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N,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine and Its Analogues as Hypodentate Ligands. Synthesis and Characterization of the Rhodium(III), Ruthenium(II), and Palladium(II) Complexes

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New complexes of Rh(III), Ru(II), and Pd(II) with *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) and its analogues have been prepared. The reaction of $RhCl_3{\cdot}nH_2O$ with tpen is slow and allows one to isolate the products of three consecutive substitution steps: Rh_2Cl_6(tpen) (**1**), *cis*-$[RhCl_2(\eta^4\text{-tpen})]^+$ (**2**), and $[RhCl(\eta^5\text{-tpen})]^{2+}$ (**3**). In acetonitrile the reaction stops at the step of the formation of *cis*-$[RhCl_2(\eta^4\text{-tpen})]^+$, whereas $[RhCl(\eta^5\text{-tpen})]^{2+}$ is the final product of the further reaction in ethanol. Fully chelated $[Rh(tpen)]^{3+}$ could not be obtained. Bis(acetylacetonato)-palladium(II), $Pd(acac)_2$, reacts with tpen and its analogues, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn) and *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-*(R)*-1,2-propylenediamine (*R*-tppn), to give $[Pd(\eta^4\text{-tpen})]^{2+}$ (**4**), $[Pd(\eta^4\text{-tppn})]^{2+}$ (**5**), and $[Pd(\eta^4\text{-tptn})]^{2+}$ (**6**), respectively. Two pyridyl arms remain uncoordinated in these cases. The formation of unstable Pd(III) complexes from these Pd(II) complexes in solution was suggested on the basis of electrochemical measurements. Ruthenium(III) trichloride, $RuCl_3{\cdot}nH_2O$, is reduced to give a Ru(II) complex with fully coordinated tpen, $[Ru(tpen)]^{2+}$ (**7**). The same product was obtained in a more straightforward reaction of $Ru^{II}Cl_2$(dimethyl sulfoxide)$_4$ with tpen. Electrochemical studies showed a quasi-reversible $[Ru(tpen)]^{2+/3+}$ couple for [**7**]$(ClO_4)_2$ ($E_{1/2} = 1.05$ V vs Ag/AgCl). Crystal structures of [**2**]$(PF_6){\cdot}2CH_3CN$, [**3**]$(PF_6)_2{\cdot}CH_3CN$, [**6**]$(ClO_4)_2$, and [**7**]$(ClO_4)_2{\cdot}0.5H_2O$ were determined. Crystal data: [**2**]$(PF_6){\cdot}2CH_3CN$, monoclinic, *C*2, $a = 16.974(4)$ Å, $b = 8.064(3)$ Å, $c = 13.247(3)$ Å, $\beta = 106.37(2)°$, $V = 1739.9(8)$ Å^3, $Z = 2$; [**3**]$(PF_6)_2{\cdot}CH_3CN$, triclinic, $P\bar{1}$, $a = 11.430(1)$ Å, $b = 19.234(3)$ Å, $c = 8.101(1)$ Å, $\alpha = 99.43(1)°$, $\beta = 93.89(1)°$, $\gamma = 80.10(1)°$, $V = 1729.3(4)$ Å^3, $Z = 2$; [**6**]$(ClO_4)_2$, orthorhombic, *Pnna*, $a = 8.147(1)$ Å, $b = 25.57(1)$ Å, $c = 14.770(4)$ Å, $V = 3076(3)$ Å^3, $Z = 4$; [**7**]$(ClO_4)_2{\cdot}0.5H_2O$, monoclinic, $P2_1/c$, $a = 10.046(7)$ Å, $b = 19.049(2)$ Å, $c = 15.696(3)$ Å, $\beta = 101.46(3)°$, $V = 2943(2)$ Å^3, $Z = 4$.

Introduction

A hypodentate ligand is defined as a ligand in which fewer than the maximum possible number of donor atoms are bonded to metal centers.[1] Complexes with a hypodentate ligand are important in several respects. For example, uncoordinated donor atoms can be further attached to another metal atom making possible a controllable building of heterometallic complexes or supramolecular aggregates. When the coordination number changes with the change in the oxidation states of the metal center, a hypodentate ligand may play an important role by dissociation or coordination of pendant arms accompanied by the redox reaction. Also, the complexes offer an opportunity to study intramolecular donor site exchange reactions between free and coordinated groups.[2]

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[1] Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67.

[2] For example: (a) Gelling, A.; Orrell, K. G.; Osborne, A. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1998**, 937. (b) Hunter, G.; McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1998**, *27*, 2634. (c) Xu, L.; Abe, M.; Sasaki, Y. *Chem. Lett.* **1999**, 163.

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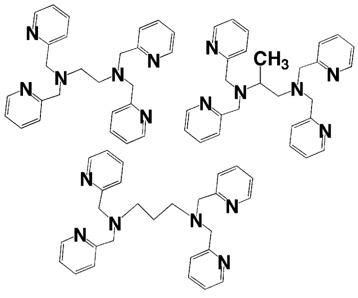
Chart 1. Schematic View of tpen (Top Left), tppn (Top Right), and tptn (Bottom)



To force a ligand to coordinate in a hypodentate binding mode, one can either employ a kinetically inert (e.g., d^6) metal center or a metal center with coordination number less than the number of donor atoms in the ligand (typically, square planar Pd(II) and Pt(II) with penta- and hexadentate ligands). Another approach is to employ so-called "misfit" ligands, i.e., those which would have too high a sterical strain to allow all their potential donor sites to coordinate to the same metal center. There are many examples of oligopyridines exhibiting a hypodentate binding mode even in the case of rather simple ligands such as 2,2′-bipyridine (bpy),[3] 1,10-phenanthroline (phen),[4] or 2,2′:6′,2″-terpyridine (tpy).[5] With a potentially tetradentate polypyridyl ligand, tris(2-pyridylmethyl)amine (tpa), we have prepared a series of Re(V), Re(VII), and Re(I) complexes where tpa is coordinated in a η^3-fashion, leaving one pyridyl arm uncoordinated.[6]

A potentially hexadentate ligand *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) and its analogues (Chart 1) are known to give more variety of hypodentate coordination modes and are among the most promising hypodentate ligands. Examples are [Fe(SO$_4$)(tpen)][7a] and [V(η^5-tpen)(η^2-SO$_4$)]$^{2+}$ [7b] in which pentadentate tpen is found. Pentadentate coordination is also found in [Fe(η^5-Me$_2$tpen)(H$_2$O)]$^{2+}$ (Me$_2$tpen = *N*,*N′*-bis(6-methyl-2-pyridylmethyl)-*N*,*N′*-bis(2-pyridylmethyl)ethylenediamine).[7c] In [VO$_2$(η^4-tpen)]$^{+}$ [7d] and VO(SO$_4$)(η^4-tpen),[7e] tpen acts as a tetradentate ligand. A tridentate tpen has recently been found in [Re^{VII}O$_3$(η^3-tpen)]$^{+}$.[7f] In all these cases, however, metal ions are substitution labile, and upon reaction with another metal ion the complexes may cause some rearrangements or dissociation of the hypodentate ligand.

In this work, we have chosen substitution inert d^6 (Rh(III), Ir(III), Ru(II), and Os(II)) and square-planar d^8 (Pd(II) and Pt(II)) to obtain a series of complexes with stable hypodentate coordination. Potentially hexadentate ligands used here are tpen and its analogues, *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn), and *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-(*R*)-1,2-propylenediamine (*R*-tppn). Among the above metal ions, Rh(III), Ru(II), and Pd(II) gave well-defined complexes bearing uncoordinated 2-pyridylmethyl arms. On the other hand, a fully coordinated tpen complex was prepared with Ru(II). In this paper we wish to report the preparation and crystal structures of the new complexes. Further studies on their reactivities will be reported elsewhere.

Experimental Section

Reagents. Ligands *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen), *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn), and *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-(*R*)-1,2-propylenediamine (*R*-tppn) were prepared by the reported procedures.[8] We found, however, that the recrystallization from hexane was necessary to obtain pure colorless crystals of the ligands. The metal chloride salts "$RhCl_3\cdot nH_2O$" and "$RuCl_3\cdot nH_2O$" were purchased from Wako Pure Chemical Industries, Ltd. Palladium acetylacetonate, Pd(acac)$_2$, was obtained from Aldrich. Other commercially available reagents were used as purchased.

Preparation of the Complexes. All manipulations were carried out in air.

CAUTION! *All the metal perchlorates containing organic ligands are potentially explosive and must be treated with a great care. Although we did not experience any accident while handling the perchlorate salts described in this paper, we recommend strongly to use hexafluorophosphates or tetraphenylborates instead. The only reason we prepared the perchlorates was their superior quality of single crystals.*

Rh$_2$Cl$_6$(tpen) (1), *cis*-[RhCl$_2$(η^4-tpen)]PF$_6$·2CH$_3$CN ([2]PF$_6$·2CH$_3$CN), and *cis*-[RhCl$_2$(η^4-tpen)]ClO$_4$ ([2]ClO$_4$). An acetonitrile solution (20 mL) of $RhCl_3\cdot nH_2O$ (155 mg, ca. 0.60 mmol) and tpen (355 mg, 0.83 mmol) was refluxed for 7 h. Yellow microcrystalline material was separated by filtration, washed with methanol and diethyl ether, successively, and dried. Yield: 100 mg (38%). Anal. Calcd for $Rh_2Cl_6C_{26}H_{28}N_6$ (**1**): C, 37.03; H, 3.35; N, 9.97; Cl, 25.23. Found: C, 36.83; H, 3.48; N, 10.46; Cl, 24.65. FAB MS (*m*/*z* (*I*, %)): 807 (18), [Rh$_2$Cl$_5$(tpen)]$^+$; 772 (10), [Rh$_2$Cl$_4$(tpen)]$^+$; 735 (6), [Rh$_2$Cl$_3$(tpen)]$^+$; 596 (39), [RhCl$_2$(tpen-H)]$^+$; 566 (13). [RhCl(tpen)]$^+$; 527 (9), [RhCl(tpen)]$^+$; 424 (12), [tpen]$^+$. Insolubility of the complex in organic solvents (including DMF and DMSO) prevented its further characterization.

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After the separation of **1** the solution was evaporated. The oily residue was dissolved in 10 mL of water. To the resulting yellow solution was added an aqueous solution of 2 g of NH_4PF_6, causing immediate appearance of voluminous yellow precipitate. It was filtered off, dissolved in acetonitrile, and loaded onto a Wakogel-300 column. A yellow band was eluted with acetonitrile. Yellow crystals were grown from the eluate by vapor diffusion of diethyl ether. Yield: 150 mg (42%). Anal. Calcd for $C_{26}H_{28}N_6RhCl_2PF_6 \cdot 2CH_3CN$ ([**2**]$(PF_6)\cdot 2CH_3CN$): C, 43.61; H, 4.15; N, 13.57; Cl, 8.59. Found: C, 43.39; H, 4.23; N, 13.33; Cl, 8.53. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 365 (345), 415 sh (183).

The perchlorate salt was prepared similarly. Anal. Calcd for $C_{26}H_{28}N_6RhCl_3O_4$ ([**2**](ClO_4)): C, 44.75; H, 4.04; N, 12.04; Cl, 15.24. Found C, 43.45; H, 4.05; N, 12.04; Cl, 15.17. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 365 (300), 415 (153, sh).

[RhCl(η^5-tpen)]$(PF_6)_2\cdot CH_3CN$ ([3]$(PF_6)_2\cdot CH_3CN$). An ethanol solution (20 mL) of $RhCl_3\cdot nH_2O$ (155 mg, ca. 0.60 mmol) and tpen (355 mg, 0.83 mmol) was refluxed for 10 h. A small amount of yellow microcrystalline **1** was precipitated which was filtered off. The solution was evaporated, and the oily residue was dissolved in 10 mL of water. Upon addition of an aqueous solution of 2 g of NH_4PF_6 to the solution, a voluminous yellowish solid was precipitated which was filtered off, dissolved in acetonitrile, and loaded onto a Wakogel-300 column. A pale yellow band was eluted with acetonitrile. Colorless needle-shaped crystals of [**3**]$(PF_6)_2\cdot CH_3CN$ were grown from the eluate by vapor diffusion of diethyl ether. The crystals were found to contain CH_3CN as solvent of crystallization. Yield: 300 mg (55%). Anal. Calcd for $C_{28}H_{31}N_7RhClP_2F_{12}$ ([**3**]$(PF_6)_2\cdot CH_3CN$): C, 37.62; H, 3.50; N, 10.97; Cl, 3.97. Found: C, 37.70; H, 3.61; N, 11.46; Cl, 3.94. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 350 (386).

[Pd(η^4-tpen)]$(PF_6)_2$ ([4]$(PF_6)_2$), [Pd(η^4-tpen)]$(BPh_4)_2$ ([4]$(BPh_4)_2$), and [Pd(η^4-tpen)]$(ClO_4)_2$ ([4]$(ClO_4)_2$). A chloroform solution (10 mL) containing $Pd(acac)_2$ (100 mg, 0.33 mmol) and tpen (150 mg, 0.35 mmol) was allowed to evaporate in an open beaker. The resulting oil was dissolved in water, and the crude product was precipitated by adding NH_4PF_6. The precipitate was filtered off, dissolved in acetone, and loaded onto a Wakogel-300 column. On eluting with acetone, a pale-yellow eluate was obtained. The residue obtained by evaporation of the eluate under vacuum was then dissolved in 1:1 acetone/methanol mixture. Slow evaporation of the solution gave light-yellow crystals of [**4**]$(PF_6)_2$. Yield: 250 mg (92%). Anal. Calcd for $C_{26}H_{28}N_6PdP_2F_{12}$: C, 38.04; H, 3.44; N, 10.24. Found: C, 37.60; H, 3.57; N, 10.16. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 300 (1480, sh). FAB-MS (*m*/*z*, (*I*, %)): 675 (18), $\{[Pd(tpen)](PF_6)\}^+$; 549 (32), $[Pd(tpen)F]^+$; 424 (18), $(tpen)^+$.

The tetraphenylborate salt [**4**]$(BPh_4)_2$ was prepared similarly by adding $NaBPh_4$ instead of NH_4PF_6 to the aqueous solution of the crude product. The salt was purified by column chromatography and recrystallized from acetone−benzene. Anal. Calcd for $C_{74}H_{68}N_6PdB_2$: C, 76.00; H, 5.86; N, 7.19. Found: C, 75.65; H, 5.88; N, 7.17. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 305 (2090, sh).

The perchlorate salt ([**4**]$(ClO_4)_2$) was also prepared similarly by adding a methanol solution of $NaClO_4$ instead of NH_4PF_6 to the aqueous solution of the crude product. It has better solubility in water and crystallizes slowly. No column purification is needed in this case. Anal. Calcd for $C_{26}H_{28}N_6PdCl_2O_8$: C, 42.8; H, 3.9; N, 11.5; Cl, 9.7. Found: C, 42.6; H, 3.7; N, 11.1; Cl 9.7. $E_{1/2}$ (CH_3CN): 1.46 V.

[Pd(*R*-tppn)]$(ClO_4)_2$ ([5]$(ClO_4)_2$) and [Pd(tptn)]$(ClO_4)_2$ ([6]$(ClO_4)_2$). The Pd complexes of *R*-tppn ([**5**]$(ClO_4)_2$) and tptn ([**6**]$(ClO_4)_2$) were prepared by procedures analogous to that for the Pd tpen complexes. [**5**]$(ClO_4)_2$: beige powder. Yield: 60%. Anal. Calcd for $C_{27}H_{29}N_6PdCl_2O_8$: C, 43.59; H, 4.06; N, 11.3; Cl, 9.53. Found: C, 43.35; H, 4.18; N, 11.29; Cl, 9.44. $E_{1/2}$ (CH_3CN): 1.48 V. [**6**]$(ClO_4)_2$: light-yellow crystals. Recrystallized from acetonitrile−methanol. Yield: 75%. $E_{1/2}$ (CH_3CN): 1.48 V.

[Ru(tpen)]$(PF_6)_2$ ([7]$(PF_6)_2$), [Ru(tpen)]$(BPh_4)_2$ ([7]$(BPh_4)_2$), and [Ru(tpen)]$(ClO_4)_2$ ([7]$(ClO_4)_2$). Ruthenium complex $[RuCl_2(S\text{-dmso})_3(O\text{-dmso})]$ (dmso = dimethyl sulfoxide)[9] (160 mg, 0.33 mmol) and the ligand tpen (140 mg, 0.33 mmol) were refluxed for 18 h in 20 mL of acetonitrile until a clear orange-yellow solution was obtained.[10] The solution was rotary-evaporated, and the residue was dissolved in water. Crude PF_6^- salt [**7**]$(PF_6)_2$ was precipitated by adding NH_4PF_6 to the aqueous solution. The precipitate was filtered off, dissolved in acetone, and passed through a Wakogel C-200 column. The eluate was diluted with methanol (1:1), and a yellow microcrystalline precipitate was separated after slow evaporation in an open beaker. Yield: 210 mg (78%). Anal. Calcd for $C_{26}H_{28}N_6RuP_2F_{12}$: C, 38.29; H, 3.46; N, 10.30; Cl, 0; S, 0. Found: C, 37.36; H, 3.72; N, 10.20; Cl, 0; S, 0. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 366 (17200). FAB-MS (*m*/*z*, (*I*, %)): 671 (40), $\{[Ru(tpen)PF_6]\}^+$; 545 (65), $[Ru(tpen)F]^+$; 523 (33), $[Ru(tpen\text{-}H)]^+$.

The tetraphenylborate salt [**7**]$(BPh_4)_2$ was prepared using $NaBPh_4$ instead of NH_4PF_6 and recrystallized from acetonitrile−benzene as yellow crystals. Anal. Calcd for $C_{74}H_{68}N_6RuB_2$: C, 76.35; H, 5.89; N, 7.22. Found: C, 76.48; H, 5.99; N, 7.33; Cl, 0. UV−vis (CH_3CN, λ (nm) (ϵ ($M^{-1}\cdot cm^{-1}$))): 366 (17200).

The perchlorate salt [**7**]$(ClO_4)_2$ was obtained as lemon-yellow single crystals ([**7**]$(ClO_4)_2\cdot 0.5H_2O$) containing water molecules by slow evaporation of a 1:1 water−methanol solution containing $[Ru(tpen)]^{2+}$ and excess $NaClO_4$. Anal. Calcd for $C_{26}H_{28}N_6RuCl_2O_8$ ([**7**]$(ClO_4)_2$): C, 43.1; H, 3.9; N, 11.6; Cl, 9.8. Found: C, 41.9; H, 4.0; N, 11.3; Cl, 9.7. Yield: 75%. $E_{1/2}$ (CH_3CN): 1.05 V.

Electrochemistry. Cyclic voltammetry was performed with a BAS CV-50W voltammetric analyzer and software package. The working and counter electrodes were glassy carbon and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 100 mV/s. The sample solutions (ca. 1 mM) in 0.1 M Bu_4NClO_4/CH_3CN were deoxygenated with a stream of argon. The reference electrode was Ag/AgCl, against which $E_{1/2}$ for the $Fc^{+/0}$ couple was 0.43 V. A scan rate of 20 mV/s was used in DPV experiments.

Other Measurements. Electronic absorption spectra were recorded on a Hitachi 3000U spectrophotometer at 20 °C. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. ^1H NMR spectra were measured on a JEOL-EX 270 (270 MHz) spectrometer.

X-ray Crystallography. A Rigaku AFC5R diffractometer was used for data collection at room temperature. Crystals were sealed in glass capillaries with a small amount of mother liquor. A summary of selected data is given in Table 1. The raw data were corrected for absorption using ψ-scan curves. Direct methods (SIR92) were used to solve the structure, and the refinement was done using standard least-squares and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions with fixed displacement parameters ($U(H) = 1.2U_{eq}(C)$).

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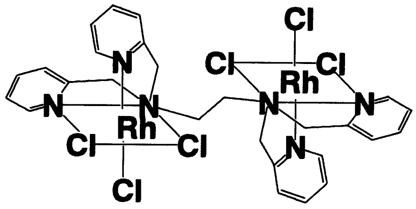
(10) The yellow precipitate is not soluble in common organic solvents. Elemental analysis suggests the formulation as $\{RuCl_2(dmso)\}_2(tpen)$. Anal. Calcd: C 39.0; H 4.4; N 9.1; S 6.9; Cl 15.3. Found: C 38.6; H 4.7; N 8.7; S 7.1; Cl 14.9. IR shows strong bands at 1020, 1055, and 1075 cm^{-1} which do not allow one to discriminate between the *S*- and *O*-bonding modes of the dmso ligand.

Table 1. Selected Crystallographic Data for [**2**](PF_6)·2CH_3CN, [**3**](PF_6)$_2$·CH_3CN, [**6**](ClO_4)$_2$, and [**7**](ClO_4)$_2$·0.5H_2O

	[**2**](PF_6)·2CH_3CN	[**3**](PF_6)$_2$·CH_3CN	[**6**](ClO_4)$_2$	[**7**](ClO_4)$_2$·0.5H_2O
formula	$C_{30}H_{34}Cl_2F_6N_8Rh$	$C_{28}H_{31}ClF_{12}N_7P_2Rh$	$C_{27}H_{30}Cl_2N_6O_8Pd$	$C_{26}H_{29}Cl_2N_6O_{8.5}Ru$
fw	825.43	893.89	743.88	733.53
space group	*C*2	$P\bar{1}$	*Pnna*	$P2_1/c$
a, Å	16.974(4)	11.430(1)	8.147(1)	10.046(7)
b, Å	8.064(3)	19.234(3)	25.57(1)	19.046(2)
c, Å	13.247(3)	8.101(1)	14.770(4)	15.696(3)
α, deg	90	99.43(1)	90	90
β, deg	106.37(2)	93.89(1)	90	101.46(3)
γ, deg	90	80.10(1)	90	90
V, Å^3	1739.9(8)	1729.3(4)	3076(3)	2943(2)
Z	2	2	4	4
λ, Å	0.71069	0.71069	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.58	1.72	1.61	1.66
T, °C	23	23	23	23
μ(Mo Kα), cm^{-1}	7.56	7.60	8.35	7.75
R^a	0.054	0.048	0.049	0.049
$R_w{}^b$	0.0870	0.064	0.049	0.047
GOF	1.16	1.03	2.48	2.17

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + p|F_o|^2$ ($p = 8.71 \times 10^{-3}$ for [**2**](PF_6)·2CH_3CN, 2.16×10^{-3} for [**3**](PF_6)$_2$·CH_3CN, 7.23×10^{-5} for [**6**](ClO_4)$_2$, and 5.63×10^{-5} for [**7**](ClO_4)$_2$·0.5H_2O).

Chart 2 Possible Structure of Rh_2Cl_6(*μ*-tpen)



Results and Discussion

Synthesis. (1) Rh(III) Complexes. The synthesis of new complexes **1**−**3** is straightforward. The primary product appeared to be insoluble dinuclear complex **1**. Due to its insolubility, it was difficult to obtain further spectroscopic evidence (particularly NMR) for the structure of **1**. In the absence of direct structural evidence we tentatively propose a dimeric structure (Chart 2) in which each $RhCl_3$ unit is coordinated by two pyridyl nitrogens and one aliphatic nitrogen at each side of the tpen ligand. It is noted that an insoluble tpen complex of V(III) has the same stoichiometry, V_2Cl_6(tpen).[11] The complex **1** reacts with an excess amount of tpen in acetonitrile to give yellow *cis*-[$RhCl_2$(η^4-tpen)]$^+$ (**2**). Further substitution was not achieved in acetonitrile. A separate experiment showed no UV−vis spectral change after keeping a solution of pure *cis*-[$RhCl_2$(η^4-tpen)](PF_6)$_2$ in acetonitrile at 50 °C for 4 h. Change of the reaction medium to ethanol, however, allows the reaction to proceed one step further to give colorless [$RhCl_2$(η^5-tpen)]$^{2+}$ (**3**). The use of ethanol to facilitate ligand substitution at a Rh(III) center is well-known.[12] Although the mechanism is still poorly understood,[12] it should be stressed that, by choosing different solvents for the reaction, the two complexes with tetradentate and pentadentate tpen have been selectively isolated. Complex **3** belongs to a rare type of pentammineacido Rh(III) complexes which otherwise are overwhelmingly represented by the numerous [Rh(NH_3)$_5$L] family, closely related [Rh(NH_2R)$_5$L] (NH_2L is aliphatic amine), and mixed [Rh(en)$_2$(NH_3)L] (en = ethylenediamine) species.[13] We were unable to prepare a fully coordinated tpen complex of Rh(III). Nevertheless, it is noteworthy that by using the substitution inert nature of Rh(III) we have prepared three stepwise chelate formation intermediates of tpen to Rh(III). The synthesis of Rh(III) complexes with lipide-soluble tpen is of interest also in connection with the proposed use of rhodium-105 as a therapeutic radionuclide.[13]

(2) Pd(II) Complexes. We initially used $PdCl_2(C_6H_5CN)_2$ to react with tpen in a 1:1 molar ratio, but obtained only a gray insoluble precipitate. On the contrary, Pd(acac)$_2$ reacted smoothly with tpen at room temperature and gave corresponding salts of [Pd(tpen)]$^{2+}$ in good yields on addition of the salt of counteranions. Complexes of Pd(II) with closely related tetradentate ligand *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (L), [PdL](ClO_4)$_2$ or [PdL](PF_6)$_2$ are known.[14] It was found that platinum(II) analogue Pt(acac)$_2$ is much more inert and did not react with tpen even after prolonged reflux in acetonitrile or methanol.

(3) Ru(II) Complexes. In the case of Ru(II), the only well-defined product was the complex with fully coordinated hexadentate tpen. When a Ru(II) complex, [$RuCl_2$(*S*-dmso)$_3$(*O*-dmso)], was used as a starting material, the substitution took place smoothly via an insoluble intermediate, {$RuCl_2$(dmso)}$_2$(tpen), which precipitated as a yellow solid and disappeared again under the reaction conditions. Its appearance as a clearly defined step is due to its insolubility. The final product was the intensely yellow colored complex [Ru(tpen)]$^{2+}$. When $RuCl_3$·$n$$H_2O$ was used as a starting material, Ru(III) was reduced to Ru(II) while the reaction proceeded via a green intermediate. Solvent acetonitrile could be a reducing reagent. A drawback of the second method is that repeated column chromatography is necessary to prepare pure [Ru(tpen)]$^{2+}$ salts. Preference for Ru(II) over Ru(III) in pyridine and oligopyridine complexes is well-documented,[15]

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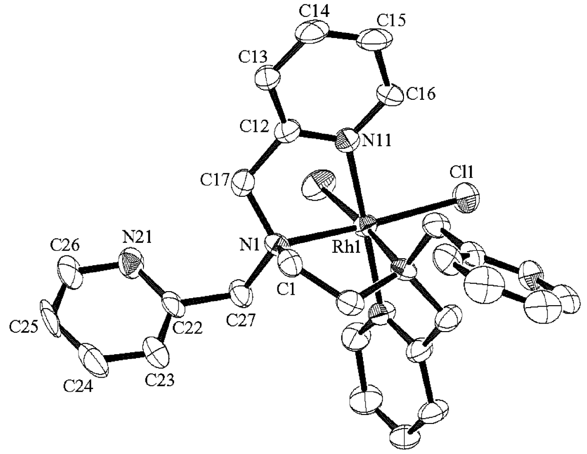

Figure 1. View of the cation *cis*-$[RhCl_2(tpen)]^+$ in the structure of [**2**]-$(PF_6)\cdot 2CH_3CN$, showing the atom-labeling scheme.

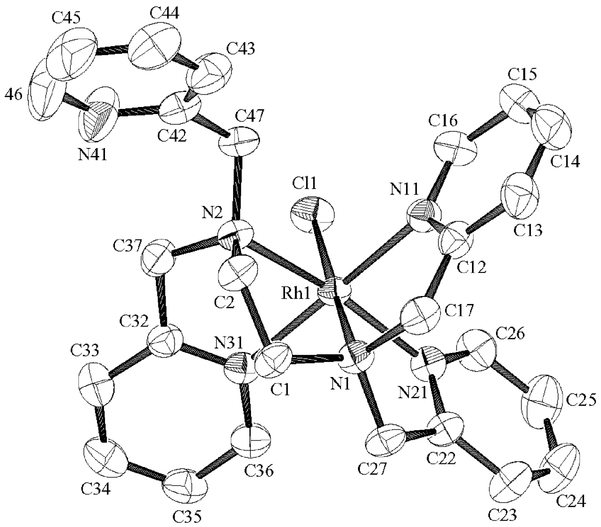

Figure 2. View of the cation $[RhCl(tpen)]^{2+}$ in the structure of [**3**]-$(PF_6)_2\cdot CH_3CN$, showing the atom-labeling scheme.

complexes such as $[Ru(py)_6]^{3+}$ and $[Ru(bpy)_3]^{3+}$ being in fact strong oxidants.[16] The tris(pyridine) complex $Ru^{III}Cl_3(py)_3$ is stable, however, and only a mild oxidant.[17] We may therefore assume that when $RuCl_3\cdot nH_2O$ reacts with tpen, the reduction to Ru(II) takes place at a later stage of the substitution, probably when the third or fourth pyridine arm of tpen coordinates to Ru (vide infra for the oxidation potential of $[Ru(tpen)]^{2+}$). The $[Ru(tpen)]^{2+}$ cation gives intensely yellow colored solutions due to a Ru(II)−N(py) charge-transfer band at 366 nm. For $[Ru(py)_6]^{2+}$ the corresponding band occurs at 341 nm.[16]

Crystal Structures. Figures 1−4 show complex cations as found in [**2**]$(PF_6)\cdot 2CH_3CN$ (Figure 1), [**3**]$(PF_6)_2\cdot CH_3CN$ (Figure 2), [**7**]$(ClO_4)_2\cdot 0.5H_2O$ (Figure 3), and [**6**]$(ClO_4)_2$ (Figure 4). Hexadentate coordination of tpen to one metal center generates five chelate rings. The only ring that does not cause appreciable strain on the octahedral geometry is the one with two sp^3 nitrogen atoms of the ethylenediamine fragment. The corresponding N−M−N angle is only slightly less than 90°: 86.1(4)° in **2** (Table 2), 87.1(1)° in **3** (Table 3), and 87.7(1)° in **7** (Table 4). The other chelate rings are

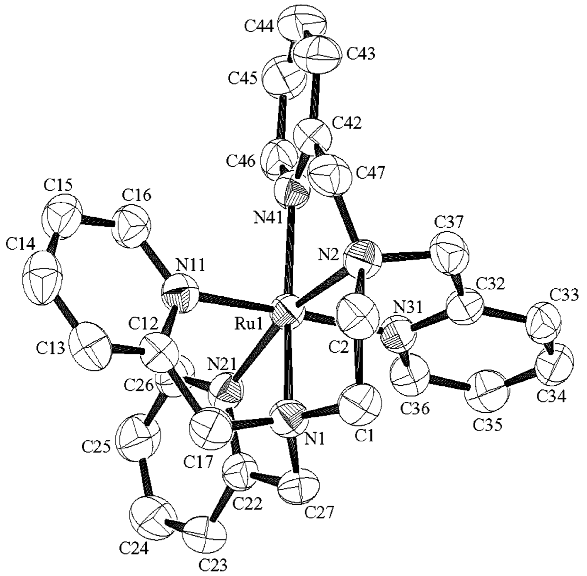

Figure 3. View of the cation $[Ru(tpen)]^{2+}$ in the structure of [**7**]$(ClO_4)_2\cdot 0.5H_2O$, showing the atom-labeling scheme.

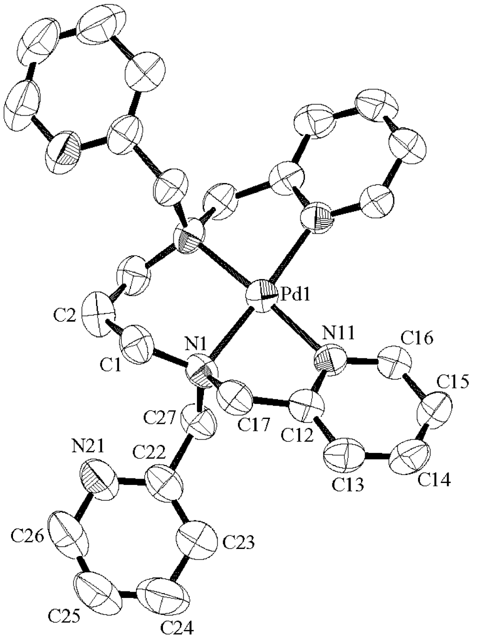

Figure 4. View of the cation $[Pd(tptn)]^{2+}$ in the structure of [**6**]$(ClO_4)_2$, showing the atom-labeling scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in *cis*-$[RhCl_2(tpen)]^+$ as Found in [**2**]$(PF_6)\cdot 2CH_3CN$

Rh1−Cl1	2.352(3)	Rh1−N11	2.036(5)
Rh1−N1	2.090(8)		
Cl1−Rh1−Cl1′	90.2(2)	N1−Rh1−N1′	86.1(4)
Cl1−Rh1−N1	175.0(3)	N1−Rh1−N11	80.3(4)
Cl1−Rh1−N1′	92.0(2)	N1−Rh1−N11′	97.6(4)
Cl1−Rh1−N11	95.3(3)	N11−Rh1−N11′	177.2(7)
Cl1−Rh1−N11′	86.7(3)		

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[RhCl(tpen)]^{2+}$ as Found in $[\mathbf{3}](PF_6)_2 \cdot CH_3CN$

Rh1−Cl1	2.344(1)	Rh1−N11	2.030(4)
Rh1−N1	2.036(3)	Rh1−N21	2.043(4)
Rh1−N2	2.103(4)	Rh1−N31	2.045(3)
Cl1−Rh1−N1	178.9(1)	N1−Rh1−N31	94.1(1)
Cl1−Rh1−N2	93.61(10)	N2−Rh1−N11	96.2(1)
Cl1−Rh1−N11	95.2(1)	N2−Rh1−N21	168.4(1)
Cl1−Rh1−N2	97.4(1)	N2−Rh1−N31	81.9(1)
Cl1−Rh1−N31	86.87(10)	N11−Rh1−N21	86.5(1)
N1−Rh1−N2	87.1(1)	N11−Rh1−N31	177.3(1)
N1−Rh1−N11	83.8(1)	N21−Rh1−N31	95.0(1)
N1−Rh1−N21	81.9(1)		

Table 4. Main Bond Lengths (Å) and Angles (deg) in $[Ru(tpen)]^{2+}$ as Found in $[\mathbf{7}](ClO_4)_2 \cdot 0.5H_2O$

Ru1−N1	2.085(4)	Ru1−N21	2.088(4)
Ru1−N2	2.070(4)	Ru1−N31	2.069(4)
Ru1−N11	2.073(4)	Ru1−N41	2.098(4)
N1−Ru1−N2	87.7(1)	N2−Ru1−N41	79.0(1)
N1−Ru1−N11	81.3(1)	N11−Ru1−N21	89.6(1)
N1−Ru1−N21	79.5(1)	N11−Ru1−N31	175.8(1)
N1−Ru1−N31	95.3(1)	N11−Ru1−N41	93.4(1)
N1−Ru1−N41	165.3(1)	N21−Ru1−N31	92.2(1)
N2−Ru1−N11	95.2(1)	N21−Ru1−N41	114.3(1)
N2−Ru1−N21	165.6(1)	N31−Ru1−N41	89.4(1)
N2−Ru1−N31	82.2(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $[Pd(tptn)]^{2+}$ as Found in $[\mathbf{6}](ClO_4)_2$

Pd1−N1	2.066(3)	Pd1−N11	2.047(3)
N1−Pd1−N1′	96.4(2)	N1−Pd1−N11′	176.7(1)
N1−Pd1−N11	80.7(1)	N11−Pd1−N11′	102.3(2)

more rigid since they include one nitrogen atom from the pyridine ring. The corresponding N−M−N angles are by about 10° less than that required for regular octahedral geometry. As a result the octahedron around Ru(II) in **7** is severely distorted with the N21−Ru1−N41 nonchelate angle as obtuse as 114.3(1)°. Similar distortion was reported for $[Fe(tpen)](ClO_4)_3$ (electronic configuration d^5, the nonchelate angle 111.2°)[18] and $[Cr(tpen)](ClO_4)_3$ (d^3, 116°).[19] In the case of low-spin d^6 Fe(II) in $[Fe(tpen)](ClO_4)_2$, the ligand field stabilization energy keeps the octahedron almost undistorted: the nonchelate N−Fe−N angle is 91°.[20] For bigger Ru(II) (d^6), however, it fails to counterbalance the distortion imposed by the ligand geometry, and for smaller Rh(III), which is also low spin d^6, even the η^6-tpen complex was not obtained. The Rh1 atom in **2** lies on crystallographically imposed 2-fold axis. The geometry of $[RhCl_2(\eta^4\text{-tpen})]^+$, with two pyridyl nitrogens coordinated trans to each other and two Cl atoms trans to the two amino nitrogen atoms and cis to each other, allows to avoid excessive strain. If four nitrogen atoms were coordinated in the same plane, the accumulation of three chelate rings would cause severe strain and the nonchelate N−M−N angle would exceed 100°. Thus the cis isomer is preferred even if it has more repulsive transannular H···H interactions than the trans isomer. For similar reasons, there are only *cis*-$[Fe(LBz_2)Cl_2](PF_6)$ (LBz_2 = *N*,*N*′-bis(benzyl)-*N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine) and *cis*-$[Fe(bispicen)Cl_2](ClO_4)_2$ (bispicen = *N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine); corresponding trans isomers remain unknown.[21]

In the case of Pd complexes the unfavorable cis coordination of two pyridyl rings is forced by the preferred square planar geometry of d^8 Pd(II). A preliminary X-ray structural analysis indicated that the tpen complex **4** in $[\mathbf{4}](ClO_4)_2$ has in fact this geometry; two pyridyl arms remain uncoordinated. However, the data set is too poor to discuss the geometry on a quantitative basis. Introduction of one extra CH_2 group into the $N-CH_2-CH_2-N$ chain leads to perceptible ease of the strain in the Pd(tptn) complex **6**. The crystallographically imposed 2-fold axis passes through Pd1 and C2 atoms. The Cl atoms of the perchlorates also lie on the 2-fold axes. In **6** the nonchelate N11−Pd1−N11′ angle is only 102.3(2)° (Table 5), because the N1−Pd1−N1′ angle within the six-membered chelate ring (96.4(2)°, i.e., almost 10° larger than in the case of tpen) partly compensates the cumulative action of two N1−Pd1−N11 angles of 80.7(1)°.

It may be interesting to compare coordination behavior of the tpen ligand and its analogues with the closely related edta (ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate) ligand. Rh(III), for example, requires very drastic conditions to form $[Rh(\eta^6\text{-edta})]^-$, which has never been isolated as a solid and easily gives $[Rh(\eta^5\text{-Hedta})(H_2O)]$ upon protonation.[22] $[Rh(\eta^5\text{-Hedta})Cl]^-$ is very stable within the pH range 1−9.[24] Ruthenium(II) complex with η^6-edta has not been reported, though $[Ru^{II}(\eta^4\text{-}H_2edta)(dppm)]$ and $[Ru^{III}(\eta^5\text{-Hedta})(PPh_3)]$ exist.[23] However, introduction of additional CH_2 links into the edta structure, either into the diamine or into the aminocarboxylate chain, enhances the stability of the η^6-N_2O_4 species by reducing the sterical strain and makes possible their isolation.[25]

Electrochemistry. The ligand tpen and its analogues are electrochemically inactive in the range −1.5 to +1.5 V vs Ag/AgCl. The Rh complexes **2** and **3** are electrochemically silent within the scan range. The Ru complex **7** gives one quasi-reversible wave at $E_{1/2} = 1.05$ V ($\Delta E_p = 96$ mV). This implies that the oxidized Ru(III) species $[Ru(tpen)]^{3+}$ is a strong oxidant, in keeping with the general tendency of py ligands to stabilize the Ru(II) oxidation state. The oxidation of Pd complexes **4** ($[\mathbf{4}](ClO_4)_2$), **5**, and **6** takes place at rather high potentials. A quasi-reversible behavior was observed at $E_{1/2} = 1.46$ V for **4**, 1.48 V for **5**, and 1.48 V for **6**. To

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determine whether Pd(II)/Pd(III) or Pd(II)/Pd(IV) is the relevant couple here, the number of electrons was estimated by integrating the peak area to compare with that of ferrocene of known concentration. The observed values are around 0.8 electron, although the determination suffers from the background current at high potentials. We believe that the oxidation produces Pd(III) species $[Pd(tpen)]^{3+}$, where octahedral coordination around Pd may be completed with the nitrogen atoms of free pyridine arms. Similar behavior was reported for $Pd([9]ane\text{-}S_3)_2^{2+}$.[23]

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Supporting Information Available: Infrared absorption spectral data for Rh_2Cl_6(tpen) (**1**), *cis*-$[RhCl_2(\eta^4\text{-tpen})](PF_6)\cdot CH_3CN$ ([**2**]-$(PF_6)\cdot CH_3CN$), $[RhCl(\eta^5\text{-tpen})](PF_6)_2$ ([**3**]$(PF_6)_2$), and [Ru(tpen)]-$(PF_6)_2$ ([**7**]$(PF_6)_2$) (Table S1). Four 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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