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Mono- and Dinuclear Palladium(II) Complexes of Uracil and Thymine Model Nucleobases and the X-ray Structure of $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2\cdot 5.5H_2O$ (Head-Head)

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Several mono- and dinuclear complexes of Pd(II) with the model nucleobase anions of 1-methyluracil (1-MeU) and 1-methylthymine (1-MeT) have been prepared and isolated: $(en)Pd(1\text{-}MeT)_2\cdot 4H_2O$ (**1a**), $(en)Pd(1\text{-}MeU)_2\cdot 5H_2O$ (**1b**), $(bpy)Pd(1\text{-}MeT)_2\cdot 4.5H_2O$ (**2a**), $(bpy)Pd(1\text{-}MeU)_2\cdot 4.5H_2O$ (**2b**), $(phen)Pd(1\text{-}MeT)_2\cdot 6.5H_2O$ (**3**), *trans*-$(NH_3)_2Pd(1\text{-}MeT)_2$ (**4a**), *trans*-$(NH_3)_2Pd(1\text{-}MeU)_2$ (**4b**), $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2\cdot 5.5H_2O$ (**5a**), $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](ClO_4)_2\cdot 4H_2O$ (**5b**), $[(bpy)Pd(1\text{-}MeT)(H_2O)]ClO_4\cdot H_2O$ (**6**), and $[(phen)Pd(1\text{-}MeT)_2Pd(phen)](NO_3)_2\cdot 4.5H_2O$ (**7**). IR, Raman, and ^1H NMR spectroscopic data and the crystal structure of **5a** are reported: triclinic space group $P\bar{1}$, a = 13.085 (4) Å, b = 14.901 (4) Å, c = 12.600 (3) Å, α = 112.61 (2)°, β = 113.47 (2)°, γ = 64.33 (2)°, V = 1963 (2) Å^3, Z = 2, R = 0.034, and R_w = 0.037 for 4854 independent reflections with $F_o^2 \gg 2\sigma(F_o^2)$ and 547 parameters. The two 1-MeT ligands coordinate to Pd through N(3) and O(4) and are arranged head-to-head, with an intramolecular Pd···Pd separation of 2.848 (1) Å. **5a** was obtained both by reaction of **2a** with $[(bpy)Pd(H_2O)_2](NO_3)_2$ and by simple acidification (HNO_3, $[Pd(H_2O)_4](NO_3)_2$) of **2a**. According to ^1H NMR spectroscopy, **5a** exists in solution (D_2O or $D_2O/(CD_3)_2CO$) in an equilibrium of several species, two of which dominate and are proposed to be two dinuclear species in slow equilibrium. A mononuclear species (**6**) converts quantitatively to the dinuclear head-head complex **5b**, which exists in solution in the same equilibrium as **5a**. Attempts to oxidize **5a** or **5b** with either Ce(IV), concentrated HNO_3, or Cl_2 to a mixed-valence dinuclear species or a dipalladium(III) species failed.

Introduction

The faster reaction kinetics of Pd(II) electrophiles as compared to the corresponding Pt(II) compounds yet otherwise similar chemistry of the two metals make the former convenient analogues for studies of Pt-nucleobase interactions.[2-5] Studies of this kind are of interest with respect to the mode of action of Pt antitumor drugs. As far as interactions between Pd(II) ($(en)PdCl_2$, *trans*-$Pd(NH_3)_2Cl_2$, $[(dien)PdCl]^+$) and the pyrimidine nucleobases uracil and thymine or derivatives of these are concerned, N(3) binding has been deduced from ^1H NMR,[6] ^{13}C NMR,[7] and Raman[8] spectroscopic studies. Stability constants (log K), determined potentiometrically[9] or by the use of ^1H NMR[10,11] for $[Pd(dien)L]^+$ (L = deprotonated uracil,[9] uridine,[9] thymidine,[9] 5′-UMP,[10,11] and 5′-TMP[10,11]) are in the 8-8.7 range, indicating a high thermodynamic stability which exceeds even that of 5′-GMP complexes.[11] Similar large log K values are reported for reactions of $[(en)Pd(H_2O)_2]^{2+}$ with uracil, uridine, and thymidine (log K_1, 8.6-9.1; log K_2, 5.9-6.8).[9,12] In moderately alkaline solution containing $(en)Pd^{II}$ and uridine, apart from mononuclear species such as $[(en)PdL(H_2O)]^+$, $(en)PdL(OH)$, and $(en)PdL_2$, also dinuclear μ-hydroxo species are formed, the stability constants of which are considerably lower, however.[12]

Preparative and/or structural work on Pd(II) nucleobase complexes to date essentially is restricted to cytosine,[13] adenine,[14] and guanine[15] derivatives. With uracil and thymine, only with 5-fluorouracil has a series of compounds been described,[16] and more recently, mixed PtPd[17] and Pt_2Pd[18] complexes of anionic 1-methyluracil (1-MeU) and anionic 1-methylthymine (1-MeT) have been prepared in our laboratory. In these mixed-metal compounds, the Pd cations (+2 and +3 oxidation state) are coordinated through the exocyclic O(4) sites of these bases. No Pd nucleobase complex was formed when $[PdCl_4]^{2-}$ and 1-propylthymine were mixed. Rather, the adduct $K_2[Pd_2Cl_6]\cdot 4(1\text{-}proTH)$ crystallized from solution.[19]

In this paper, we describe mononuclear Pd(II) complexes containing N(3)-bound 1-MeU and 1-MeT as well as dinuclear, N(3), O-bridged Pd_2 complexes. The latter were of particular interest with respect to the analogous Pt_2 and the heteronuclear PtPd complexes.

Experimental Section

Preparations. K_2PdCl_4,[20] PdX_2Cl_2 (X_2 = en, bpy[21] with en = ethylenediamine, bpy = 2,2′-bipyridine), and $[PdX_2(H_2O)]Z_2$[17] (X_2 = en, bpy; Z = NO_3^-, ClO_4^-)[22] were prepared as described. $Pd(phen)Cl_2$ (phen = 1,10-phenanthroline)[21] and from it the corresponding aqua (hydroxo) species[23] were prepared by analogy (reaction with 2 equiv of AgZ at 50 °C, filtration of AgCl from hot reaction mixture). 1-MeUH and 1-MeTH were prepared according to published procedures;[24] 1-MeUH was

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Table I. List of Pd(II) Complexes Prepared

compd	compn[a]
1a	$(en)Pd(1\text{-}MeT)_2\cdot 4H_2O$
1b	$(en)Pd(1\text{-}MeU)_2\cdot 5H_2O$
2a	$(bpy)Pd(1\text{-}MeT)_2\cdot 4.5H_2O$
2b	$(bpy)Pd(1\text{-}MeU)_2\cdot 4.5H_2O$
3	$(phen)Pd(1\text{-}MeT)_2\cdot 6.5H_2O$
4a	*trans*-$(NH_3)_2Pd(1\text{-}MeT)_2$
4b	*trans*-$(NH_3)_2Pd(1\text{-}MeU)_2$
5a	$[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2\cdot 5.5H_2O$
5b	$[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](ClO_4)_2\cdot 4H_2O$
6	$[(bpy)Pd(1\text{-}MeT)_2(H_2O)]ClO_4\cdot H_2O$
7	$[(phen)Pd(1\text{-}MeT)_2Pd(phen)](NO_3)_2\cdot 4.5H_2O$

[a] 1-MeT = $C_6H_7N_2O_2$; 1-MeU = $C_5H_5N_2O_2$.

also obtained in a slightly modified version thereof.[25]

(en)Pd(1-MeT)$_2$·4H$_2$O (1a), (en)Pd(1-MeU)$_2$·5H$_2$O (1b), (bpy)Pd(1-MeT)$_2$·4.5H$_2$O (2a), (bpy)Pd(1-MeU)$_2$·4.5H$_2$O (2b), and (phen)Pd(1-MeT)$_2$·6.5H$_2$O (3) were synthesized by analogy to the procedure for *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2\cdot 4H_2O$[26] from the corresponding diaqua species[22] $[X_2Pd(H_2O)_2]Z_2$ (X_2 = en, bpy, phen; Z = NO_3^-, ClO_4^-), to which 2 equiv of NaOH and an excess (3 equiv) of 1-MeUH (1-MeTH) had been added. Column chromatography (Sephadex G-10-120) of the crude material of **1a**, **1b**, and **2b** eventually gave yellow needles of the three compounds in 32, 34, and 80% yield, respectively. The low solubility of **2a** made a cromatographic purification unnecessary (yellow microcrystals, 88% yield). Crude **3a** always contained AgCl, which was separated through repeated filtration of hot (80 °C) aqueous suspensions of the crude material through a fine (G 5) glass filter.

***trans*-(NH$_3$)$_2$Pd(1-MeT)$_2$ (4a) and *trans*-(NH$_3$)$_2$Pd(1-MeU)$_2$ (4b)** were obtained in 60% yield each by mixing K_2PdCl_4 (3 mmol in 25 mL of water), LH (7 mmol), and NH_4OH (ca. 6 mL of 20% aqueous NH_3) and heating the solution (pH = 8) to 50 °C. Precipitation of **4a** and **4b** started rapidly. The white precipitate was filtered off after 2 h, washed with water, acetone and ether, and dried in air. From the filtrate, unreacted LH and crystalline *trans*-$(NH_3)_2PdCl_2$ were isolated.

Synthesis of the dinuclear complexes in general followed the route reported earlier for related Pt complexes[27] and mixed PtPd[17] complexes. No attempts were made to optimize yields.

[(bpy)Pd(1-MeT)$_2$Pd(bpy)](NO$_3$)$_2$·5.5H$_2$O (5a) was prepared accordingly as bright orange-yellow crystals, yield 48%. **5a** was also obtained in 24% yield from $(bpy)Pd(1\text{-}MeT)_2PdCl_2$[28] on treatment with $AgNO_3$ (1 mmol each in 20 mL of water) and addition of bpy (1 equiv) at 50 °C (pH = 3.5, 2 h), filtration of AgCl, concentration to a small volume, and crystallization at 3 °C. **5a** was also obtained on addition of **2a** to an aqueous solution of $[(en)Pd(H_2O)_2](NO_3)_2$.

[(bpy)Pd(1-MeT)$_2$Pd(bpy)](ClO$_4$)$_2$·4H$_2$O (5b) was obtained when excess $[Pd(H_2O)_4](ClO_4)_2$[18] was added to an aqueous solution of **2a**. From the deep yellow solution (pH = 1.3), yellow microcrystals started to precipitate immediately. Yield: 45%. At a later stage, free 1-MeTH crystallized as well. Recrystallization of the crude material from H_2O/acetone (1:1) at 22 °C gave long, transparent columns of **5b**. In a modified version, excess $NaClO_4$ was added to an aqueous solution of **2a** and the pH of the solution (8.0) brought to 6.5 with 0.5 M HNO_3. The yellow precipitate that formed (18 mg from 50 mg of **2a** and 150 mg $NaClO_4$ in 5 mL of H_2O) immediately was filtered off, washed with water, and dried in air. On the basis of the elemental analysis data and its IR spectrum, the compound was assigned to **[(bpy)Pd(1-MeT)(H$_2$O)]ClO$_4$·H$_2$O (6)**. Recrystallization of **6** from H_2O/acetone (1:1; 22 °C) gave single crystals of **5b** as the only product.

[(phen)Pd(1-MeT)$_2$Pd(phen)](NO$_3$)$_2$·4.5H$_2$O (7) was obtained as follows: An aqueous suspension of **3** to which excess $[Pd(H_2O)_4](NO_3)_2$ solution[18] had been added was briefly warmed to 50 °C. The resulting clear, yellow solution was concentrated and filtered off from some residue and allowed to crystallize. Orange columns of **7** were obtained in 45% yield.

Table I lists the Pd complexes prepared. Elemental analysis data, usually for C, H, N and occasionally for additional elements, were satisfactory. These data are given in the supplementary material.

Spectroscopy and Solution Studies. IR spectra were recorded on a Perkin-Elmer 783 spectrometer, Raman spectra on a Jobin Yvon U 1000 spectrometer using krypton laser excitation (647.1 nm), and ^1H NMR spectra on a Varian T 60 spectrometer with a Nicolet pulse unit and a Bruker SY 200 and AM 300 spectrometer, respectively. NMR samples were measured as D_2O or $D_2O/(CD_3)_2CO$ solutions ($[NMe_4]^+$ as internal standard, referenced to sodium 3-(trimethylsilyl)propanesulfonate.) pH values were measured by use of a glass electrode (Metrohm); for D_2O solutions, 0.4 unit was added to the meter reading. UV–vis spectra were recorded on a Perkin-Elmer Model 555 spectrometer. The oxidation studies with $Ce(SO_4)_2$ (dissolved in 0.7 M H_2SO_4) as oxidizing agent were carried out as previously described[17] by using a Pt combination electrode (Metrohm, Ag/AgCl reference).

X-ray Crystallography

Crystal Data for 5a: $[C_{32}H_{30}N_8O_4Pd_2](NO_3)_2\cdot 5.5H_2O$; fw = 1026.5; triclinic, $P\bar{1}$, a = 13.085 (4) Å, b = 14.901 (4) Å, c = 12.600 (3) Å, α = 112.61 (2)°, β = 113.47 (2)°, γ = 64.33 (2)°, V = 1963 (2) Å^3; $F(000)$ = 1038; D_{calcd} = 1.74 Mg m^{-3}; Z = 2; λ(Mo Kα) = 0.71073 Å; μ(Mo Kα) = 9.8 cm^{-1}; T = 293 K.

Crystallographic Measurements and Structure Refinement. A prismatic crystal with dimensions 0.32 × 0.18 × 0.48 mm was chosen for data collection and mounted in a Lindemann capillary tube. Cell parameters were obtained from a least-squares fit to the settings of 25 reflections in the range $15° \ll \theta \ll 20°$ centered on an Enraf-Nonius CAD4 diffractometer by using Mo Kα radiation. The intensity data were collected in the ω-scan mode for reflection widths 0.85 + 0.35 tan θ at variable speeds between 1.03 and 4.02 deg min^{-1}. A total of 5090 independent reflections ($\pm h,k,\pm l$, after averaging equivalent reflections, R_{int} = 0.010) were collected for $2\theta \leq 45°$. Three monitor reflections were measured at regular intervals; crystal decay was not observed. Lorentz, polarization, and empirical absorption corrections (μ = 9.8 cm^{-1}) based on ψ-scan data (ψ intervals = 10°; nine reflections with χ close to 90°) were applied to the reflection intensities. Relative transmission factors were 0.64 (min) and 0.78 (max). On the basis of the criterion $I > 1.0\sigma(I)$, 4854 reflections were used for structure refinement.

The coordinates for the two Pd atoms were obtained from a Patterson synthesis; those of the remaining nonhydrogen atoms were obtained from difference syntheses. Full-matrix least-squares refinement was performed with the SHELX-76[29] system. Ring hydrogen atoms were included at geometrically calculated positions with d(C–H) = 1.08 Å; 1-MeT methyl protons could not be located unambiguously in difference syntheses and were not refined. A joint isotropic temperature factor was refined for the bipyridine H atoms. Difference syntheses revealed the positions of 5.5 water oxygens in the asymmetric unit. Ow(5) and Ow(5)′ are disordered and were assigned site occupation factors of 0.6667 and 0.3333. The temperature factor for Ow(6) indicated partial occupation of this site, and a site occupation factor of 0.50 was assigned. With the exception of Ow(5)′ all non-hydrogen atoms were refined anisotropically, with joint isotropic temperature factors refined to 0.083 (1)3 and 0.086 (5) Å^2 for the 1-MeT and bpy protons, respectively. The terminal reliability indices were R = 0.034 and $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.037 with weights given by the expression $w = (\sigma^2(F_o) + 0.0001F_o^2)^{-1}$. The highest peak in the final difference map was 0.57 e Å^{-3} at 0.61 Å from Ow(6); the largest shift/esd in the final cycle was 0.03. Positional parameters with equivalent isotropic temperature factors are listed in Table II. Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 30. All calculations were performed on a MicroVAX 2000 computer.

Results and Discussion

Formation. Several mononuclear complexes of composition *cis*-$X_2PdL_2\cdot nH_2O$ with X_2 = en, bpy, or phen and L = 1-MeU or 1-MeT as well as two *trans*-X_2PdL_2 complexes have been isolated and characterized. While (en)Pd^{II} complexes of uridine are well established,[3,13] a recent report on the aqueous solution chemistry of $[(bpy)Pd(H_2O)_2]^{2+}$ and $[(phen)Pd(H_2O)_2]^{2+}$ was suggestive of an inertness of the respective μ-hydroxo species $[(phen)Pd(OH)_2Pd(phen)]^{2+}$ that might prevent any reaction with nucleophiles other than OH^-.[22] However, our data leave no doubt whatsoever, that reaction with 1-methyluracil and 1-methylthymine takes place.

The poor solubility of the two trans complexes **4a** and **4b** did not permit any solution studies.

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Table II. Positional Parameters with Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for **5a**

	x/a	y/b	z/c	U_{eq}[a]
Pd(1)	0.0971 (1)	0.1173 (1)	0.0720 (1)	34 (1)
Pd(2)	0.1645 (1)	0.2632 (1)	0.0444 (1)	28 (1)
O(2)	0.3444 (3)	0.3664 (3)	0.1941 (3)	51 (2)
O(4)	0.2228 (3)	0.1373 (2)	0.2277 (3)	43 (2)
N(1)	0.4415 (3)	0.3000 (3)	0.3551 (4)	48 (3)
N(3)	0.2857 (3)	0.2483 (3)	0.2045 (3)	32 (2)
C(2)	0.3569 (4)	0.3084 (4)	0.2480 (4)	38 (3)
C(4)	0.2928 (4)	0.1882 (3)	0.2657 (4)	35 (3)
C(5)	0.3807 (4)	0.1803 (4)	0.3766 (4)	41 (3)
C(6)	0.4516 (4)	0.2369 (4)	0.4153 (4)	50 (3)
C(11)	0.5175 (5)	0.3649 (4)	0.4066 (6)	74 (4)
C(51)	0.3908 (5)	0.1128 (4)	0.4468 (5)	59 (4)
O(2)′	0.3214 (3)	0.2375 (3)	−0.0826 (3)	49 (2)
O(4)′	0.2233 (3)	0.0133 (2)	−0.0072 (3)	44 (2)
N(1)′	0.4106 (3)	0.0665 (3)	−0.1478 (3)	42 (2)
N(3)′	0.2722 (3)	0.1287 (3)	−0.0395 (3)	32 (2)
C(2)′	0.3344 (4)	0.1492 (4)	−0.0892 (4)	37 (3)
C(4)′	0.2826 (4)	0.0322 (3)	−0.0504 (4)	33 (3)
C(5)′	0.3609 (4)	−0.0525 (3)	−0.1112 (4)	37 (3)
C(6)′	0.4207 (4)	−0.0320 (4)	−0.1573 (4)	46 (3)
C(11)′	0.4752 (5)	0.0848 (4)	−0.2070 (5)	61 (4)
C(51)′	0.3712 (5)	−0.1620 (4)	−0.1260 (5)	58 (3)
N(11)	−0.0373 (3)	0.2206 (3)	0.1348 (4)	39 (3)
C(12)	−0.0263 (5)	0.2831 (4)	0.2449 (5)	52 (4)
C(13)	−0.1227 (6)	0.3639 (4)	0.2759 (6)	66 (4)
C(14)	−0.2314 (6)	0.3797 (5)	0.1937 (7)	79 (5)
C(15)	−0.2419 (5)	0.3139 (5)	0.0790 (7)	69 (4)
C(16)	−0.1433 (4)	0.2350 (4)	0.0517 (5)	44 (3)
N(21)	−0.0345 (4)	0.0940 (3)	−0.0739 (4)	43 (3)
C(22)	−0.0208 (5)	0.0214 (4)	−0.1752 (4)	52 (4)
C(23)	−0.1182 (6)	0.0158 (5)	−0.2735 (5)	70 (5)
C(24)	−0.2274 (6)	0.0848 (6)	−0.2674 (6)	78 (5)
C(25)	−0.2394 (5)	0.1577 (5)	−0.1642 (6)	68 (4)
C(26)	−0.1417 (4)	0.1623 (4)	−0.0652 (5)	48 (3)
N(31)	0.0299 (3)	0.2815 (3)	−0.1049 (3)	30 (2)
C(32)	0.0250 (4)	0.2157 (4)	−0.2138 (4)	40 (3)
C(33)	−0.0762 (5)	0.2276 (4)	−0.3059 (4)	50 (4)
C(34)	−0.1732 (5)	0.3092 (5)	−0.2884 (5)	58 (4)
C(35)	−0.1692 (4)	0.3796 (4)	−0.1787 (5)	53 (3)
C(36)	−0.0661 (4)	0.3638 (3)	−0.0864 (4)	34 (3)
N(41)	0.0527 (3)	0.3971 (3)	0.1152 (3)	31 (2)
C(42)	0.0731 (4)	0.4528 (4)	0.2282 (4)	43 (3)
C(43)	−0.0087 (4)	0.5440 (4)	0.2662 (5)	48 (3)
C(44)	−0.1147 (5)	0.5803 (4)	0.1863 (5)	48 (3)
C(45)	−0.1369 (4)	0.5235 (4)	0.0700 (5)	43 (3)
C(46)	−0.0520 (4)	0.4308 (3)	0.0355 (4)	34 (3)
N(51)	0.2343 (6)	−0.0463 (5)	−0.4200 (5)	77 (5)
O(51)	0.1515 (6)	−0.0054 (5)	−0.3760 (7)	155 (6)
O(52)	0.2779 (7)	0.0044 (6)	−0.4302 (6)	149 (7)
O(53)	0.2717 (4)	−0.1380 (4)	−0.4455 (5)	98 (4)
N(61)	0.2396 (9)	0.3724 (5)	0.5597 (9)	104 (7)
O(61)	0.3061 (7)	0.4197 (4)	0.5783 (7)	143 (6)
O(62)	0.2762 (6)	0.3198 (5)	0.6324 (6)	128 (6)
O(63)	0.1497 (7)	0.3753 (6)	0.4819 (6)	151 (7)
Ow(1)	0.0981 (5)	0.2061 (4)	0.5333 (5)	102 (4)
Ow(2)	−0.1275 (6)	0.2107 (6)	0.3863 (6)	158 (7)
Ow(3)	0.7536 (6)	0.4284 (7)	0.5200 (6)	164 (6)
Ow(4)	0.4516 (5)	0.4537 (7)	0.1238 (9)	201 (8)
Ow(5)	0.5361 (7)	0.6588 (6)	0.0775 (8)	108 (7)
Ow(6)	0.4775 (8)	0.6392 (8)	0.2596 (10)	112 (8)
Ow(5)′	0.4913 (18)	0.3547 (15)	0.8396 (20)	131 (6)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. [b] Ow(5)′ was refined isotropically.

The dipalladium(II) complexes $[X_2PdL_2PdY_2]^{2+}$ ($X_2 = Y_2 =$ bpy, phen) were prepared according to the general route

$$cis\text{-}X_2ML_2 + cis\text{-}[(H_2O)_2M'Y_2]^{2+} \rightarrow [X_2ML_2M'Y_2]^{2+} + 2H_2O \quad (1)$$

used in the preparation of diplatinum(II)[27] and mixed Pt(II), Pd(II) complexes (M = Pt, M′ = Pd),[17] leading to products with head-to-head oriented nucleobases L. In Pt_2 and PtPd complexes, X_2 was variable ($(NH_3)_2$, en, bpy, phen), whereas in the Pd_2 complexes described here, formation was found to be restricted to the aromatic amine ligands bpy and phen. Attempts to prepare Pd_2 complexes with X_2 = en and Y_2 = en, bpy, or phen failed due to the sensitivity of $(en)PdL_2$ toward H^+. For example, as deduced from ^1H NMR spectroscopy, liberation of 1-MeUH from (en)Pd(1-MeU)$_2$ (**1b**) starts at pD ~ 6, leading initially to $[(en)Pd(1\text{-}MeU)(D_2O)]^+$ and, at pD ≪ 2, to $[(en)Pd(D_2O)_2]^{2+}$ and free 1-MeUH. Although, in principle, formation of both head-head and head-tail dinuclear species might be expected in the course of this reaction (Figure 1), detectable amounts of these species are not formed under the conditions of our experiment. Analogous Pt(II) complexes behave differently in that (i) they permit isolation of the initial protonated specis *cis*-$[X_2PtL(LH)]^+$,[31] (ii) they lose LH from the complex only slowly, and (iii) they form both head-tail[27c,32] and head-head dinuclear complexes.

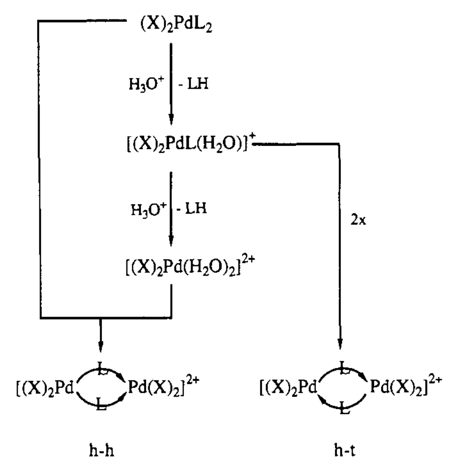

Figure 1. Scheme for possible reactions of X_2PdL_2 complexes with H^+ in the absence of a well-coordinating anion.

Attempts to isolate mixed-amine Pd_2 complexes with Y_2 = en failed as well. Addition of $[(en)Pd(H_2O)_2]^{2+}$, a strong acid, to a solution of X_2PdL_2 (X_2 = bpy, phen) gave dinuclear complexes $[X_2PdL_2PdX_2]^{2+}$ that did not contain the en ligand.

Similarly, simple acidification of X_2PdL_2 (X_2 = bpy) with HNO_3 or $[Pd(H_2O)_4]^{2+}$ (pH ≤ 2) afforded dipalladium(II) complexes according to (2). With one exception (compound **6**),

$$2X_2PdL_2 + 2H^+ \rightarrow [X_2PdL_2PdX_2]^{2+} + 2LH \quad (2)$$

compounds with a Pd:L = 1:1 stoichiometry were not obtained via this route.

It thus appears that the heterocyclic amine ligands, in contrast to en, stabilize the dinuclear complexes and prevent further decomposition by acid. It is likely that ring stacking is responsible for this effect, but poor solubility in water, and possibly also the choice of counterion, may be important as well.

Ligand Orientation. The arrangement of the two bridging L ligands has unambiguously been confirmed (by X-ray analysis) for $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2$ (**5a**). This compound was obtained via route 1. It reveals a head-head arrangement, as might be expected from the manner of preparation. However, the apparent lability of the Pd-N(3)L bond toward acid (e.g. $[X_2Pd(H_2O)_2]^{2+}$) should, in principle, also have allowed formation of a head-tail dimer. This argument applies even more to formation of dinuclear complexes according to eq 2. At least with compound **5a**, routes 1 and 2 give identical products as judged by IR and ^1H NMR spectroscopy, however.

A slight modification of the procedure leading to dinuclear Pd complexes according to (2) yielded a mononuclear compound of composition $[(bpy)Pd(1\text{-}MeT)(H_2O)]ClO_4{\cdot}H_2O$ (**6**),[33] which,

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(31) (a) Lippert, B. *Inorg. Chim. Acta* **1981**, *55*, 5. (b) Schöllhorn, H.; Thewalt, U.; Lippert, B. *J. Am. Chem. Soc.* **1989**, *111*, 7213.

(32) Thewalt, U.; Neugebauer, D.; Lippert, B. *Inorg. Chem.* **1984**, *23*, 1713.

(33) Although ν_3 of ClO_4^- is split into three components (1095, 1125, 1155 cm^{-1}), it is felt that low site symmetry or a perturbation of tetrahedral symmetry by a water molecule might explain this feature better than coordination to Pd. Cf.: Hezel, A.; Ross, S. D. *Spectrochim. Acta* **1966**, *22*, 1949.

Table III. Selected Bond Lengths (Å) and Angles (deg) in **5a**

Pd(2)–Pd(1)	2.848 (1)	O(4)–Pd(1)	2.013 (3)
O(4)′–Pd(1)	2.007 (3)	N(11)–Pd(1)	1.978 (4)
N(21)–Pd(1)	1.992 (4)	N(3)–Pd(2)	2.031 (3)
N(3)′–Pd(2)	2.056 (3)	N(31)–Pd(2)	2.013 (3)
N(41)–Pd(2)	2.015 (3)	C(2)–O(2)	1.214 (8)
C(4)–O(4)	1.271 (7)	C(2)–N(1)	1.372 (5)
C(6)–N(1)	1.355 (9)	C(11)–N(1)	1.477 (9)
C(2)–N(3)	1.383 (7)	C(4)–N(3)	1.343 (8)
C(5)–C(4)	1.421 (6)	C(6)–C(5)	1.346 (9)
C(51)–C(5)	1.513 (10)	C(2)′–O(2)′	1.225 (7)
C(4)′–O(4)′	1.273 (8)	C(2)′–N(1)′	1.371 (5)
C(6)′–N(1)′	1.377 (8)	C(11)′–N(1)′	1.485 (10)
C(2)′–N(3)′	1.384 (8)	C(4)′–N(3)′	1.342 (7)
C(5)′–C(4)′	1.411 (6)	C(6)′–C(5)′	1.323 (10)
C(51)′–C(5)′	1.519 (8)		

O(4)–Pd(1)–Pd(2)	79.7 (1)	O(4)′–Pd(1)–Pd(2)	83.9 (1)
O(4)′–Pd(1)–O(4)	89.2 (1)	N(11)–Pd(1)–Pd(2)	95.3 (2)
N(11)–Pd(1)–O(4)	95.9 (1)	N(11)–Pd(1)–O(4)′	174.6 (1)
N(21)–Pd(1)–Pd(2)	105.2 (2)	N(21)–Pd(1)–O(4)	174.4 (2)
N(21)–Pd(1)–O(4)′	93.9 (1)	N(21)–Pd(1)–N(11)	81.2 (2)
N(3)–Pd(2)–Pd(1)	84.2 (1)	N(3)′–Pd(2)–Pd(1)	80.2 (1)
N(3)′–Pd(2)–N(3)	89.6 (1)	N(31)–Pd(2)–Pd(1)	91.7 (1)
N(31)–Pd(2)–N(3)	173.2 (2)	N(31)–Pd(2)–N(3)′	95.1 (1)
N(41)–Pd(2)–Pd(1)	101.3 (1)	N(41)–Pd(2)–N(3)	94.4 (1)
N(41)–Pd(2)–N(3)′	175.9 (1)	N(41)–Pd(2)–N(31)	81.1 (1)
C(4)–O(4)–Pd(1)	130.9 (4)	C(6)–N(1)–C(2)	120.7 (5)
C(11)–N(1)–C(2)	118.7 (5)	C(11)–N(1)–C(6)	120.5 (4)
C(2)–N(3)–Pd(2)	114.5 (3)	C(4)–N(3)–Pd(2)	122.7 (3)
C(4)–N(3)–C(2)	122.7 (4)	N(1)–C(2)–O(2)	121.8 (5)
N(3)–C(2)–O(2)	121.4 (4)	N(3)–C(2)–N(1)	116.8 (5)
N(3)–C(4)–O(4)	122.1 (4)	C(5)–C(4)–O(4)	118.1 (5)
C(5)–C(4)–N(3)	119.8 (5)	C(6)–C(5)–C(4)	116.4 (6)
C(51)–C(5)–C(4)	120.8 (5)	C(51)–C(5)–C(6)	122.8 (4)
C(5)–C(6)–N(1)	123.5 (4)	C(4)′–O(4)′–Pd(1)	126.5 (3)
C(6)′–N(1)′–C(2)′	119.8 (6)	C(11)′–N(1)′–C(2)′	119.2 (5)
C(11)′–N(1)′–C(6)′	120.9 (4)	C(2)′–N(3)′–Pd(2)	110.9 (3)
C(4)′–N(3)′–Pd(2)	127.1 (4)	C(4)′–N(3)′–C(2)′	122.0 (4)
N(1)′–C(2)′–O(2)′	121.0 (6)	N(3)′–C(2)′–O(2)′	121.7 (4)
N(3)′–C(2)′–N(1)′	117.4 (5)	N(3)′–C(4)′–O(4)′	122.0 (4)
C(5)′–C(4)′–O(4)′	117.7 (5)	C(5)′–C(4)′–N(3)′	120.3 (6)
C(6)′–C(5)′–C(4)′	117.1 (5)	C(51)′–C(5)′–C(4)′	120.6 (6)
C(51)′–C(5)′–C(6)′	122.3 (4)	C(5)′–C(6)′–N(1)′	123.4 (4)
C(12)–N(11)–Pd(1)	124.3 (3)	C(16)–N(11)–Pd(1)	114.6 (3)
C(22)–N(21)–Pd(1)	124.7 (3)	C(26)–N(21)–Pd(1)	114.1 (3)
C(32)–N(31)–Pd(2)	126.1 (3)	C(36)–N(31)–Pd(2)	114.2 (3)
C(42)–N(41)–Pd(2)	126.6 (3)	C(46)–N(41)–Pd(2)	114.0 (3)

however, on recrystallization from water/acetone (1:1, 22 or 60 °C) converted instantaneously to the dinuclear complex **5b**. On the basis of IR, Raman (solid state), and, in particular, ^{1}H NMR spectra (D_2O or $D_2O/(CD_3)_2CO$), the cation of **5b** is identical with that of the structurally characterized species **5a**, and hence a head–head arrangement of the two 1-MeT ligands in the solid state exists. Unambiguous confirmation has now been obtained through X-ray crystallography.[34] These results imply a rapid linkeage isomerization process, either at the stage of the mononuclear species **6** or alternatively at the stage of a dinuclear head–tail isomer[35] to be formed in a condensation reaction of **6**.

Description of the Structure of 5a. Figure 2 depicts the molecular cation of $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2\cdot5.5H_2O$. As can be seen, both Pd(II) are coordinated to a bpy ligand and bridged by two 1-MeT ligands. Pd(2) is bound to two N(3) sites of 1-MeT, while Pd(1) coordinates to two exocyclic oxygens. Unlike in dinuclear Pt(II) complexes of 1-MeT,[17,27,36,37a] the X-ray analysis allows an unambiguous assignment as O(4) for the oxygen atoms that bind to the metal. Table III lists selected bond distances and angles of the cation. Complete lists are to be found in the supplementary material.

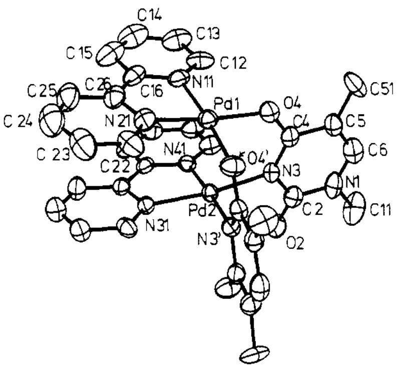

Figure 2. Molecular cation of **5a**. For clarity, the atom numbering is given for one 1-MeT and one bpy ligand only. Other ligands are numbered accordingly as indicated by the coordinating atoms.

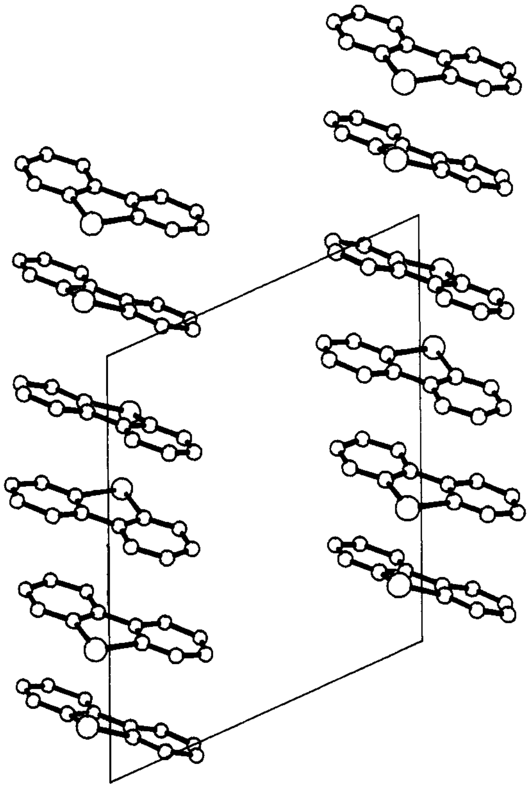

Figure 3. Stacking of Pd(bpy) entities in **5a** along the *b* axis. 1-MeT ligands are not shown.

The coordination geometry of both Pd atoms is square planar with rather small deviations of the ligating atoms (maximum for the Pd(1) plane 0.060 Å, for the Pd(2) plane 0.055 Å) from the five atoms defining the coordination plane, and somewhat variable angles about the heavy metals (e.g. bite angles of bpy of 81.2 (2) and 81.1 (1)°). A comparison of the bond lengths about the Pd atoms reveals that distances to the N donors of the bpy ligands are significantly shorter (maximum of 13σ) than to the trans positioned N(3) and O donors of the 1-MeT rings. Expectedly, the trans influence of oxygen on the Pd–bpy bond is weaker than that of N(3) of 1-MeT.

Bond lengths and angles of bpy and 1-MeT ligands are not unusual. Interestingly, **5a** represents the first example of a thymine complex to show the expected difference in bond length between free and coordinated keto group (C(2)–O(2), 1.214 (8) and 1.225 (7) Å; C(4)–O(4), 1.271 (7) and 1.273 (8) Å; 6–7σ), consistent with a proposed electron distribution for N(3)-platinated uracil or thymine.[26,31,38]

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(34) **6** crystallizes in space group *C*2/*c*, with a = 21.792 Å, b = 14.159 Å, c = 13.677 Å, α = 100.00°, V = 4160 Å^3, and Z = 4. Despite severe disorder of cations and anions, the head–head orientation of 1-MeT rings is apparent, Pd···Pd being 2.827 (4) Å.

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Table IV. Chemical Shifts (δ, ppm) of 1-MeT and 1-MeU Resonances[a]

	chem shift					
	H(6)	H(5)	N(1)-CH$_3$	C(5)-CH$_3$	solv	pD
1-MeTH	7.45 q		3.33 s	1.86 d	D_2O	0–8
1-MeTH	7.51 q		3.35 s	1.87 d	$D_2O/(CD_3)_2CO$	7.8
1-MeT	7.33 s		3.30 s	1.83 s	D_2O	10.6
1a	7.29 q		3.33 s	1.81 d	D_2O	9.5
2a	7.30 s		3.33 s; 3.32 s	1.83 s; 1.81 s	$D_2O/(CD_3)_2CO$	
5a	7.57 s		3.48 s; 3.46 s	2.02 s; 1.98 s	D_2O	6
5a	7.64 s		3.51 s; 3.49 s	2.04 s; 2.01 s	$D_2O/(CD_3)_2CO$	
1-MeUH	7.60 d	5.78 d	3.36 s		D_2O	0–8
1-MeU	7.45 d	5.71 d	3.31 s		D_2O	11
1b	7.31 d	5.50 d	3.25 s		D_2O	7.7
2b	7.45 d	5.59 d; 5.587 d	3.34 s		$D_2O/(CD_3)_2CO$	7.8

[a] Key: s = singlet; d = doublet; q = quartet.

The two Pd coordination planes are tilted by 15.8°, giving rise to a Pd(1)–Pd(2) separation of 2.848 (1) Å. This distance is significantly shorter than that in diplatinum(II)[27,36,37] and mixed Pt(II)–Pd(II)[17] complexes of 1-MeT and 1-MeU ligands as well as an acetato-bridged dipalladium(II) complex.[39] In dipalladium(II) complexes containing four bridging ligands (6-methyl-2-hydroxypyridinate,[40] 6-chloro-2-hydroxypyridinate,[40] pyridine-2-thiolate,[41] thioacetate[42]), Pd–Pd separation are clearly shorter, however, with distances between 2.55 and 2.75 Å.

Figure 3 gives a view of the arrangement of dinuclear cations of **5a**. For clarity, the bridging 1-MeT ligands are omitted. Stacking is along the *b* axis with intermolecular Pd–Pd distances of 4.593 (1) and 6.747 (1) Å.

Vibrational Spectra. A differentiation of binding patterns (N(3) vs N(3), O) in the Pd(II) complexes described here is possible on the basis of several marker bands in the IR and Raman spectra. As previously reported for Pt(II) analogues,[27c,38] the position of an intense IR mode for 1-MeT (and similarly for 1-MeU) at 1580–1590 cm^{-1} is characteristic for monodentate binding through N(3), whereas a shift of this band to ca. 1510 cm^{-1} indicates strong metal binding to both N(3) and an exocyclic oxygen, most likely O(4). The other intense IR band in the double-bond stretching region, at ca. 1660 cm^{-1}, is frequently split in 1-MeT compounds (Δ = 15–40 cm^{-1}). Among the most intense Raman bands of the 1-MeT ring, the ring deformation mode (e.g. 787 cm^{-1} in $(bpy)Pd(1\text{-}MeT)_2$ (**2a**), 805 cm^{-1} in $[(bpy)Pd(1\text{-}MeT)_2Pd(bpy)](NO_3)_2$ (**5a**)) and the ring stretching mode (1238 cm^{-1} in **2a**, 1201 and 1253 cm^{-1} in **5a**) have been found to be good indicators for Pd-binding modes (cf. supplementary material) and are affected in a manner similar to coordination of Pt(II) at N(3) and Mn(II) at O(4).[43]

The monodentate binding mode of 1-MeT in **6** was deduced from the IR bands pattern in the 1700–1500-cm^{-1} range, especially the absence of any strong band around 1500 cm^{-1}. We noted, however, that with moist samples of **6**, the IR spectrum (KBr) indicated partial formation of a N(3), O-bridged species (growing bands at 1510 cm^{-1} at the expense of the 1580-cm^{-1} band) (Figure 4).

^{1}H NMR Spectra. N(3) metal coordination in *cis*-X_2PdL_2 was deduced from the upfield shifts of H(5) and/or H(6) resonances relative to those of free LH (Table IV).

The ^{1}H chemical shifts of the 1-MeU ligands in the Pd complexes are, as with related Pt compounds, influenced in several ways. A comparison of 1-MeU resonances of 1-MeUH, 1-MeU, $(en)Pd(1\text{-}MeU)_2$ (**1b**), and $(bpy)Pd(1\text{-}MeU)_2$ (**2b**) shows that deprotonation of 1-MeUH expectedly causes upfield shifts of all 1-MeU resonances and that, due to ring current effects, the resonances of the two cis-arranged rings in **1b** move further upfield. This shielding effect apparently overcomes the opposite effect of the metal, which normally causes downfield shifts. In **2b**, this trend is reversed, which suggests that the bpy ligand apparently accepts electron density from the metal. In turn, the 1-MeU rings might act as a better σ-donor toward the metal.

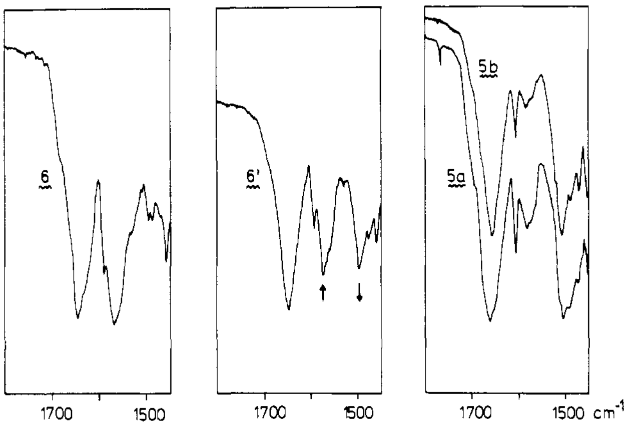

Figure 4. Sections (1800–1450 cm^{-1}) of IR spectra (KBr) of $[(bpy)Pd(1\text{-}MeT)(H_2O)]^+$ (**6**), of a moist sample of **6** (**6′**), and of dinuclear complexes **5a** and **5b**.

Attempts to infer N(3)–Pd binding from pD-dependent downfield shifts of aromatic protons was impossible due to instantaneous decomposition of the Pd complex on addition of acid

$$X_2PdL_2 + D^+ \xrightarrow{D_2O} [X_2PdL(D_2O)]^+ + LD \qquad (3a)$$

$$[X_2PdL(D_2O)]^+ + D^+ \xrightarrow{D_2O} [X_2Pd(D_2O)_2]^{2+} + LD \qquad (3b)$$

or secondary reactions (see above). On the other hand, these reactions indirectly confirmed complex formation of Pd with L. Decomposition reactions (eq 3) at the same time prevented any determination of ligand basicity as in related Pt(II) compounds,[31] but the fact that reaction 3a proceeds quantitatively at pH = 5.5–6 strongly suggests that basicity of the exocylic oxygen(s) of L in the Pd(II) complexes is higher than in the case of *cis*-$(NH_3)_2PtL_2$;[45] hence, the Pd–N(3) bond is weaker. This assumption is indeed reasonable, considering the lower equilibrium constants of Pd nucleobase complexes as compared to those for the corresponding Pt analogues.[12]

A common feature of the ^{1}H NMR spectra of $(bpy)ML_2$ complexes is the doubling of some of the resonances, frequently observed under high resolution only. For example, with M = Pt or Pd and L = 1-MeU, H(5) is doubled, as in the related $[(bpy)Au(1\text{-}MeU)_2]^+$ cation.[46] With the corresponding 1-MeT

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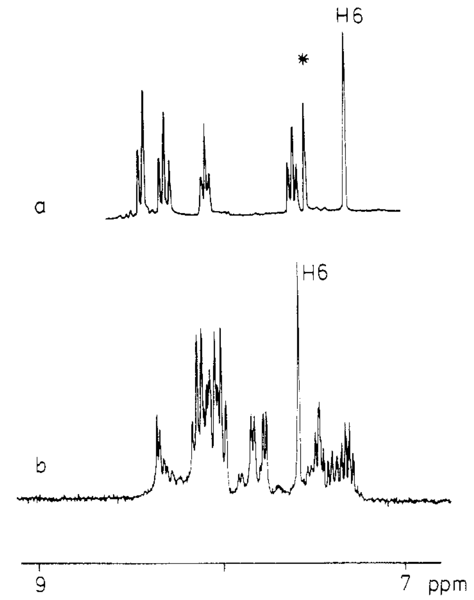

Figure 5. 300-MHz ^{1}H NMR spectra of bpy and H(6) (1-MeT) resonances of (a) mixture of **2a** and 1-MeTH (✱) ($D_2O/(CD_3)_2CO$; pD = 7.8) and (b) **5b** (D_2O; pD = 6). The spectrum of **5a** is identical with that of **5b** in the same solvent. In $(CD_3)_2CO/D_2O$ (not shown), the bpy pattern of **5** is less complex, and shifts of both H(6) and bpy resonances are somewhat different.

complexes of Pt and Pd, both N(1)–CH_3 and C(5)–CH_3 signals are doubled (1:1), but not C(6)–H. We attribute these doublings to the existence of the two rotamers of (bpy)ML_2 (with approximately C_2 and C_s symmetry) in solution.

Compared to that of **2a**, the ^{1}H NMR spectra of **5a** and **5b** are considerably more complex. The doubling of C(5)–CH_3 and N(1)–CH_3 resonances is also observed, but relative intensities are 3:2 and depend on the solvent composition (addition of acetone-d_6 to D_2O favors one of the two main species). Moreover, there is indication that additional minor species are present (two to three additional CH_3 resonances). As with **2b**, only a single H(6) resonances is observed for **5**, which is shifted downfield by ca. 0.27 ppm in D_2O compared to the former. The bpy resonances in the dinuclear complexes are upfield from those in **2b**, as expected for intramolecular ring stacking, and are more numerous (Figure 5). Compared to **2a**, a doubling of bpy resonances is to be expected both for single species of head–head *and* head–tail dinuclear complexes, but the pattern of **5** is clearly more complex. As far as the two major species present in D_2O solution are concerned, a slow (head–head) ⇌ (head–tail) equilibrium (N(3),O(4)–Pd binding each) or different head-head isomers (N(3),O(4)–, N(3),O(2)–Pd binding) could account for the two major CH_3 resonances of 1-MeT ligands *and* the multiplicity of bpy resonances. Equilibria 4 and 5 between di- and mononuclear complexes appear not to play any significant role, since distinct H(6) resonances due to **2b** or **6** are not detected.

$$\underset{\text{(h-h)}}{[(bpy)_2Pd_2L_2]^{2+}} \xrightleftharpoons{D_2O} \underset{\mathbf{2b}}{(bpy)PdL_2} + [(bpy)Pd(D_2O)_2]^{2+} \qquad (4)$$

$$\underset{\text{(h-t)}}{[(bpy)_2Pd_2L_2]^{2+}} \xrightleftharpoons{D_2O} \underset{\mathbf{6}}{2[(bpy)PdL(D_2O)]^+} \qquad (5)$$

Whatever the exact equilibrium may be, it is restricted to the solution state. Evaporation of a solution of **5** eventually gives **5a** and **5b** more or less quantitatively.

Oxidation Behavior. No oxidation through Ce(IV) was detected for any of the following mononuclear Pd(II) compounds: K_2PdCl_4, (en)Pd(1-MeU)$_2$, **1b**, $[(en)Pd(H_2O)_2]^{2+}$, and $[Pd(H_2O)_4]^{2+}$.[47] Likewise, attempts to oxidize the Pd_2 complex **5** to either a mixed-valent Pd or a dipalladium(III) complex were unsuccessful. This is in contrast to analogous $[Pt^{II}]_2$ complexes, which are oxidized both to $[Pt^{2.25}]_4$ and $[Pt^{III}]_2$ species.[17]

Concentrated nitric acid failed as well, giving aqueous (bpy)Pd$(NO_3)_2$ only,[48] and oxidation of **5** with chlorine gave the known Pd(IV) compound (bpy)$PdCl_4$.[49]

Our findings are not inconsistent with reports on the difficulty encountered in the generation of $[Pd^{III}]_2$ complexes electrochemically. Apparently a rather short Pd···Pd separation of 2.6 Å or less is required in the $[Pd^{II}]_2$ compound to permit oxidation,[50] but even then oxidation can occur at the ligand rather than the metal.[51]

Comparison with PtPt and PtPd Compounds. The dinuclear PdPd complex **5a** described in this report represents the third structurally characterized example of the four possible combinations—PtPt, PtPd, PdPt, and PdPd—involving two d^8 metal ions (Pd(II) and Pt(II)) and two mixed N,O donors (1-methyluracil and/or 1-methylthymine) in head-head arrangement. PtPt[17,27] and PtPd[17] species have previously been described. The fourth combination, PdPt (Pd bound to N(3), Pt bound to O) has not been obtained as yet due to principal problems of its preparation (slow kinetics of Pt binding, H^+ sensitivity of Pd–N bond).[17] Of the three types now prepared, the PtPt combination is the most versatile one, considering the number of compounds obtainable and its redox chemistry (mixed-valence-state compounds, diplatinum(III) species). While intracomplex metal–metal distances do not differ greatly in PtPt (2.927 (1), 2.937 (1) Å) and PtPd (2.927 (1) Å), the PdPd separation in **5a** is substantially shorter (2.848 (1) Å). The solution chemistry in water of the three compounds is markedly different. While the dinuclear structure of PtPt is essentially retained in solution, PtPd shows a marked tendency to dissociate into mononuclear Pt and Pd species. In contrast, the PdPd compound **5a** exists in solution in an equilibrium of two dinuclear species. Oxidation with preservation of the dinuclear entity is observed for PtPt only.

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Supplementary Material Available: Tables of elemental analysis data and positional and thermal parameters, bond lengths, and bond angles for **5a** and Raman spectra of **2a** and **5a** (12 pages); a listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(47) Prepared according to: Elding, L. I. *Inorg. Chim. Acta* **1972**, *6*, 647.

(48) (bpy)Pd$(NO_3)_2$ crystallized as yellow rhombohedra when the solution was diluted with H_2O and left at room temperature for several days. According to the IR spectrum, nitrate is coordinated to Pd.

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