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## Syntheses, Properties, and Electrochemistry of Transition-Metal Complexes of the Macrocycle 1,4,7-Tris(2-pyridylmethyl)-1,4,7-triazacyclononane (L). Crystal Structures of $[\text{NiL}](\text{ClO}_4)_2$ , $[\text{MnL}](\text{ClO}_4)_2$ , and $[\text{PdL}](\text{PF}_6)_2$ Containing a Distorted-Square-Base-Pyramidal $\text{Pd}^{\text{II}}\text{N}_5$ Core

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1,4,7-Tris(2-pyridylmethyl)-1,4,7-triazacyclononane (L),  $\text{C}_{24}\text{H}_{30}\text{N}_6$ , a new hexadentate N macrocycle, has been prepared. Methanolic solutions of the ligand and  $\text{MCl}_2 \cdot x\text{H}_2\text{O}$  (1:1; M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)) yielded upon addition of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  the corresponding complexes  $[\text{ML}](\text{ClO}_4)_2$ . Oxidation of  $[\text{CoL}](\text{ClO}_4)_2$  and  $[\text{FeL}](\text{ClO}_4)_2$  with 30%  $\text{H}_2\text{O}_2$  yielded the complexes  $[\text{LM}](\text{ClO}_4)_3$  (M = Co(III), Fe(III)).  $[\text{LRu}]^{2+/3+}$  and  $[\text{LCr}]^{3+}$  complexes were also prepared as  $\text{PF}_6^-$  salts. The reaction of palladium(II) acetate with L in methanol yielded red  $[\text{LPd}]^{2+}$ , which was isolated as a  $\text{PF}_6^-$  salt. The crystal structures of  $[\text{MnL}](\text{ClO}_4)_2$  (1) and of  $[\text{NiL}](\text{ClO}_4)_2$  (2) show the metal ions to be in a distorted-prismatic environment of six nitrogen donors for the former and in a distorted-octahedral environment for the latter. For compound 1 the crystals are monoclinic ( $P2_1/c$ ) with  $a = 8.478$  (3) Å,  $b = 17.050$  (4) Å,  $c = 20.247$  (6) Å,  $\beta = 101.52$  (2)°,  $V = 2867.7$  (12) Å<sup>3</sup>, and  $Z = 4$ . Compound 2 forms trigonal crystals ( $P3$ ) with  $a = 17.155$  (3) Å,  $c = 7.892$  (2) Å,  $V = 2011$  (1) Å<sup>3</sup>, and  $Z = 3$ . Crystals of  $[\text{LPd}](\text{PF}_6)_2$  (3) are triclinic ( $P1$ ) with  $a = 9.060$  (4) Å,  $b = 10.372$  (4) Å,  $c = 17.683$  (6) Å,  $\alpha = 102.44$  (3)°,  $\beta = 92.28$  (3)°,  $\gamma = 112.01$  (3)°,  $V = 1491$  (2) Å<sup>3</sup>, and  $Z = 2$ . In  $[\text{LPd}]^{2+}$  the ligand is pentadentate with one dangling pyridylmethyl arm and the geometry around the palladium center is distorted square base pyramidal with an averaged equatorial Pd-N bond distance of 2.035 Å and an axial Pd-N distance of 2.580 (3) Å. The cyclic voltammograms of  $[\text{ML}](\text{ClO}_4)_2$  (M = Mn, Fe, Co, Ni) complexes in acetonitrile show a reversible or quasi-reversible one-electron-transfer process. The redox potentials and electronic spectra of all complexes are reported.

### Introduction

N-functionalization of the macrocycle 1,4,7-triazacyclononane yields a variety of novel hexadentate ligands, which form very stable complexes with divalent and trivalent first-row transition elements:<sup>3-6</sup>

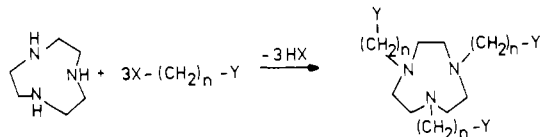
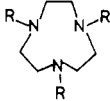
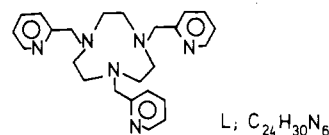


Chart I summarizes the potentially hexadentate ligands of this kind synthesized to date. Here we wish to report the synthesis

Chart I. N-Functionalized Derivatives of 1,4,7-Triazacyclononane

R	Ref.
	
-CH <sub>2</sub> COOH	3, 4, 5, 6, 7
-CH <sub>2</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	8
-CH <sub>2</sub> CH <sub>2</sub> -SO <sub>3</sub> H	8
-CH <sub>2</sub> CH <sub>2</sub> -OH	9
-CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	10, 11
-CH <sub>2</sub> -PO <sub>3</sub> H <sub>2</sub>	12, 13
-CH <sub>2</sub> -P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	14, 15, 16

of the analogous ligand 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane (L) and its coordination chemistry with transition



metals. The crystal structures of  $[\text{LMn}](\text{ClO}_4)_2$ ,  $[\text{LNi}](\text{ClO}_4)_2$ , and  $[\text{LPd}](\text{PF}_6)_2$  have been determined. In addition, the redox potentials of the couples  $\text{ML}^{2+}/\text{ML}^{3+}$  have been measured by cyclic voltammetry. During our investigations the work of Christiansen et al.<sup>17</sup> was brought to our attention, who have independently synthesized the ligand and have also prepared the complexes  $[\text{FeL}](\text{ClO}_4)_2$ ,  $[\text{CoL}](\text{ClO}_4)_3$ , and  $[\text{NiL}](\text{ClO}_4)_2$ . Where their results and ours overlap, excellent agreement of data is observed. These authors also report the crystal structure of  $[\text{FeL}](\text{ClO}_4)_2$ .

### Experimental Section

**Caution:** Perchlorate salts are potentially explosive, especially when heated.

**Synthesis of 1,4,7-Tris(2-pyridylmethyl)-1,4,7-triazacyclononane.** To an aqueous solution (250 mL) of 1,4,7-triazacyclononane (12.9 g, 100 mmol) was added 2-picolyl chloride hydrochloride (49.2 g, 0.3 mol). To the slurry was added solid sodium hydroxide at 20 °C in small amounts with stirring until a clear, alkaline (pH ~11) solution was obtained, from which a red oil separated out upon standing. The aqueous phase was

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**Table I.** Crystal Data for [LMn](ClO<sub>4</sub>)<sub>2</sub>, [LNi](ClO<sub>4</sub>)<sub>2</sub>, and [LPd](PF<sub>6</sub>)<sub>2</sub>

	[LMn](ClO <sub>4</sub> ) <sub>2</sub>	[LNi](ClO <sub>4</sub> ) <sub>2</sub>	[LPd](PF <sub>6</sub> ) <sub>2</sub>
empirical formula	C <sub>24</sub> H <sub>30</sub> N <sub>6</sub> MnCl <sub>2</sub> O <sub>8</sub>	C <sub>24</sub> H <sub>30</sub> N <sub>6</sub> NiCl <sub>2</sub> O <sub>8</sub>	C <sub>24</sub> H <sub>30</sub> N <sub>6</sub> PdP <sub>2</sub> F <sub>12</sub>
mol wt	656.38	660.15	798.87
color of cryst	colorless	violet	red
cryst dimens, mm	0.23 × 0.34 × 0.76	0.3 × 0.4 × 0.3	0.2 × 0.4 × 0.4
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 3	<i>P</i> 1̄
temp, °C	22	22	22
<i>a</i> , Å	8.478 (3)	17.155 (3)	9.060 (4)
<i>b</i> , Å	17.050 (4)	17.155 (3)	10.372 (4)
<i>c</i> , Å	20.247 (6)	7.892 (2)	17.683 (6)
<i>α</i> , deg	90.00	90.00	102.44 (3)
<i>β</i> , deg	101.52 (2)	90.00	92.28 (3)
<i>γ</i> , deg	90.00	120.0	112.01 (3)
<i>Z</i> (molecules/cell)	4	3	2
vol, Å <sup>3</sup>	2867.7	2011	1491
calcd density, g/cm <sup>3</sup>	1.52	1.635	1.78
instrument	AEDII (Siemens)	AEDII (Siemens)	Syntex R3
scan	<i>ω</i>	<i>ω</i>	<i>θ</i> -2 <i>θ</i>
octant	± <i>h,k,l</i>	± <i>h,k,l</i>	+ <i>h,±k,±l</i>
radiation (Mo K $\alpha$ ), Å	$\lambda$ = 0.71069	$\lambda$ = 0.71069	$\lambda$ = 0.71069
linear abs coeff, cm <sup>-1</sup>	6.4	7.1	8.2
transmission factors	0.69–0.83	0.88–0.98	0.86–1.00
2 <i>θ</i> range, deg	2.5–62	2–65	3.0–70
no. of unique intens	3335	3714	13 000
no. of reflexns with <i>I</i> ≥ <i>nσ</i> ( <i>I</i> )	3276 ( <i>n</i> = 3.0)	3692 ( <i>n</i> = 3.0)	10 376 ( <i>n</i> = 2.0)
no. of parameters refined	346	349	444
<i>R</i> ( <i>F</i> )	0.076	0.063	0.053
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.066	0.058	0.054
goodness of fit for the last cycle	3.5	5.2	4.6

discarded, and the product was washed several times with cold water and finally dissolved in chloroform (200 mL). The solution was dried over CaO. Chloroform was then removed on a rotary evaporator under reduced pressure. The resulting reddish oil crystallized upon standing in the refrigerator overnight (yield 20 g (50%)). The mass spectrum exhibited the correct molecular ion peak at *m/z* = 402. <sup>1</sup>H NMR ( $\delta$ , 22 °C, CD<sub>3</sub>CN): singlet (12 ring methylene protons), 2.78; singlet (6 picolyl methylene protons), 3.75; multiplet (12 pyridine ring protons), 7.15–8.45. From a perchloric acid solution the trihydroperchlorate of the ligand was obtained as colorless crystals. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>·3HClO<sub>4</sub>: C, 40.96; H, 4.30; N, 11.94; ClO<sub>4</sub>, 42.38. Found: C, 41.0; H, 4.35; N, 11.9; ClO<sub>4</sub>, 42.5.

**Syntheses of [LM](ClO<sub>4</sub>)<sub>2</sub> Complexes (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)).** To a solution of the ligand 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane (L, C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>; 0.40 g, 1 mmol) in methanol (40 mL) was added 1 mmol of the respective dichloride, MCl<sub>2</sub>·*x*H<sub>2</sub>O. The solution was stirred at 60 °C for 30 min, after which time sodium perchlorate hydrate (0.3 g) was added. When the solutions were cooled to 5 °C, the desired complexes precipitated as perchlorate salts, which were filtered off, washed with ethanol and ether, and air-dried (yield 60%). Recrystallization from a minimum amount of hot acetonitrile yielded crystals of X-ray quality. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>MnCl<sub>2</sub>O<sub>8</sub>: C, 43.92; H, 4.61; N, 12.80; Mn, 8.32; ClO<sub>4</sub>, 30.33. Found: C, 43.85; H, 4.65; N, 12.9; Mn, 8.2; ClO<sub>4</sub>, 30.8. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>FeCl<sub>2</sub>O<sub>8</sub>: C, 43.86; H, 4.60; N, 12.78; Fe, 8.49; ClO<sub>4</sub>, 30.28. Found: C, 43.9; H, 4.6; N, 12.8; Fe, 8.4; ClO<sub>4</sub>, 29.9. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>CoCl<sub>2</sub>O<sub>8</sub>: C, 43.66; H, 4.58; N, 12.72; Co, 8.92; ClO<sub>4</sub>, 30.14. Found: C, 43.5; H, 4.7; N, 12.7; Co, 8.7; ClO<sub>4</sub>, 30.8. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>NiCl<sub>2</sub>O<sub>8</sub>: C, 43.67; H, 4.58; N, 12.73; Ni, 8.89; ClO<sub>4</sub>, 30.12. Found: C, 43.63; H, 4.8; N, 12.7; Ni, 8.7; ClO<sub>4</sub>, 29.8. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>CuCl<sub>2</sub>O<sub>8</sub>: C, 43.36; H, 4.55; N, 12.63; Cu, 9.55; ClO<sub>4</sub>, 29.90. Found: C, 43.2; H, 4.6; N, 12.6; Cu, 9.3; ClO<sub>4</sub>, 29.8.

**Syntheses of [LM](ClO<sub>4</sub>)<sub>3</sub> Complexes (M = Fe(III), Co(III)).** [LM](ClO<sub>4</sub>)<sub>2</sub> (1 mmol; M = Fe(II), Co(II)) was dissolved in 10 mL of 30% hydrogen peroxide, and NaClO<sub>4</sub>·H<sub>2</sub>O (0.28 g) was added. This solution was stirred 12 h at 20 °C. After 5 mL of water was added, yellow microcrystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried (yield 65%). The crude products were recrystallized from acetonitrile. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>CoCl<sub>3</sub>O<sub>12</sub>: C, 37.95; H, 3.98; N, 11.06; Co, 7.75; ClO<sub>4</sub>, 39.26. Found: C, 38.0; H, 4.0; N, 11.1; Co, 7.7; ClO<sub>4</sub>, 39.2. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>FeCl<sub>3</sub>O<sub>12</sub>: C, 38.10; H, 3.99; N, 11.10; Fe, 7.37; ClO<sub>4</sub>, 39.45. Found: C, 38.2; H, 4.0; N, 11.2; Fe, 7.3; ClO<sub>4</sub>, 39.3.

**[LRu](PF<sub>6</sub>)<sub>2</sub>.** A solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.49 g, 2 mmol) in dimethyl sulfoxide (Me<sub>2</sub>SO, 50 mL) was heated in an open vessel at 150 °C for 15 min until a clear yellow solution was obtained, to which the ligand (0.81 g, 2 mmol) was added. The solution was stirred for 8 h at 60 °C, after which time NaPF<sub>6</sub> (0.68 g, 4 mmol) was added. After reduction

of the volume of the solution under reduced pressure (~10 mL) and addition of ethanol (20 mL) a greenish brown precipitate formed, which was recrystallized from hot acetonitrile to give green-brown crystals of [LRu](PF<sub>6</sub>)<sub>2</sub> (yield 0.8 g). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 36.33; H, 3.78; N, 10.59. Found: C, 36.2; H, 3.9; N, 10.6.

**[LCr](PF<sub>6</sub>)<sub>3</sub>.** This yellow compound was prepared analogously. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>CrP<sub>3</sub>F<sub>18</sub>: C, 32.41; H, 3.40; N, 9.45. Found: C, 32.2; H, 3.5; N, 9.6.

**[LRu](PF<sub>6</sub>)<sub>3</sub>.** [LRu](PF<sub>6</sub>)<sub>2</sub> (0.79 g, 1 mmol) was dissolved in concentrated nitric acid (5 mL) and stirred at room temperature for 30 min. Addition of NaPF<sub>6</sub> (0.34 g, 2 mmol) and water (10 mL) initiated the precipitation of yellow-orange crystals of [LRu](PF<sub>6</sub>)<sub>3</sub>, which were collected by filtration, washed with ethanol and ether, and air-dried (yield 0.4 g). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>RuP<sub>3</sub>F<sub>18</sub>: C, 30.71; H, 3.20; N, 8.95. Found: C, 31.0; H, 3.3; N, 9.1.

**[LRh](PF<sub>6</sub>)<sub>3</sub>.** A solution of the ligand (0.41 g, 1 mmol) and RhCl<sub>3</sub>·*x*H<sub>2</sub>O (0.21 g, 1 mmol) in methanol (40 mL) was stirred for 1 h at 60 °C, after which time NaPF<sub>6</sub> (0.51 g, 3 mmol) was added. A yellow precipitate formed, which was collected by filtration, washed with ethanol and ether, and air-dried (yield 0.4 g). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>RhP<sub>3</sub>F<sub>18</sub>: C, 30.63; H, 3.19; N, 8.93. Found: C, 31.0; H, 3.3; N, 9.1.

**[LPd](PF<sub>6</sub>)<sub>2</sub>.** To a solution of the ligand (1.21 g, 3 mmol) in methanol (50 mL) was added palladium(II) acetate (0.45 g) in small amounts over a 1-h period at 50 °C. After this solution was stirred for a further 1 h, NaPF<sub>6</sub> (0.68 g, 4 mmol) was added, which initiated the immediate formation of a pink precipitate. Recrystallization from hot acetone yielded deep red crystals of X-ray quality (yield 1 g). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>6</sub>PdP<sub>2</sub>F<sub>12</sub>: C, 36.07; H, 3.79; N, 10.51. Found: C, 36.2; H, 3.8; N, 10.6.

**Collection and Reduction of X-ray Data for [LMn](ClO<sub>4</sub>)<sub>2</sub> (1), [LNi](ClO<sub>4</sub>)<sub>2</sub> (2), and [LPd](PF<sub>6</sub>)<sub>2</sub> (3).** Crystals of 1 (colorless), 2 (violet), and 3 (red) were grown from acetonitrile solution at room temperature. The crystals of 1–3 used for data collection were a fraction of a columnaric crystal, a small fragment from a large twinned crystal, and a small triclinic parallelepiped, respectively. There was no apparent deterioration of the samples during data collection. The crystals were found to be acceptable on the basis of  $\omega$  scans of several low-angle reflections ( $\Delta\omega_{1/2}$  = 0.3° (maximal)). Compound 1 crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, 2 in the trigonal, polar space group *P*3, and 3 in the triclinic space group *P*1̄. Crystal parameters and additional details of the data collection are given in Table I. The unit cell parameters listed in Table I were obtained by a least-squares fit to the automatically centered settings for 25 reflections, respectively. The data were corrected for Lorentz, polarization, and anomalous dispersion effects. An empirical absorption correction was also carried out in all cases ( $\psi$  scans).

**Structure Solution and Refinement.** The structures were solved by standard Patterson and difference Fourier methods and refined by using

Table II. Atom Coordinates for [LMn](ClO<sub>4</sub>)<sub>2</sub>

atom	x/a	y/b	z/c
Mn	0.8707 (1)	0.2520 (1)	0.36010 (5)
N1	0.8664 (7)	0.3608 (3)	0.4251 (2)
N2	0.9800 (7)	0.2088 (3)	0.4666 (2)
N3	1.1313 (7)	0.2944 (3)	0.3752 (2)
N4	0.9654 (7)	0.1976 (3)	0.2770 (2)
N5	0.6813 (7)	0.3263 (3)	0.3008 (2)
N6	0.7121 (7)	0.1534 (3)	0.3784 (2)
C1	0.9129 (10)	0.3434 (4)	0.4992 (3)
C2	0.8944 (9)	0.2552 (4)	0.5109 (3)
C3	1.1581 (8)	0.2188 (4)	0.4829 (3)
C4	1.2219 (9)	0.2333 (4)	0.4189 (3)
C5	1.1468 (9)	0.3730 (4)	0.4055 (3)
C6	0.9849 (10)	0.4133 (4)	0.4010 (4)
C11	1.1033 (9)	0.2268 (4)	0.2665 (3)
C12	1.1784 (10)	0.1935 (5)	0.2180 (4)
C13	1.1073 (11)	0.1325 (5)	0.1792 (4)
C14	0.9589 (11)	0.1054 (5)	0.1893 (4)
C15	0.8964 (9)	0.1392 (4)	0.2382 (3)
C16	1.1738 (9)	0.2953 (4)	0.3074 (3)
C21	0.6175 (9)	0.3157 (5)	0.2362 (3)
C22	0.4911 (11)	0.3632 (6)	0.2014 (4)
C23	0.4397 (10)	0.4231 (6)	0.2358 (4)
C24	0.5103 (10)	0.4367 (6)	0.3034 (4)
C25	0.6296 (9)	0.3873 (4)	0.3331 (3)
C26	0.7019 (9)	0.3944 (4)	0.4078 (3)
C31	0.5670 (9)	0.1377 (5)	0.3411 (3)
C32	0.4723 (10)	0.0772 (5)	0.3561 (4)
C33	0.5290 (12)	0.0316 (5)	0.4110 (4)
C34	0.6793 (11)	0.0475 (5)	0.4495 (4)
C35	0.7687 (9)	0.1087 (4)	0.4316 (3)
C36	0.9356 (9)	0.1256 (4)	0.4689 (3)
C11	0.4974 (3)	0.1277 (1)	0.0864 (1)
C12	0.9398 (3)	0.4426 (2)	0.1607 (1)
O11	0.3364 (8)	0.0983 (3)	0.0638 (2)
O12	0.6115 (9)	0.0656 (4)	0.0822 (3)
O13	0.5253 (10)	0.1891 (4)	0.0438 (3)
O14	0.5161 (9)	0.1493 (4)	0.1544 (3)
O21	0.882 (1)	0.4484 (6)	0.2235 (5)
O22	0.806 (1)	0.3928 (7)	0.1216 (5)
O23	0.897 (2)	0.5203 (8)	0.1333 (6)
O24	1.080 (2)	0.4199 (10)	0.1390 (7)
O31	1.004 (2)	0.132 (1)	0.6530 (7)
O32	1.077 (3)	0.006 (1)	0.6645 (10)
O33	0.835 (2)	0.029 (1)	0.6119 (8)
O34	0.966 (2)	0.4384 (8)	0.2284 (6)

anisotropic thermal parameters for all non-hydrogen atoms of the respective cation [LM]<sup>2+</sup>. The perchlorate anions in **1** and **2** were found to be disordered. In **1** the anisotropic thermal coefficients for the oxygen atoms of one ClO<sub>4</sub><sup>-</sup> group were abnormally large, but no discrete disorder pattern was found in the final refinement cycle, and consequently, isotropic thermal parameters were used. For the second ClO<sub>4</sub><sup>-</sup> anion in **1** two distinct positions for each oxygen atom were detected in the difference Fourier map and these positions were refined with occupancy factors of 0.5 and isotropic thermal parameters, respectively. In **2** three oxygen atoms of each ClO<sub>4</sub><sup>-</sup> group are disordered. Two distinct positions of each of these three oxygen atoms were refined with isotropic thermal parameters (and occupancy factors 0.5). Finally, in **3** one of the PF<sub>6</sub><sup>-</sup> anions was found to be disordered. The difference Fourier map clearly indicated two different positions of the fluorine atoms, the positions of which were successfully refined with isotropic thermal parameters and occupancy factors 0.5.

Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 18. All hydrogen atoms were placed at calculated positions with  $d(C-H) = 0.96 \text{ \AA}$ . The function minimized during refinement was  $\sum_w (|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(I)$ .<sup>19</sup> Toward the end of the refinement of **2** a test was made to check that the choice of polarity was correct. The largest ratio of parameter shift to estimated standard deviation in the final cycle of refinement without consideration of disordered oxygen or fluorine atoms was 0.1 in all cases.

Table III. Atom Coordinates for [LNi](ClO<sub>4</sub>)<sub>2</sub>

atom	x/a	y/b	z/c
Ni1	0	0	0
N11	0.0856 (3)	0.1155 (3)	-0.1243 (6)
N12	-0.0018 (3)	0.0935 (3)	0.1709 (6)
C11	0.1402 (4)	0.1245 (4)	-0.2539 (7)
C12	0.1891 (4)	0.2042 (4)	-0.3394 (7)
C13	0.1830 (4)	0.2787 (4)	-0.2887 (8)
C14	0.1281 (4)	0.2692 (4)	-0.1572 (7)
C15	0.0795 (4)	0.1882 (4)	-0.0761 (7)
C16	0.0168 (4)	0.1724 (4)	0.0650 (7)
C17	0.0706 (4)	0.1199 (4)	0.2990 (8)
C18	-0.0918 (4)	0.0470 (4)	0.2450 (7)
Ni3	0.3333	0.6667	-0.1478 (2)
N31	0.4326 (3)	0.6545 (3)	-0.0123 (5)
N32	0.3506 (3)	0.5818 (3)	-0.3120 (5)
C31	0.4867 (4)	0.7089 (4)	0.1141 (7)
C32	0.5541 (4)	0.6970 (4)	0.1817 (7)
C33	0.5687 (4)	0.6320 (5)	0.1181 (9)
C34	0.5154 (4)	0.5789 (4)	-0.0143 (9)
C35	0.4478 (4)	0.5914 (4)	-0.0734 (7)
C36	0.3838 (4)	0.5326 (4)	-0.2082 (7)
C37	0.2618 (4)	0.5244 (4)	-0.3861 (8)
C38	0.4188 (4)	0.6397 (4)	-0.4418 (7)
Ni2	0.6667	0.3333	-0.0148 (2)
N21	0.6575 (3)	0.2248 (3)	-0.1420 (5)
N22	0.5592 (3)	0.2614 (3)	0.1557 (6)
C21	0.5989 (4)	0.1786 (4)	-0.2669 (7)
C22	0.5085 (4)	0.4024 (4)	-0.3441 (8)
C23	0.4240 (4)	0.3439 (4)	-0.2920 (8)
C24	0.4099 (4)	0.2837 (4)	-0.1582 (8)
C25	0.7140 (4)	0.1991 (4)	-0.0863 (8)
C26	0.4770 (4)	0.2229 (4)	0.0517 (8)
C27	0.5607 (4)	0.3264 (4)	0.2855 (7)
C28	0.5789 (4)	0.1924 (4)	0.2300 (8)
C11	0.0351 (1)	0.6668 (1)	0.2509 (2)
O1	0.0665 (7)	0.6758 (7)	0.084 (1)
O2	0.073 (1)	0.626 (1)	0.356 (2)
O3	-0.0466 (6)	0.6648 (6)	0.293 (1)
O4	0.097 (1)	0.758 (1)	0.323 (2)
C12	0.3310 (1)	0.0440 (1)	0.5750 (3)
O5	0.2497 (8)	0.0427 (9)	0.552 (2)
O6	0.3397 (7)	0.0649 (6)	0.762 (1)
O7	0.4047 (7)	0.1147 (7)	0.503 (1)
O8	0.6283 (6)	0.6625 (7)	-0.413 (1)
O11	-0.022 (1)	0.566 (1)	0.237 (2)
O12	0.086 (2)	0.692 (2)	0.394 (3)
O14	0.080 (1)	0.726 (1)	0.105 (3)
O15	-0.065 (1)	0.227 (1)	0.703 (3)
O16	-0.007 (1)	0.247 (1)	0.476 (2)

No peaks with density greater than background in the final difference Fourier maps were observed except for a few peaks in the vicinity of disordered ClO<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> groups (0.7–0.4 e/Å<sup>3</sup>). There were no significant systematic errors among final observed and calculated structure factors.

The final positional parameters for all refined atoms are listed in Table II for **1**, Table III for **2**, and Table IV for **3**. Listings of the thermal parameters, calculated hydrogen atom positions, and intraligand bond distances and angles are available in the supplementary material.

**Instrumentation.** The magnetic susceptibility of powdered samples of complexes were measured by the Faraday method (Sartorius microbalance, Bruker B-E 100088 research magnet, and Bruker B-VT 1000 automatic temperature control) between 100 and 298 K; diamagnetic corrections were applied with use of Pascal's constants.

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer (200–1500 nm). The apparatus used for electrochemical measurements has been described previously.<sup>7</sup> Cyclic voltammograms were measured in dry acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, ~10<sup>-3</sup> M sample, and 10<sup>-3</sup> M ferrocene as internal standard.

## Results and Discussion

**Preparation of Complexes.** The ligand 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane was prepared by the reaction of 1,4,7-triazacyclononane with 2-picoly chloride and sodium hydroxide in aqueous solution at 20 °C. A reddish oil separated out, which crystallized slowly upon standing in the refrigerator. The colorless trihydroperchlorate crystallized readily from a 0.1

(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(19) Computations were carried out on an Eclipse computer using the program package STRUCSY (structure computation system, Stoe, Darmstadt, FRG) and SHELXTL (Sheldrick, G. M., Universität Göttingen, revision 30, 1981).

**Table IV.** Atom Coordinates ( $\times 10^4$ ) for [LPd](PF<sub>6</sub>)<sub>2</sub>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pd	1641 (1)	233 (1)	2101 (1)
N1	3622 (4)	2095 (3)	2250 (2)
C1	4893 (5)	1607 (5)	2496 (3)
C2	4440 (5)	940 (5)	3167 (3)
N2	2705 (4)	-76 (4)	3026 (2)
C3	1859 (6)	173 (5)	3722 (2)
C4	1739 (6)	1629 (5)	3912 (2)
N3	1063 (4)	1925 (3)	3239 (2)
C5	1987 (5)	3259 (4)	3045 (3)
C6	3633 (5)	3372 (4)	2851 (3)
C40	3713 (5)	2349 (5)	1445 (3)
C41	2076 (5)	2099 (4)	1092 (3)
C42	1749 (7)	2959 (5)	674 (3)
C43	185 (8)	2626 (6)	377 (3)
C44	-1010 (7)	1457 (6)	501 (3)
C45	-637 (5)	647 (5)	947 (2)
N4	883 (4)	948 (3)	1233 (2)
C50	2492 (6)	-1618 (5)	2794 (3)
C51	846 (5)	-2520 (4)	2356 (2)
C52	80 (7)	-3983 (5)	2328 (3)
C53	-1371 (7)	-4760 (5)	1868 (4)
C54	-2058 (6)	-4082 (5)	1474 (3)
C55	-1280 (5)	-2648 (4)	1543 (2)
N5	154 (4)	-1875 (3)	1965 (2)
C60	9321 (5)	1538 (4)	3185 (2)
C61	-1194 (4)	2551 (4)	3740 (2)
C62	8250 (5)	2295 (5)	4427 (3)
C63	7735 (6)	3228 (6)	4892 (3)
C64	7798 (6)	4422 (6)	4663 (3)
C65	8382 (6)	4638 (5)	3985 (3)
N6	8869 (4)	3731 (4)	3520 (2)
P1	3838 (1)	2389 (1)	6178 (1)
F11	5670 (3)	3287 (3)	6533 (2)
F12	2030 (4)	1490 (4)	5810 (2)
F13	3335 (4)	3433 (4)	6795 (2)
F14	3656 (4)	1404 (3)	6764 (2)
F15	4042 (4)	3403 (4)	5605 (2)
F16	4372 (5)	1371 (4)	5558 (2)
P2	4351 (2)	-2419 (2)	668 (1)
F21	5615 (9)	-1362 (8)	1430 (4)
F22	3581 (9)	-1280 (8)	916 (4)
F23	3745 (9)	-2565 (8)	-249 (4)
F24	4824 (9)	-3773 (8)	421 (4)
F25	5925 (9)	-1528 (8)	377 (4)
F26	3619 (9)	-3430 (8)	1253 (4)
F31	5772 (12)	-2832 (11)	413 (6)
F32	2603 (13)	-3714 (11)	518 (7)
F33	2967 (12)	-2066 (11)	1001 (6)
F34	5007 (14)	-2330 (12)	1507 (6)
F35	4765 (13)	-894 (11)	503 (6)
F36	3274 (14)	-3271 (12)	-87 (7)

**Table V.** Selected Bond Distances (Å) for [LMn](ClO<sub>4</sub>)<sub>2</sub>, [LNi](ClO<sub>4</sub>)<sub>2</sub>, and [LPd](PF<sub>6</sub>)<sub>2</sub>

[LMn] <sup>2+</sup>			
Mn-N1	2.278 (6)	Mn-N4	2.207 (5)
Mn-N2	2.291 (5)	Mn-N5	2.203 (6)
Mn-N3	2.286 (6)	Mn-N6	2.229 (6)
[LNi] <sup>2+</sup>			
Ni1-N11	2.034 (4)	Ni2-N22	2.111 (4)
Ni1-N12	2.108 (5)	Ni3-N31	2.108 (4)
Ni2-N21	2.051 (4)	Ni3-N32	2.078 (4)
[LPd] <sup>2+</sup>			
Pd-N1	2.041 (3)	Pd-N4	2.040 (4)
Pd-N2	2.010 (4)	Pd-N5	2.048 (3)
Pd-N3	2.580 (3)		

M perchloric acid solution of the ligand.

Complexes containing the new ligand and divalent first-row transition-metal ions, [LM]<sup>2+</sup>, formed from methanolic solutions of the ligand and the respective transition-metal dichloride, MCl<sub>2</sub>·xH<sub>2</sub>O (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)). Addition of sodium perchlorate caused precipitation of the diperchlorate salts, respectively. The corresponding [LRu](PF<sub>6</sub>)<sub>2</sub>

**Table VI.** Selected Bond Angles (deg) for MN<sub>6</sub> Cores of [LMn](ClO<sub>4</sub>)<sub>2</sub>, One Cation in [LNi](ClO<sub>4</sub>)<sub>2</sub>, and [PdL](PF<sub>6</sub>)<sub>2</sub>

[LMn] <sup>2+</sup>			
N1-Mn-N2	76.6 (3)	N1-Mn-N4	146.4 (7)
N1-Mn-N6	116.0 (4)	N2-Mn-N4	116.2 (3)
N2-Mn-N6	75.3 (2)	N3-Mn-N5	118.1 (4)
N4-Mn-N5	99.4 (3)	N5-Mn-N6	97.3 (3)
N1-Mn-N3	78.0 (3)	N1-Mn-N5	75.7 (2)
N2-Mn-N3	77.1 (2)	N2-Mn-N5	144.2 (6)
N3-Mn-N4	75.3 (2)	N3-Mn-N6	144.6 (7)
N4-Mn-N6	97.6 (3)		
[LNi] <sup>2+</sup>			
N11-Ni1-N11'	98.7 (3)	N12-Ni1-N12'	83.4 (2)
N11-Ni1-N12''	96.7 (3)	N11-Ni1-N12	81.1 (2)
N11'-Ni1-N12''	164.3 (2)		
[LPd] <sup>2+</sup>			
N1-Pd-N2	86.2 (1)	N1-Pd-N3	77.9 (1)
N2-Pd-N3	78.8 (1)	N1-Pd-N4	83.0 (1)
N2-Pd-N4	168.8 (1)	N3-Pd-N4	96.0 (1)
N1-Pd-N5	163.3 (2)	N2-Pd-N5	83.2 (1)
N3-Pd-N5	112.4 (1)	N4-Pd-N5	108.0 (1)

**Table VII.** Physical Data of Complexes (UV-Visible,<sup>a</sup> Magnetic Moments)

complex	$\lambda_{\max}$ , nm ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> )	color	$\mu_{\text{eff}}$ (298 K), $\mu_{\text{B}}$
[LCr](PF <sub>6</sub> ) <sub>3</sub>	475 (134), 373 (106), 310 (sh)	orange	3.87 (4)
[LMn](ClO <sub>4</sub> ) <sub>2</sub>		colorless	5.82 (4)
[LFe](ClO <sub>4</sub> ) <sub>2</sub>	432 (1.24 × 10 <sup>4</sup> )	brown-red	0.26-0.63
[LCo](ClO <sub>4</sub> ) <sub>2</sub>	472 (272)	gray	4.79 (4)
[LNi](ClO <sub>4</sub> ) <sub>2</sub>	886 sh (24), 810 (36), 515 (27)	violet	3.17 (4)
[LCu](ClO <sub>4</sub> ) <sub>2</sub>	695 (121)	blue	2.20 (4)
[LRu](PF <sub>6</sub> ) <sub>2</sub>	362 (8700), 246 (1.3 × 10 <sup>4</sup> )	green-brown	diamag
[LPd](PF <sub>6</sub> ) <sub>2</sub>	453 (76)	red	diamag
[LFe](ClO <sub>4</sub> ) <sub>3</sub>	439 (408), 357 (sh) (960)	yellow-orange	2.71 (4)
[LRu](PF <sub>6</sub> ) <sub>3</sub>	383 (6500), 250 (1.4 × 10 <sup>3</sup> )	orange	not measd
[LCo](ClO <sub>4</sub> ) <sub>3</sub>	474 (296), 343 (284)	yellow	diamag
[LRh](PF <sub>6</sub> ) <sub>3</sub>	299 (1100)	yellow	diamag

<sup>a</sup> Measured in CH<sub>3</sub>CN.

was prepared from the reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O dissolved in dimethyl sulfoxide (Me<sub>2</sub>SO) at 150 °C, which yielded a clear yellow solution of [Ru(Me<sub>2</sub>SO)<sub>6</sub>]<sup>2+</sup>, to which the ligand was added at 60 °C. Addition of NaPF<sub>6</sub> initiated the precipitation of greenish brown crystals of [LRu](PF<sub>6</sub>)<sub>2</sub>. Yellow [LCr](PF<sub>6</sub>)<sub>3</sub> was prepared analogously with CrCl<sub>3</sub>·6H<sub>2</sub>O as starting material.

The reaction of palladium(II) acetate in a methanolic solution of the ligand at 50 °C yielded a red solution from which, upon addition of NaPF<sub>6</sub>, red crystals of [LPd](PF<sub>6</sub>)<sub>2</sub> precipitated, which were recrystallized from hot acetone, yielding large, deep red crystals of X-ray quality.

Oxidation of [LM](ClO<sub>4</sub>)<sub>2</sub> (M = Fe(II), Co(II)) in aqueous solution with hydrogen peroxide (30%) and addition of sodium perchlorate afforded the complexes [LM](ClO<sub>4</sub>)<sub>3</sub> (M = Fe(III), Co(III)). [LRu](PF<sub>6</sub>)<sub>3</sub> was obtained from the reaction of [LRu](PF<sub>6</sub>)<sub>2</sub> with concentrated nitric acid, and [LRh](PF<sub>6</sub>)<sub>3</sub> was prepared from RhCl<sub>3</sub>·xH<sub>2</sub>O and the ligand dissolved in methanol at 60 °C. Yellow crystals of [LRh](PF<sub>6</sub>)<sub>3</sub> precipitated upon addition of NaPF<sub>6</sub>. Christiansen et al.<sup>17</sup> have reported independently the syntheses of [LM](ClO<sub>4</sub>)<sub>2</sub> (M = Fe(II), Ni(II)) and [LCo](ClO<sub>4</sub>)<sub>3</sub> using similar preparative routes.

The complexes have been characterized through their analytical data, electronic spectra, magnetic susceptibility data, and cyclic voltammograms. The crystal structures of [LMn](ClO<sub>4</sub>)<sub>2</sub>, [LNi](ClO<sub>4</sub>)<sub>2</sub>, and [LPd](PF<sub>6</sub>)<sub>2</sub> have been determined. The crystal structure of [LFe](ClO<sub>4</sub>)<sub>2</sub> has been reported by Christiansen et al.<sup>17</sup>

**Electronic Spectra and Magnetic Properties of Complexes.** Table VII summarizes the physical data of [LM]<sup>2+/3+</sup> complexes.

**Table VIII.** Redox Potentials of  $[LM]^{3+}/[LM]^{2+}$  Couples at 22 °C (vs. Ferrocene/Ferrocene)<sup>a</sup>

M	$E_{1/2}$ , V	$\Delta E$ , <sup>b</sup> mV	electrode <sup>c</sup>	reacn <sup>d</sup>
Cr	-1.88	120	HMD	rev
Mn	+0.77	245	glassy carbon	quasi-rev
Fe	+0.35	70	platinum	rev
Ru	+0.565	90	platinum	rev
Co	-0.32	90	HMD	rev
Ni	+1.01	105	platinum	quasi-rev

<sup>a</sup> Measured in  $CH_3CN$  with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte:  $10^{-3}$  M sample;  $10^{-3}$  M ferrocene. <sup>b</sup> Separation between the anodic and cathodic peaks of the cyclic voltammogram at a scan rate of 50 mV/s. <sup>c</sup> HMD = hanging mercury drop. <sup>d</sup> rev = reversible.

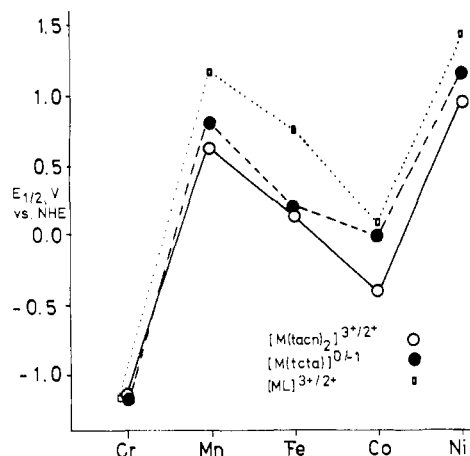
The electronic spectra of  $[LM]^{2+}$  complexes (Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Ru(II)) indicate  $MN_6$  cores; i.e., the ligand is six-coordinate. In the cases of  $[LFe]^{2+}$  and  $[LRu]^{2+}$  an intense metal-to-ligand charge-transfer band typical for low-spin iron(II) and ruthenium(II) complexes is detected, respectively. The corresponding manganese(II) complex is colorless, indicating a high-spin  $d^5$  electronic configuration ( $\mu_{eff} = 5.82 \mu_B$ ).  $[LCo]^{2+}$  has a nondescriptive gray color and is high spin ( $\mu_{eff} = 4.79 \mu_B$ ).

In the electronic spectrum of  $[LNi]^{2+}$  two bands in the visible region typical of octahedral nickel(II) are observed and a value of  $12350 \text{ cm}^{-1}$  for  $10 Dq$  was deduced. This value indicates a strong ligand field of the macrocycle, which is only slightly weaker than that in bis(1,4,7-triazacyclononane)nickel(II) ( $10 Dq = 12500 \text{ cm}^{-1}$ ).<sup>20</sup> Consequently,  $[LFe]^{3+}$  and  $[LFe]^{2+}$  are low spin ( $d^5$ ,  $\mu_{eff} = 2.71 \mu_B$ ;  $d^6$ , diamagnetic), as has been reported for their bis(1,4,7-triazacyclononane) analogues.<sup>21,22</sup> It is noted that magnetic susceptibility data on  $[LFe](ClO_4)_2$ , which was carefully recrystallized twice, showed a small residual paramagnetism; the magnetic moments varied from 0.24 to  $0.63 \mu_B$  between 98 and 298 K. These values are somewhat smaller than those reported by Christiansen et al.,<sup>17</sup> who found magnetic moments of 1.20–1.26  $\mu_B$  between 303 and 406 K. This paramagnetism has been ascribed to temperature-independent paramagnetism<sup>17</sup> or, alternatively, to small impurities of  $[LFe]^{3+}$ .

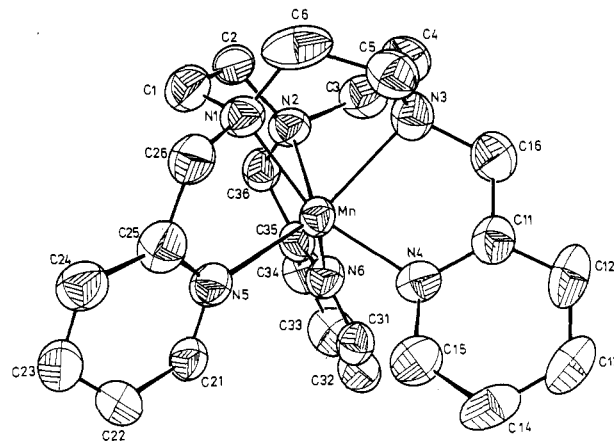
In the electronic spectrum of  $[LCu]^{2+}$  one d–d transition at 695 nm is observed, which is typical for octahedral copper(II). It is expected that the  $CuN_6$  chromophore shows some kind of Jahn–Teller distortion.

In  $[LPd]^{2+}$  the palladium(II) center ( $d^8$ ) is in a square-based-pyramidal geometry of three tertiary amine nitrogen atoms and two pyridine nitrogen atoms and one pendant pyridylmethyl arm is uncoordinated (see below). The electronic spectrum of  $[LPd](PF_6)_2$  both in solution and in the solid state exhibits a weak absorption maximum at 453 nm, which is assigned to a d–d transition of the low-spin, square-based  $PdN_5$  chromophore.<sup>25–30</sup>

**Electrochemistry.** Cyclic voltammograms of  $[LM]^{2+}$  species, where M represents Mn(II), Fe(II), Ru(II), Co(II), and Ni(II), in acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte) exhibited one wave in the potential range +1.7 to -1.5 V vs. Ag/AgCl at 20 °C. The peak-to-peak separations (Table VIII) and an  $i_{pa}/i_{pc}$  ratio of approximately unity, which are independent of the scan rate, indicated the electro-



**Figure 1.** Redox potentials (V vs. NHE) for the couples  $[M(tacn)_2]^{3+}/2+$  (values taken from ref 21),  $[M(tcta)_2]^{3+}/2+$  (ref 7), and  $[ML]^{3+}/2+$  (lines drawn only to guide the eyes).



**Figure 2.** Structure of  $[LMn]^{2+}$  and atom-labeling scheme.

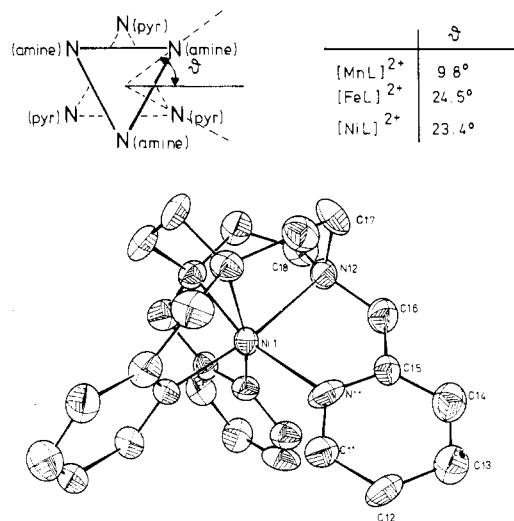
chemical reversibility or quasi-reversibility for the respective one-electron-redox process. Formal redox potentials summarized in Table VIII indicate a moderate stabilization of the oxidation state +3 for the cobalt complex, with the reduced form being a weak reductant, whereas the  $[NiL]^{3+}$  species containing a nickel(III) ion is a very strong one-electron oxidant.  $[LPd]^{2+}$  and  $[LRh]^{3+}$  were found to be redox-inactive in the potential range investigated.

Figure 1 shows the redox potentials for first-row transition-metal ions containing the hexadentate ligand 1,4,7-triazacyclononane- $N,N',N''$ -triacetate (tcta) and 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane and those of bis(1,4,7-triazacyclononane)metal complexes. The redox potential of +0.965 V for the couple  $[LRu]^{3+}/2+$  may be compared with that reported for the couple  $[Ru(tacn)_2]^{3+}/2+$  ( $tacn = 1,4,7$ -triazacyclononane) at +0.37 V vs. NHE.<sup>23</sup> The potentials of metal complexes containing the pure  $\sigma$ -donor 1,4,7-triazacyclononane are in all cases more negative by  $\sim 400$  mV than those of  $[LM]^{3+}/2+$  couples containing a ligand with three tertiary amine nitrogen atoms as well as three pyridine nitrogen atoms, which are weak  $\pi$ -acceptors stabilizing the respective +II oxidation state. This is a clear indication for the  $\pi$ -acceptor capability of the macrocycle 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, which is most pronounced for ruthenium(II).  $[LRu^{III}]^{3+}$  is a strong one-electron oxidant, which is stable in aqueous solution, in contrast to  $[Ru(tacn)_2]^{3+}$ , which decomposes with oxidation of the ligand.<sup>23</sup>

**Description of the Structure of  $[LMn](ClO_4)_2$ .** Crystals of  $[LMn](PF_6)_2$  consist of well-separated  $[LMn]^{2+}$  cations and perchlorate anions. There are no strong intermolecular contacts or hydrogen bonds. Figure 2 shows the structure of the cation and the atomic labeling scheme. The manganese(II) ions are in a pseudo-trigonal-prismatic environment of six nitrogen atoms, i.e. three tertiary amine nitrogen atoms and the pyridine nitrogen

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Chart II

Figure 3. Structure of [LNi]<sup>2+</sup> and atom-labeling scheme.

atoms. The ligand acts as a hexadentate ligand. The weighted mean Mn–N(pyridine) and Mn–N(tertiary amine) distances are 2.213(6) and 2.285(6) Å, respectively. The three five-membered chelate rings of the coordinated triazacyclononane entity of the ligand are not planar; they adopt either the  $\lambda\lambda\lambda$  or  $\delta\delta\delta$  conformation. Since [LMn](ClO<sub>4</sub>)<sub>2</sub> crystallizes in the nonpolar space group *P*2<sub>1</sub>/*c*, both enantiomers are present in the unit cell (two of each kind); i.e., crystals of [LMn](ClO<sub>4</sub>) contain the racemate.

The three five-membered rings formed by coordination of the three pendant pyridylmethyl arms to manganese(II) are also puckered. If the conformation of the coordinated cyclononane moiety is  $\delta\delta\delta$ , these rings also adopt the  $\delta\delta\delta$  conformation and the three coordinated pyridine rings are then fixed; they adopt the  $\Delta$  configuration and resemble a right-handed three-bladed screw propeller. In the enantiomeric form all conformations are  $\lambda\lambda\lambda$  and a left-handed screw propeller is formed by the coordinated pyridine ligands.

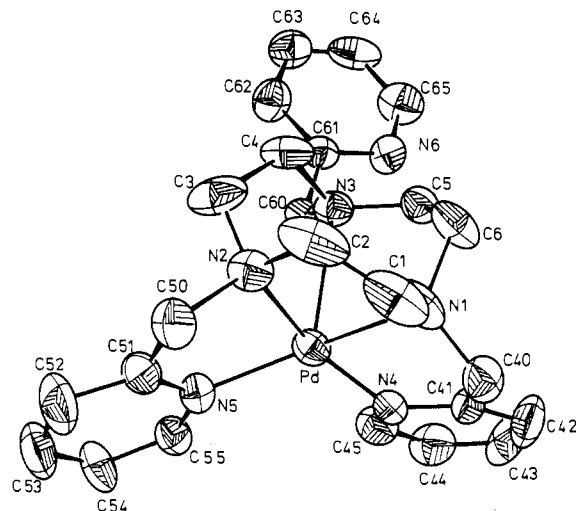
The degree of distortion from the regular octahedral arrangement of the N<sub>6</sub> donor set may be expressed by the twist angle,  $\vartheta$ , defined in Chart II.  $\vartheta$  is 0° for a prismatic and 30° for an octahedral arrangement. The observed angle  $\vartheta$  is 9.8°.

[LMn]<sup>2+</sup> is a high-spin complex (d<sup>5</sup>), and therefore, no electronic preference of an octahedral environment over any other geometry is to be expected in terms of simple ligand field stabilization energy arguments. The macrocyclic ligand is expected to favor a trigonal-prismatic structure, especially when coordinated to a large metal ion, in order to minimize the ligand strain energy. The same effect has been observed for a series of transition-metal complexes containing the hexadentate macrocycle 1,4,7-triazacyclononane-*N,N',N''*-triacetate.<sup>5,4,7</sup>

**Description of the Structure of [LNi](ClO<sub>4</sub>)<sub>2</sub>.** This complex is isostructural with the corresponding complex [LFe](ClO<sub>4</sub>)<sub>2</sub>.<sup>17</sup> Both crystallize in the polar trigonal space group *P*3 with very similar unit cell dimensions. There are three [LNi]<sup>2+</sup> cations in the unit cell; each cation has a C<sub>3</sub> axis perpendicular to the two planes defined by the three pyridine nitrogen atoms and the three tertiary amine nitrogen atoms, respectively.

Figure 3 shows the structure of one of the three cations. All three crystallographically different cations have very similar dimensions. Tables V and VI give a list of selected bond angles and distances of one of these cations. Dimensions for the other two cations are available in the supplementary material.

The macrocyclic ligand coordinates to the nickel(II) through six nitrogen atoms, forming a pseudooctahedral NiN<sub>6</sub> core. The twist angle  $\vartheta$  is 23.4°. The three five-membered chelate rings of the coordinated triazacyclononane are again not planar; all three cations in the unit cell of the crystal investigated adopt the  $\lambda\lambda\lambda$  conformation for each set of chelate rings. The three five-membered rings formed by coordination of the pendant pyridylmethyl

Figure 4. Structure of [LPd]<sup>2+</sup> and atom-labeling scheme.

arms to nickel(II) are also puckered; they adopt the  $\delta\delta\delta$  conformation. The configuration of the coordinated pyridine ligands is then fixed; they adopt the  $\Delta$  configuration and resemble a right-handed, three-bladed screw propeller. Thus, crystals of [LNi](ClO<sub>4</sub>)<sub>2</sub> spontaneously resolve on crystallization. The same observation has been reported for [LFe](ClO<sub>4</sub>)<sub>2</sub>, and the rate of its racemization has been measured in dimethylformamide solution with <sup>13</sup>C NMR spectroscopy by dissolving one crushed single crystal.<sup>17</sup>

The averaged Ni–N(amine) and Ni–N(pyridine) distances are 2.109(5) and 2.054(5) Å, respectively. In [Ni(tacn)]<sub>2</sub>(NO<sub>3</sub>)·Cl·H<sub>2</sub>O a Ni–N(amine) distance of 2.104 Å has been reported,<sup>24</sup> which agrees well with the corresponding value found in [NiL](ClO<sub>4</sub>)<sub>2</sub>.

It is noted that for [LM]<sup>2+</sup> complexes two different conformers are observed, as is exemplified by the manganese(II) and nickel(II) species. Since the coordinated base fragment triazacyclononane of the ligand is chiral, the pendant pyridylmethyl arms attach themselves in a clockwise or anticlockwise fashion for one given arrangement of the base fragment. In [LMn]<sup>2+</sup> the conformations of the chelate rings formed by the triazacyclononane fragment and by the pendant arms are the same; both adopt  $\lambda\lambda\lambda$  or  $\delta\delta\delta$  conformations. In contrast, in [LNi]<sup>2+</sup> these conformations are  $\lambda\lambda\lambda$  and  $\delta\delta\delta$  or vice versa for each of the two enantiomers. Hancock et al. have carried out an empirical force field (EFF) analysis of both structure types of 1,4,7-triazacyclononane-*N,N',N''*-triacetate complexes, which have stereochemical properties very similar to those of complexes described here. They have shown that the structure of [Ni(tcta)]<sup>−</sup> where both sets of chelate ring conformations are identical, is more stable by 4 kcal mol<sup>−1</sup> than the other conformer, which is favored only when angle-bending force constants are lowered to 10% of their value for Ni(II).

[LMn]<sup>2+</sup> is high spin, and the Mn–N distances are significantly longer than those in [LNi]<sup>2+</sup>, leading to somewhat reduced angle-bending force constants. In addition, for nickel(II) there is a significant ligand field stabilization of an octahedral geometry over a trigonal-prismatic arrangement. Thus we suggest that a combination of electronic (ligand field stabilization energy) and steric (strain energy minimization) factors lead to the two structure types observed in this study.

**Description of the Structure of [LPd](PF<sub>6</sub>)<sub>2</sub>.** Crystals of this material consist of well-separated [LPd]<sup>2+</sup> cations and PF<sub>6</sub><sup>−</sup> anions. Figure 4 shows the structure and atom-labeling scheme; Tables V and VI summarize selected bond distances and angles of the PdN<sub>5</sub> core, respectively. The palladium(II) center is in a distorted-square-base-pyramidal environment of five coordinated nitrogen atoms, two of which are pyridine nitrogen atoms in equatorial positions. Three tertiary amine nitrogen atoms, two of which complete the basal plane and one occupies the apical position, are also coordinated to palladium(II). The averaged in-plane Pd–N(amine) distance is 2.03 Å whereas the corre-

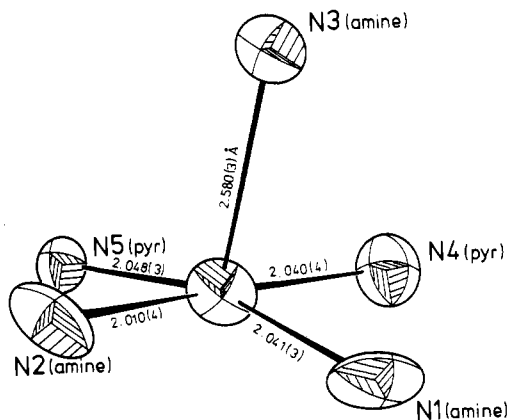


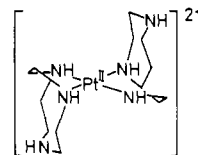
Figure 5. Schematic representation of the square-based-pyramidal  $\text{PdN}_5$  core in  $[\text{LPd}]^{2+}$ .

sponding axial bond distance is 2.580 (3) Å and the averaged  $\text{Pd-N}(\text{pyr})$  bond length is 2.044 Å (Figure 5). The macrocycle acts as a pentadentate ligand; the third pendant arm is bent away from the palladium(II) center.

$[\text{LPd}]^{2+}$  represents to the best of our knowledge the first example of a structurally characterized complex containing a square-based-pyramidal  $\text{PdN}_5$  core. A number of five-coordinate palladium(II) complexes with trigonal-bipyramidal geometry around the Pd(II) center containing sulfur, selenium, phosphorus, and arsenic as donor ligands have been reported.<sup>25-29</sup> Five-coordinate Pd complexes containing 2,2'-bipyridine and *o*-phenanthroline (phen) ligands have also been described.<sup>30-32,38</sup> Only very recently Yamazaki<sup>33</sup> reported the crystal structure of  $[\text{PdCl}(\text{PPh}_3)_2(\text{phen})](\text{BF}_4) \cdot (\text{CH}_3)_2\text{CO}$ , where the phenanthroline ligand is coordinated via one normal  $\text{Pd-N}$  bond (2.09 (5) Å) and one very weak  $\text{Pd-N}$  bond (2.68 (4) Å) and the geometry around the Pd(II) center may be described as square-based pyramidal. Louw et al.<sup>37</sup> have reported the square-based-pyramidal  $\text{PdCl}_2$ -

$(\text{PMe}_2\text{Ph})_3$  complex, which contains a weak  $\text{Pd-Cl}$  bond in the apical position ( $\text{Pd-Cl} = 2.96$  Å).

It is of interest to note that 1,4,7-triazacyclononane does not enforce out of steric necessity coordination of all three nitrogen atoms, forming one very weak  $\text{Pd-N}$  interaction. In  $[\text{Pt}(\text{tacn})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$  the platinum(II) center is surrounded by two nitrogen atoms of each ligand in a square-planar fashion and two nitrogen atoms (one of each ligand) are not coordinated to platinum(II); they are in fact bent away from the *z* axis perpendicular to the  $\text{PtN}_4$  plane:



The analogous palladium(II) complex is isostructural.<sup>36</sup> Canty et al.<sup>35</sup> have recently shown that, in the complex  $[\text{Pd}\{\text{HB}(\text{pz})_3\}_2]$  (*pz* = pyrazolyl), the strong potentially tridentate ligand hydro-tripyrzolyborate (1-) is present as an *N,N'* bidentate ligand to give square-planar  $\text{PdN}_4$  geometry.

Since the electronic spectrum of  $[\text{LPd}]^{2+}$  both in solution and in the solid state displays one weak *d-d* transition at 453 nm ( $\epsilon = 76 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), we suggest that the square-based-pyramidal  $\text{PdN}_5$  moiety is also present in solution.

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**Supplementary Material Available:** Listings of thermal parameters, calculated hydrogen positions, and intraligand bond distances and angles of  $[\text{LMn}](\text{ClO}_4)_2$ ,  $[\text{LNi}](\text{ClO}_4)_2$ , and  $[\text{LPd}](\text{PF}_6)_2$  (11 pages); listings of calculated and observed structure factors for the Mn and Pd compounds (78 pages). Ordering information is given on any current masthead page.

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