Figure 4. Schematic representation of Pd_3 double cone with separations within triangles of same atoms indicated.

The three Pd ions are at the corners of an almost ideal equilateral triangle, with Pd···Pd distances of 5.166(3)−5.175(2) Å, and angles between 59.98(3)° and 60.10(3)° within the triangle. The three bases are inclined by 74.7(3)° (ring E), 67.1(3)° (ring F), and 71.8(2)° (ring G) with respect to the Pd_3 plane. The three N(4) atoms likewise form a triangle (3.329(8)−3.427(8) Å), as do the N(3) atoms (4.443(8)−4.522(8) Å) and the N(1)CH_3 groups (5.408(10)−5.708(9) Å). These triangles are no longer equilateral as a consequence of the different inclinations of the three nucleobases relative to the Pd_3 plane. Overall, the three 1-MeC^{-} rings provide a cone of approximately 3-fold symmetry. The three tmeda entities likewise form a cone, which at its base is wider than that formed by the three nucleobases. Thus, distances between equivalent amine-N atoms of the tmeda ligands are 6.98(1), 7.12(1), and 7.12(1) Å (N atoms of tmeda opposite to N(3) sites of 1-MeC^{-}) and 7.92(1), 8.01(1), and 8.10(1) Å (N atoms of tmeda opposite to N(4) sites of 1-MeC^{-}), and distances between methyl groups of the tmeda ligands furthest apart are 9.52(1), 9.78(1), and 10.19(1) Å (CH_3 groups at N(2) opposite to N(4) of 1-MeC^{-}, pointing away from 1-MeC^{-} ligands). Thus, the Pd_3 cation has the shape of a double cone, which is wider at the tmeda Pd "bottom" than at the 1-methylcytosine "top" (Figure 4). The structure of Pd_3 thus is similar to that of *cis*-$[\{(PMe)_3Pt(1\text{-}MeC^{-})\}_3]^{3+}$ reported by Longato et al.[17]

Geometries about the Pd^{II} ions are normal. As expected, the bite angles of the tmeda ligands deviate markedly from 90° (ca. 85°, av), but the N3−Pd−N4 angles are virtually ideal (Table 3). The two other angles are consequently larger than 90°, ca. 92°. As to Pd−N bond lengths, they are normal (2.015(6)−2.086(6) Å), displaying a trend of Pd−N(tmeda) > Pd−N3(1-MeC^{-}) > Pd−N4(1-MeC^{-}). There are no major changes in the cytosine rings of Pd_3 as compared to free 1-MeC, Pd−(1-MeC-*N*3), and HT1 of *cis*-$(NH_3)Pd^{II}$.[34] This statement includes C(2)−O(2) and C(4)−N(4) bond lengths.

As pointed out above, the major difference between the here-described trinuclear species and related dinuclear *cis*-$[\{L_2M(1\text{-}MeC^{-})\}_2]^{2+}$ compounds with HT1 structure (L_2M = *cis*-$(NH_3)_2Pd^{II}$,[34] *cis*-$(NH_3)_2Pt^{II}$,[35] *cis*-$(PMe_3)_2Pt^{II}$ [16]) is the *anti* orientation of the metal at N(4) with respect to the metal at N(3) of the same nucleobase. It is this swing of the metal

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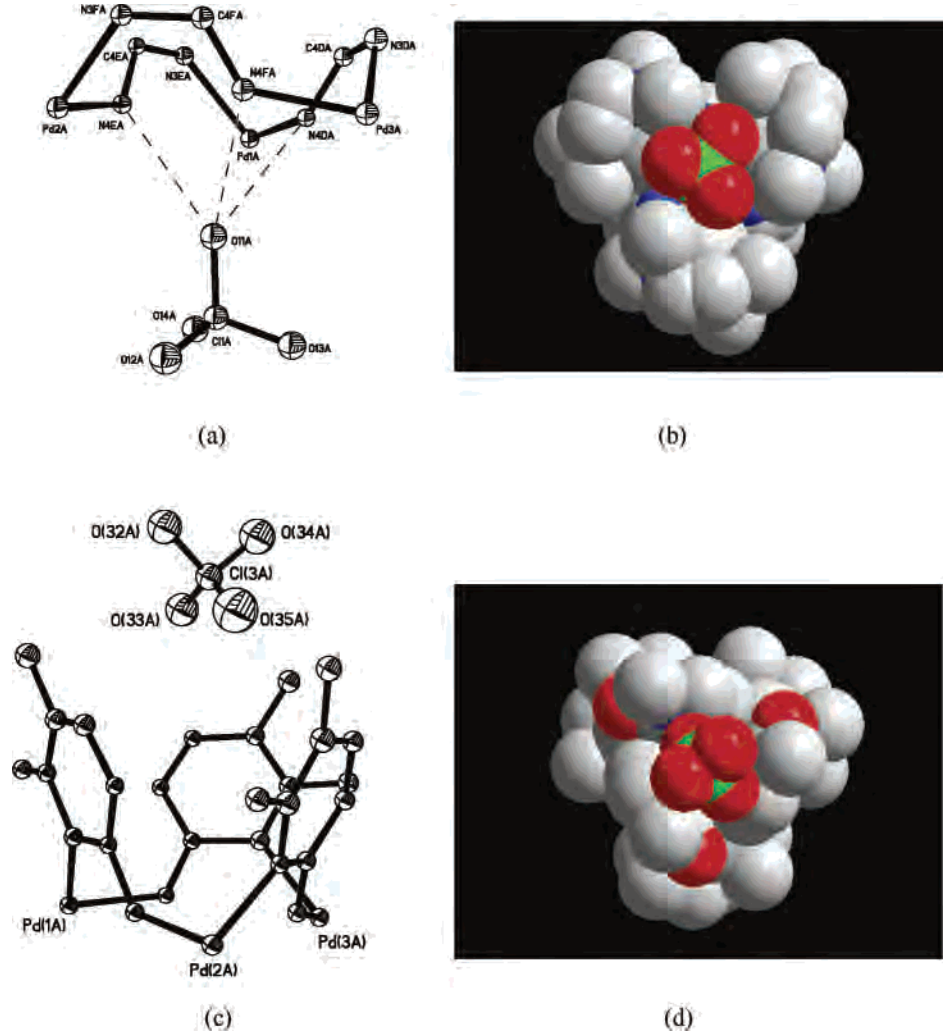

Figure 5. Interactions of two of the four ClO_4^- anions with Pd_3 cation: (a) Interaction of O(11A) with three N(4)H sites ("bottom" of double cone). Only the 12-membered ring is shown. (b) Space filling representation of interaction of this ClO_4^- with bottom cone. (c) Interaction of second ClO_4^- with top cone (tmeda ligands are omitted for clarity). (d) Space filling representation of top cone with ClO_4^-.

at N(4) around the C(4)−N(4) bond which enables the large M···M separation of ca. 5.175(2) Å and hence formation of a cyclic trimer. There are moderate deviations of the metal entities at N(4) from ideal *anti* arrangement, which are reflected by the distances of the three Pd ions from the best nucleobase planes, namely 0.19(2) Å (Pd(1) to ring E), 0.06(2) Å (Pd(2) to ring F), and 0.15(2) Å (Pd(3) to ring G). The values compare with estimated 1.7−2 Å values for the hypothetical HT2 dimer.

A major difference between the previously reported Pt_3 complex[17] and the here-described Pd_3 species refers, despite identical ClO_4^- anions, to the interactions between the trinuclear cations and the anions. While cations and anions are well-separated in Pt_3, in the here-described Pd_3 species two distinct interaction patterns between Pd_3 and ClO_4^- are seen (Figure 5). Thus in Pd_3, two of the three counteranions approach the openings of the double cone: One ClO_4^- anion (Cl(1A)) interacts via O(12A) with the N(4)H triangle from the "bottom". While the protons at the N(4) groups were not located in the X-ray structure determination, inspection of a model clearly reveals that the three protons of N(4)H are pointing toward the perchlorate oxygen atom, with distances of ca. 3.02−3.07 Å between N(4) sites and O(12A). There are additional weak contacts between the other three oxygen atoms of the ClO_4^- and protons of 3 out of the 12 methyl groups of the three tmeda chelate rings which are close to the lower cone C(3A), C(4B), and C(6C); see also the paragraph labeled "Pd_3 as Receptor for Fluoride" below. A second ClO_4^- anion (Cl(3A)) approaches the double cone from the "top". Comparison of the thermal ellipsoids of the atoms of the two anions clearly shows that the one approaching from the top is less fixed and more flexible. It appears that the interaction between one of the oxygen atoms of this second ClO_4^- (O(31A)) involves weak hydrogen bonds with the methyl group in the N(1F) position of the nucleobase (3.327(14) Å). There are two additional positions for ClO_4^- anions: one has a 50% occupancy (Cl(2A)), and one has a 50% occupancy as well and is at the same time disordered (Cl(5A) and Cl(5B)). Neither of these is immediately associated with the Pd_3 cations but rather located in hydrophobic cavities between Pd_3 cations formed by aromatic H5 and H6 protons as well as methyl groups of tmeda ligands. There is a weak hydrogen bond (3.175(16) Å) between O(24A) and C(6E) of the nucleobase.

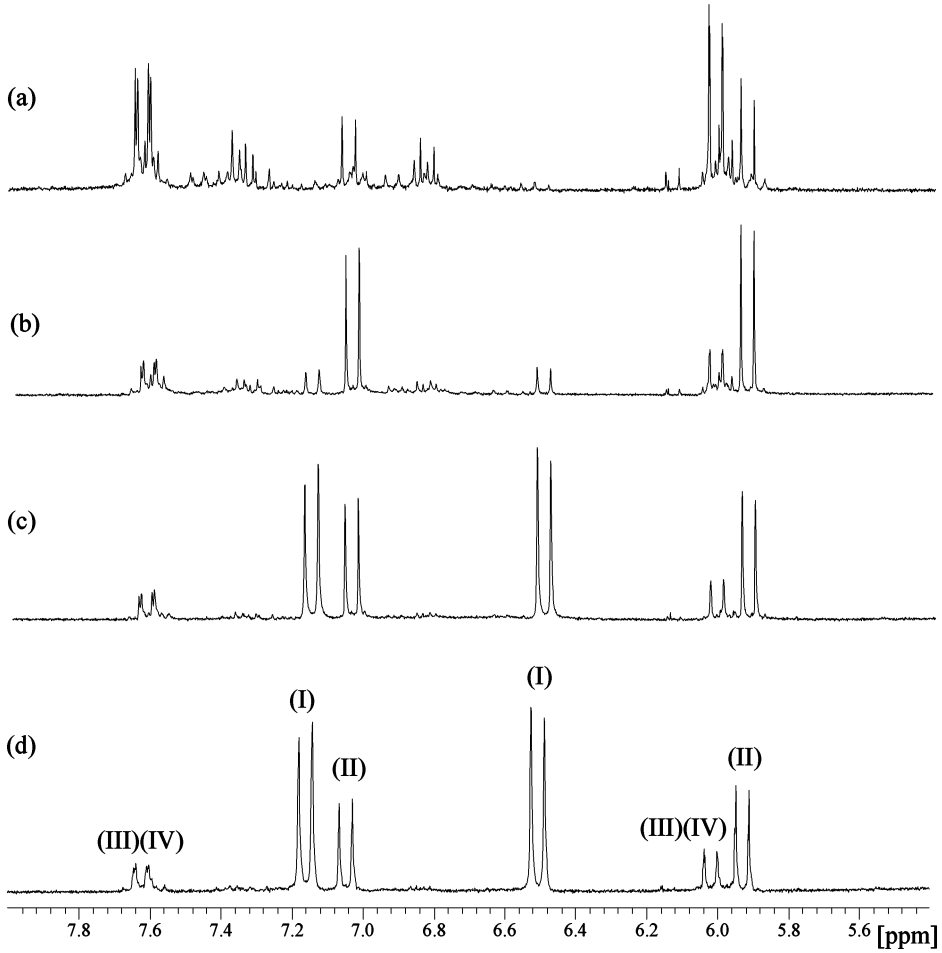

Figure 6. Lowfield sections of ^{1}H NMR spectra (D_2O) obtained upon mixing $[(tmeda)Pd(1\text{-}MeC\text{-}N3)_2]^{2+}$ and $[(tmeda)Pd(H_2O)_2]^{2+}$ (1:1) and addition of NaOD: (a) immediately after adjusting pD to 10.4; (b) after 3 days at 25 °C, pD has dropped to 9.2; (c) after heating to 60 °C for 25 h, pD 9.2; (d) after additional heating to 60 °C for 3 days, pD 9.2. For assignment of I−V, see text.

^{1}H NMR Spectra: Formation of Pd_3 and Evidence for *anti* Orientation of 1-MeC$^-$ in Pd_3. Isolation of the cyclic Pd trimer was preceded by ^{1}H NMR spectroscopic studies on the interaction of the μ-OH dimer $[\{(tmeda)Pd(OH)\}_2]^{2+}$ with 1-MeC and that of $[(tmeda)Pd(1\text{-}MeC\text{-}N_3)_2]^{2+}$ with $[(tmeda)Pd(D_2O)_2)]^{2+}$ at alkaline pD. In both cases, the region of the aromatic cytosine protons is rather complex at the beginning of the reaction but simplifies greatly as the reaction proceeds. Eventually, only a limited number of sets of resonances remain. In Figure 6, ^{1}H NMR spectra obtained by mixing $[(tmeda)Pd(1\text{-}MeC\text{-}N3)_2]^{2+}$ with $[(tmeda)Pd(D_2O)_2]^{2+}$ at alkaline pH are given. In sequence of relative intensities, the following cytosine resonances are eventually observed: Doublets (I) correspond to those of Pd_3, as unambiguously confirmed by recording a spectrum of the isolated compound. Its 1-MeC$^-$ resonances (D_2O, pD 7.7) are observed at 7.17 ppm (H6, d, ^3J = 7.6 Hz), 6.56 ppm (H5, d), and 3.12 ppm (N(1)CH_3, s). Somewhat surprisingly, the N(4)H protons exchange only very slowly against ^{2}D (days) and give rise to a singlet at 5.20 ppm. The tmeda ligands of Pd_3 display two CH_2 quartets centered at approximately 3.0 ppm and four individual methyl singlets at 2.85, 2.83, 2.75, and 2.40 ppm. In wet DMSO-d_6, these resonances are observed at 7.36 ppm (H6; d), 6.38 ppm (H5; d), 5.0 ppm (N(4)H; s), 3.16 ppm (N(1)CH_3; s), and 2.9 ppm (tmeda-CH_2; m) as well as at 2.77, 2.76, 2.65, and 2.33 ppm (tmeda-CH_3; s, each). Already prior to isolation of Pd_3 and its X-ray crystallographic confirmation as a cyclic trimer, we had speculated that I must be a species in which the 1-methylcytosine base is anionic, bridging two Pd^{II} ions, and in particular is in an *anti* orientation relative to the Pd^{II} at N(3). Thus, the upfield shift of H6 as compared to free 1-MeC (7.56 ppm) or typical (1-MeC-*N*3)Pd^{II} species (ca. 7.6 ppm) was consistent with an anionic 1-methylcytosine base being present. On the other hand, the remarkable downfield shift of the H5 doublet relative to free 1-MeC (5.95 ppm) or (1-MeC-*N*3)Pd^{II} (ca. 6.0 ppm) could only be rationalized if a second metal was reasonably close to H5, a situation realized only with this metal being bonded at N4 and present in an *anti* arrangement with respect to N(3). We have previously reported an even larger downfield shift of H5 resonances in pyrimidine nucleobase complexes, namely in complexes derived from (tmeda)Pt(1-MeU-*N*3)$_2$ (1-MeU = 1-methyluracilate).[36] This situation was interpreted in terms of a "face-back" arrangement of the two metals, hence an *anti* orientation of the metal at O(4). The steric bulk of the

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tmeda ligand obviously prevented an arrangement with the second metal being *syn*. We propose that the larger downfield shift of H5 in the case of the 1-MeU compounds (1.64 ppm)[36] relative to 0.5 ppm in Pd_3 is largely due to the fact that in the 1-MeU complex the nucleobase was already anionic. In contrast, in the case of Pd_3, binding of the second metal at N(4) is accompanied by deprotonation of the nucleobase. As the two effects of base deprotonation and metal binding counteract each other as far as the H5 shift is concerned, this effect is smaller in the case of the 1-MeC$^-$ compound.

The nature of the second compound (II) with its H6 doublet at 7.05 ppm and its H5 doublet at 5.93 ppm was identified by analyzing the relative intensities of the 1-MeC$^-$ and the methyl resonances of the tmeda ligands. Integrals of the various resonances gave a ratio of two tmeda ligands per 1-methylcytosine. As the H5 and H6 resonances are constistent with a μ(1-MeC$^-$-*N*3,*N*4) mode, we assign this species a dinuclear structure, either [{(tmeda)Pd(OH)}$_2$(μ-1-MeC$^-$-*N*3,*N*4)]$^+$ or [{(tmeda)Pd}$_2$(μ-OH)(μ-1-MeC$^-$-*N*3,*N*4)]$^{2+}$. Attempts to isolate this compound in pure form have not been successful as yet. We originally also considered the possibility that (II) is the *head*−*tail* dimer (HT1) [{(tmeda)Pd(1-MeC$^-$-*N*3,*N*4)}$_2$]$^{+2}$, in analogy to the situation in the *cis*-(PMe$_3$)$_2$Pt^{II}/1-MeC system.[16,17] There it was shown that HT1 forms as the kinetic product, while the cyclic trimer Pt_3 only formed after long reactions times as the thermodynamic product. However, the chemical shifts of the cytosine resonances of II, when compared with those of the closely related ht dimers [{enPd(1-MeC$^-$-*N*3,*N*4)}$_2$]$^{2+}$ (H6, 6.89 ppm; H5, 5.69 ppm)[34] and *cis*-[{(NH$_3$)$_2$Pt(1-MeC$^-$-*N*3,*N*4)}$_2$]$^{2+}$ (H6, 6.91 ppm; H5, 5.71 ppm),[34] do not agree with a dinuclear structure, even though there is general good agreement ($\leq$0.04 ppm) in 1-MeC chemical shifts of 1:1 and 1:2 complexes of *cis*-a$_2$Pd^{II} (a = NH$_3$, a$_2$ = en, a$_2$ = tmeda).

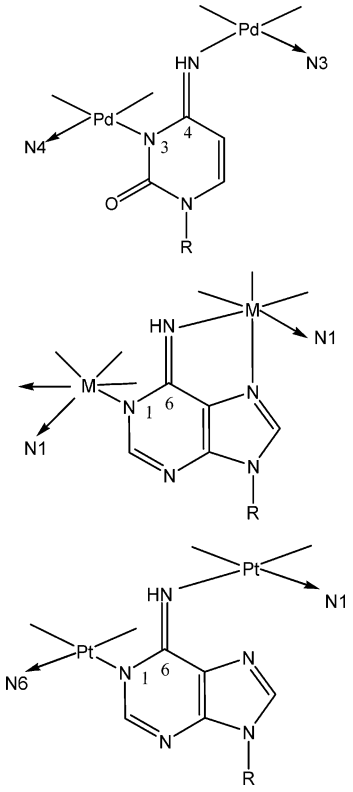
Resonances of the two species III and IV are closely similar and overlap. Although in some of the spectra these sets look like two double doublets, addition of [(tmeda)Pd(1-MeC-*N*3)$_2$]$^{2+}$ leads to an intensity increase of only one of the two doublets (III: H6, 7.63 ppm; H5, 6.02 ppm, ^3J = 7.4 Hz) (Supporting Information). The remaining doublet (IV: H6, 7.62 ppm; H5, 6.00 ppm, ^3J = 7.4 Hz) is tentatively assigned to [(tmeda)Pd(1-MeC-*N*3)(OH)]$^+$.

Occasionally, yet not in the example given in Figure 6, also a fifth set of 1-MeC resonances is observed, which unambiguously can be assigned to free 1-MeC (H6, 7.56 ppm; H5, 5.95 ppm; N(1)CH$_3$, 3.36 ppm at pD 7.2).

The fact that, as demonstrated above, Pd_3 also forms from the 1:2 complex [(tmeda)Pd(1-MeC-*N*3)$_2$]$^{2+}$ clearly demonstrates that the Pd−(1-MeC-*N*3) bond is labile and hence a self-assembly process is taking place.

Relationship of Pd_3 with Cyclic Adeninato Complexes. The cyclic 1-methylcytosinato-bridged Pd_3 compound described here bears a close resemblance with a series of cyclic trinuclear complexes with adenine nucleobases and six-coordinate metal entities such as Rh^{III}(η^5-C$_5$-Me$_5$),[37,38] Ru^{II}(η^6-arene),[39] or *fac*-Pt^{IV}(CH$_3$)$_3$[40] as well as the four-coordinate *cis*-(PMePh$_2$)$_3$Pt^{II} entity.[41] Like in Pd_3, in all cases the metal bound to the exocyclic, deprotonated amino group is in an

Scheme 1



anti orientation relative to the metal at the endocyclic N(1) site. In the compounds with octahedral metal ions, this situation is reinforced by the additional interaction of the metal with N(7) (Scheme 1). The metal triangles in the adeninato compounds containing octahedral metal ions have dimensions exceeding slightly those of the Pd triangle, with M···M distances of ca. 5.6 Å.[38] In the Pt triangle,[41] the Pt···Pt distances are between 5.20 and 5.32 Å and hence very similar to those of Pd_3. The presence of the fused imidazole ring extends the available π-surface in the adenine triangles, however, and in the case of the nucleosides adenosine and 2-deoxyadenosine, the upper cavity is further enlarged by the sugar entities. Consequently, a rich receptor chemistry has been reported for cyclic adenine nucleoside trimers.[42]

Analogy of Pd_3 with Metallacrowns. There is a close conceptional analogy between the classical crown ethers and the azacrowns, in which some or all of the oxygen atoms are replaced by NH functionalities.[43,44] This analogy has

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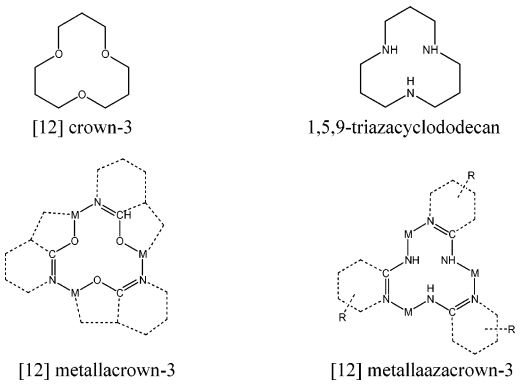

Figure 7. Analogy between crowns, azacrowns, metallacrowns, and metallaazacrowns.

lately been extended by Pecoraro et al. to cyclic metal complexes termed "metallacrowns" (Figure 7). They represent inorganic analogues of crown ethers.[45] According to this concept, CH_2 groups are substituted by heteroatoms such as N atoms and transition metal ions. For example, [12]crown-3 can be converted into the [12]metallacrown-3 by taking advantage of the self-assembly process of a Ru half-sandwich complex and 3-hydroxy-2-pyridone ligands (Figure 7).[46] This compound displays a high affinity for Li^+ cations, for example.[46a,46b,47] Following similar considerations, the here-described Pd_3 compound could be regarded as a [12]metallaazacrown-3 ([12] mac-3). It is obvious that its receptor properties no longer are those of a crown ether and likewise not those of an azacrown in that the NH group, originating from N(4)H of 1-MeC$^-$, has no available electron lone pair. Consequently, no receptor chemistry of Pd_3 toward metal ions is to be expected, but both the positive charge of Pd_3 and the presence of NH functions make this compound a potential anion receptor (vide infra).

Pd_3 as Receptor for Fluoride. The association of two of the ClO_4^- counterions with the Pd_3 cation, as seen in the solid-state structure (Figure 5) and the positioning of the three protons of the N(4) groups, prompted us to look into the potential of Pd_3 to act as a fluoride host. Fluoride was chosen because of its size and spherical shape.

Anion receptors based on directed hydrogen bonding interactions between host and guest are a field of topical interest,[48] with fluoride binding and sensing representing a particular challenge.[49] After applying ^{1}H NMR spectroscopy and concentrating on the N(4)H resonance, there was no evidence for any host−guest chemistry between Pd_3 and F^- found in D_2O as the solvent, presumably as a consequence of efficient solvation of host and guest. In DMSO-d_6, however, shifts of several ^{1}H resonances of the trinuclear Pd_3 cation in the presence of F^- were detected (Figure 8). Thus, addition of increasing amounts of [NMe_4]F to a solution of Pd_3 resulted in a marked downfield shift of the N(4)H resonance, moderate downfield shifts of two of the four CH_3 resonances of the tmeda ligand, and minor upfield shifts of the aromatic protons of the 1-MeC$^-$ ligand. A saturation behavior was seen with more than 2 equiv of F^- added. For example, chemical shift changes of Pd_3 (ClO_4^- salt, 4 mmol/L) in the presence of 4 equiv of [NMe_4]F amounted to $\Delta\delta = 3.75$ ppm for N(4)H, 0.20 and 0.10 ppm, respectively, for tmeda-CH_3, −0.18 ppm for H6, and −0.04 ppm for H5 (Figure 8). Attempts to analyze the chemical shift data and to determine an association constant were hampered by the fact that water was introduced into DMSO-d_6 by both the Pd_3 compound (water of crystallization) and the hygroscopic [NMe_4]F salt and the fact that the N(4)H resonance proved quite sensitive to the presence of water.[50] Deliberate additon of D_2O to DMSO-d_6 solutions of Pd_3 and F^- indeed caused a partial reversal of the chemical shifts mentioned above. Consequently, the slope of $\Delta\delta$ for N(4)H as a function of the ratio (r) between F^- guest and Pd_3 receptor is artificially lowered with the break in the curve reached near $r \approx 2$ (Supporting Information). We do not consider this evidence for a 2:1 stoichiometry (two F^- bound per Pd_3) but rather a consequence of the introduction of water in the system.

As pointed out above, only two of the four methyl resonances of the tmeda ligands proved sensitive for F^-. It was the one furthest downfield (2.77 ppm in DMSO-d_6) and the one furthest upfield (2.33 ppm) which underwent downfield shifts with increasing F^- amounts. It either reflects CH···F hydrogen bonding, averaged over the protons of CH_3 groups involved, or is due to a reorganization of the lower cone in the presence of fluoride. From the structure provided in Figure 3, it appears that at least the methyl groups C(3A), C(4B), and C(6C), which are closest to the cavity with the three N(4)H's at its bottom, are affected by F^- binding.

Concerning the long-term stability of the Pd_3-F^- adduct in Me_2SO-d_6, gradual ^{1}H NMR spectroscopic changes were observed within days at 25 °C only in cases of high F^- excess ($r \geq 4$). A sign of secondary reactions taking place was the appearance of sharp resonances in the 2.1−2.7 ppm region of the spectrum.

(44) With all oxygen atoms replaced by NH groups, these ligands are also termed polyamine macrocycles or azacorands.

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(50) The amount of water being present in solution was determined from the integrated intensities of the H_2O signal (ca. 3.34 ppm) relative to that of the [NMe_4]$^+$ signal (ca 3.09 ppm) and those of the H6 and H5 resonances of the cytosine ligands. A typical situation was found as follows: $c_{Pd3} = 4$ mmol/L, $c_{[NMe4]F} = 5.92$ mmol/L; 32.4 equiv of water per F^- present; δ N(4)H, 6.92 ppm.

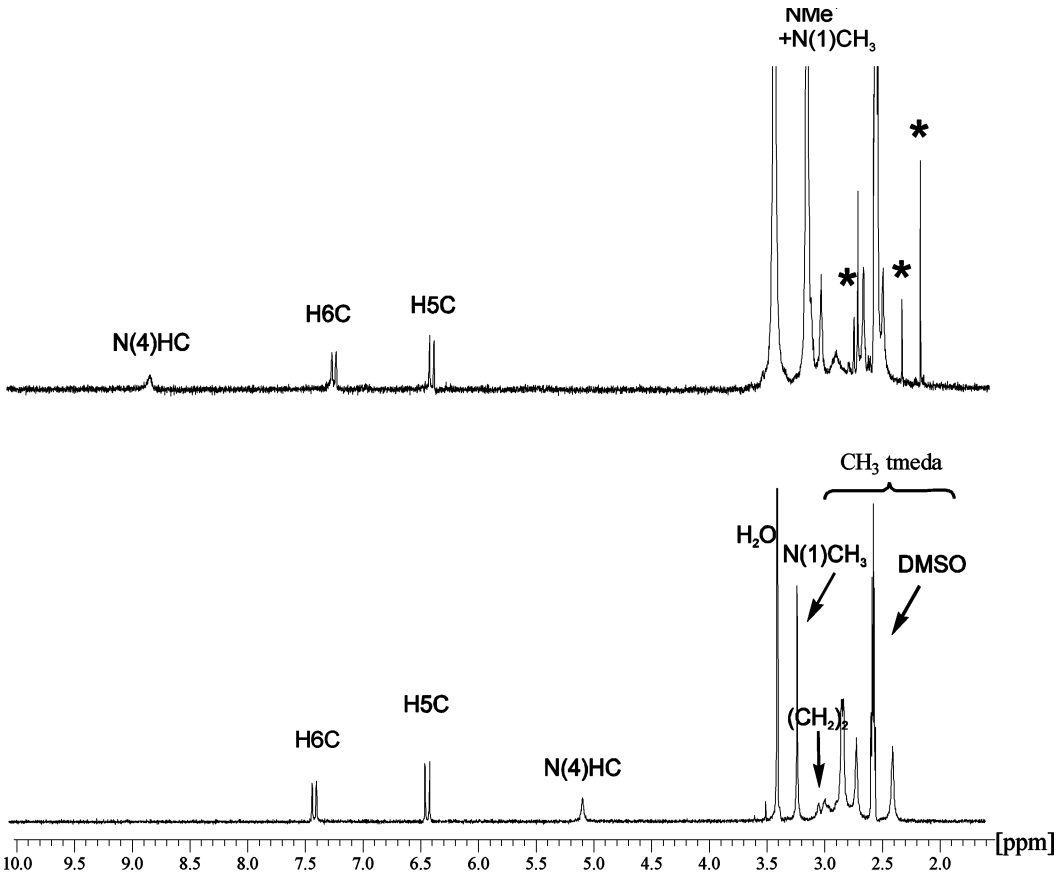

Figure 8. ^{1}H NMR spectra (DMSO-d_6, $c = 4 \times 10^{-3}$ M) of Pd_3 compound (bottom) and in the presence of 4 equiv of $[NMe_4]F$ (top). Note that the water peak increases strongly upon addition of the fluoride salt. Signals with asterisks refer to unknown species.

Summary

A trinuclear cyclic Pd^{II} complex containing 1-methylcytosinato ligands with *N*3,*N*4-anti-bridging modes has been synthesized and characterized. The trimer forms instead of two feasible *head*−*tail* dimers (HT1 and HT2), presumably because of the steric bulk exercised by the tmeda ligands, and unfavorable angles about the exocyclic N(4) donor, respectively. The title compound Pd_3 can be considered formally a [12] metallaazacrown-3 species. Due to the presence of three cyclic N(4)H protons, it acts as a receptor for the small anion fluoride.

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Supporting Information Available: Crystallographic data and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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