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Synthesis, Characterization, and Molecular Mechanics Studies on the Metal Complexes of 1,5,9-Tris(2-pyridylmethyl)-1,5,9-triazacyclododecane, $[ML^1](PF_6)_2$ (M = Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Pd(II))

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1,5,9-Tris(2-pyridylmethyl)-1,5,9-triazacyclododecane (L^1) and its metal complexes, $[ML^1](PF_6)_2$ (M = Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Pd(II)), have been prepared and characterized. The effective magnetic moments at room temperature are 5.68, 6.00 4.38, 3.23, and 2.10 μ_B, respectively, for the Fe(II), Mn(II), Co(II), Ni(II), and Cu(II) complexes, and Pd(II) complex is diamagnetic. Cyclic voltammetry provided the potentials for the reversible redox couples Fe(III)/Fe(II), Mn(III)/Mn(II), Cu(II)/Cu(I), and Pd(II)/Pd(I): 1.22, 1.48, −0.21, and −0.77 V vs NHE, respectively. $[Co^{II}L^1]^{2+}$, $[Ni^{II}L^1]^{2+}$, and $[Pd^{II}L^1]^{2+}$ are irreversibly oxidized at 1.49, 1.9, and 1.27 V vs NHE. The new complexes are much more resistant to oxidation than the analogous derivatives of 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane. This difference in behavior is rationalized on the basis of molecular mechanics calculations that show the minimum strain energy M−N(sp^3) distances to be 2.37 Å for a 1,5,9-tris-(2-pyridylmethyl)-1,5,9-triazacyclododecane complex and 2.12 Å for a 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane complex. The influence of the triaza ring size on the physical properties of the complexes is also discussed.

Introduction

The tetraazacycloalkanes are among the most studied polyaza compounds and they are persistently featured in reviews and books on macrocyclic compounds.[1−9] The effect of ring size on the structures and properties of complexes with tetraaza macrocycles has been discussed at length.[7,8,10,11] Although triaza macrocyclic compounds have also received a great deal of attention, most of that work has focused on 9-membered 1,4,7-triazacyclononane and its derivatives. Various functional groups have been appended to the three N atoms of 1,4,7-triazacyclononane to form hexadentate ligands (Figure 1),[12−31] and, like the N-functionalized tetraaza macrocycles, which can have as many as eight available coordinating atoms, the triaza derivatives can form stable hexacoordinated complexes that completely envelope a metal ion. Since most first-row transition metals prefer forming six-coordinate complexes, the structures of the complexes of N-bearing pendant ligands of tridentate macrocycles are much simpler than those of tetraza derivative complexes. 1,4,7-Tris(2-pyridylmethyl)-1,4,7-triazacyclononane (L^2, Figure 2) is one of most studied ligands among the triaza derivatives. Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Ru(III), and Pd(II) complexes of L^2 have been synthesized and characterized.[30,31] The electrochemistry, elec-

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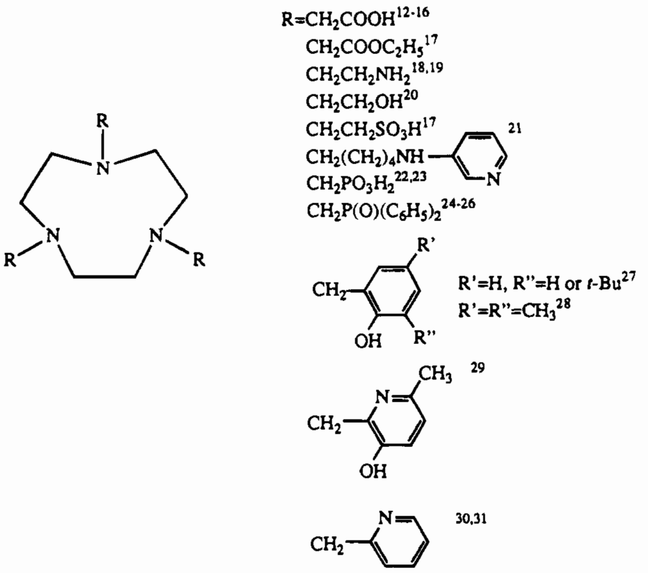

Figure 1. The N-functionalized 1,4,7-triazacyclononane ligands.

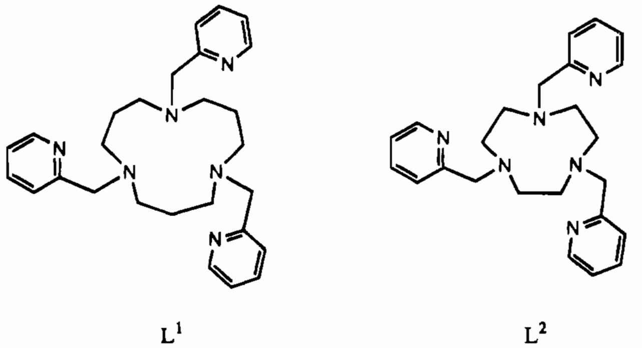

Figure 2. 1,5,9-Tris(pyridylmethyl)-1,5,9-triazacyclododecane (L^1) and 1,4,7-tris(pyridylmethyl)-1,4,7-triazacyclononane (L^2).

tronic spectra, and magnetic properties of the complexes have been reported. It was found that the Fe(II), Fe(III), Co(III), Pd(II), and Rh(III) complexes are low spin while the Mn(II), Ni(II), and Co(II) complexes are high spin. Moreover, the crystal structures of the Fe(II), Ni(II), Mn(II), and Pd(II) complexes have been determined.[30,31] The coordination geometries of Fe(II) and Ni(II) complexes were found to be slightly distorted octahedra while the Mn(II) complex adopts a distorted trigonal prismatic geometry. Pd(II) forms a pentacoordinated complex with an uncoordinated pyridine group. In contrast to studies on L^2, relatively little work has been done on analogous ligands based on other triaza macrocycles. Christiansen et al.[30] reported the Fe(II), Ni(II), and Co(III) complexes of 1,5,9-tris-(2-pyridylmethyl)-1,5,9-triazacycdodecane (L^1, Figure 1), stating that Fe(II) complex is high spin, in contrast with the low-spin Fe(II) complex of L^2,[30,31] but no data were presented to support the compositions of the compounds and little characterization was provided. Because the difference between the ring sizes of L^1 and L^2 results in a change in the spin state of Fe(II), we sought to investigate this ring size effect further. Attempts to synthesize the ligand L^1 by the literature procedure[30] were unsuccessful, and the difficulty can be attributed to the extremely high proton affinity of the triaza macrocycle. The equilibrium constant for the first protonation step of 1,5,9-triazacyclododecane is around 10^{13},[32,33] much higher than that of 1,4,7-triazacyclononane ($<10^{11}$).[34,35] A reliable procedure has been developed to prepare L^1, and Fe(II), Mn(II), Co(II), Ni(II), Cu(II), and Pd(II) complexes were prepared and characterized, and their magnetic properties, electronic spectra, and electrochemistry have been studied. The effect of the triaza ring size has been studied further by the methods of molecular mechanics.

Table 1. Elemental Analyses for the Complexes of 1,5,9-Tris(2-pyridylmethyl)-1,5,9-triazacyclododecane, $[ML^1](PF_6)_2$

complex		% C	% H	% N
$[FeL^1](PF_6)_2$	calc	41.03	4.59	10.68
	found	40.78	4.70	10.43
$[CuL^1](PF_6)_2$	calc	40.63	4.55	10.53
	found	40.63	4.60	10.28
$[CoL^1](PF_6)_2$	calc	40.87	4.57	10.59
	found	40.87	4.40	10.18
$[PdL^1](PF_6)_2$	calc	38.56	4.31	9.99
	found	38.38	4.50	9.90
$[MnL^1](PF_6)_2$	calc	41.08	4.60	10.64
	found	40.98	4.80	10.48
$[NiL^1](PF_6)_2$	calc	40.88	4.57	10.59
	found	40.68	4.80	10.19

Experimental Section

Chemicals. 3,3'-Iminobis(propylamine) (98%), 1,3-propanediol (98%), p-tosyl chloride (98%), and 2-picolyl chloride hydrodrochloride (98%) were purchased from Aldrich Chem. Co. All the solvents were of reagent grade and were used without further purification.

Syntheses. (a) 1,5,9-Triazacyclododecane Tris(dihydrogen sulfate). This compound was prepared from 3,3'-iminobis(propylamine) and 1,3-propanediol by using a multistep procedure described in the literature.[36,37] High-dilution conditions were used for the ring-closure reaction to increase the yield. All of the intermediate products were purified. *N,N',N''*-Tritosyliminobis(propylamine) and 1,3-bis(tosyloxy)-propane were recrystallized from boiling methanol and ethanol, respectively. 1,5,9-Tritosyl-1,5,9-triazacyclododecane was purified by column chromatography using chloroform as an eluent, and the product was in the most mobile fraction.

(b) 1,5,9-Tris(2-pyridylmethyl)-1,5,9-triazacyclododecane. Picolyl chloride hydrochloride (30 mmol) was added to 1,5,9-triazacyclododecane tris(dihydrogen sulfate) (10 mmol) in 50 mL of water. The mixture was chilled to 0 °C, and in order to produce a pH between 11 and 12, an aqueous solution of NaOH (120 mmol) was added over a period of 40 h under vigorous stirring. The solution was stirred at low temperature during the first 3 days, and a sticky, brownish, oil-like product precipitated. After the mixture was stirred at room temperature for another 3 days, the product was converted to a light brown solid, which was collected by suction filtration and dried in a vacuum oven. Yield: 6.5 mmol or 65%. Mp: 98−99 °C. Anal. Calc for $C_{27}H_{36}N_6$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.98; H, 8.45; N, 18.89. The mass spectrum showed a strong peak at $m/z = 445$ (M + 1). ^1H NMR (in $CDCl_3$), ppm: 1.67, quintet (6H); 2.52, triplet (12H); 3.62, singlet (6H); 7.07, triplet (3H); 7.40, doublet (3H), 7.58, triplet (3H); 8.43, doublet (3H). ^{13}C NMR: 22.2, 50.0, 61.5, 122.2, 123.2, 136.7, 149.2, 160.8 ppm.

(c) $[ML^1](PF_6)_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)). Metal salt, $M^{II}X_2$ ($X = Cl^-$ or CH_3COO^-) (1 mmol), in 2 mL of methanol was slowly added, with stirring, to a methanolic solution of 1,5,9-tris-(2-pyridylmethyl)-1,5,9-triazacyclododecane. After the resulting solution was heated for several hours and cooled to room temperature, it was filtered. In order to precipitate the complex, 0.5 g of ammonium hexafluorophosphate in methanol was added to the filtrate. The solid was filtered off, washed with methanol, and dried in a vacuum oven. Yield: 50−80%. Elemental analyses are reported in Table 1. The Fe(II), Cu(II), Mn(II), and Co(II) complexes were recrystallized from acetonitrile/ethanol to yield X-ray-quality crystals.

(d) $[PdL^1](PF_6)_2$. The ligand (0.44 g in 10 mL of methanol) was added to a suspension of $PdCl_2$ in 10 mL of methanol, and the mixture

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was refluxed for 5 h. Upon cooling, a black precipitate formed, which appeared similar to the starting material, $PdCl_2$. Water (1 mL) was added to the mixture, and the solution was refluxed for another hour before it was cooled and filtered. The filtrate became cloudy after 0.70 g of ammonium hexafluorophosphate was added, and a pale yellow solid (0.085 g) was isolated by filtration. When the sample was allowed to stand overnight, yellow crystals formed in the filtrate; these were collected and dried in a vacuum oven. Yield: 0.385 g. Elemental analyses appear in Table 1. The mass spectra of the complexes showed strong peaks corresponding to $[ML^1PF_6]^+$ and $[ML^1F]^+$.

Physical Measurements. Magnetic susceptibilities were determined by Evans' method[38,39] on a QE 300 Plus NMR instrument. Several milligrams of $[ML^1](PF_6)_2$ was dissolved in 0.500 mL of deuterated acetonitrile in an NMR tube before an inner tube with a narrow end containing pure deuterated acetonitrile was inserted into the solution containing the complex. The paramagnetic solute caused the resonance peaks of the solvent (outer tube) to shift downfield compared to the resonances of the pure solvent (inner tube). Diamagnetic corrections were made by using Pascal's constants. ^1H and ^{13}C NMR spectra were determined with a QE 300 Plus spectrometer, and some ^1H spectra were acquired using a Varian 500 NMR instrument.

Electrochemical experiments were performed on a Princeton Applied Research Model 175 programmer and Model 173 potentiostat. The output was recorded on paper using a Houston Instruments recorder. A glassy carbon electrode, a silver wire, and a platinum wire were used as working, reference, and secondary electrodes, respectively. Under nitrogen, acetonitrile solutions of the complexes (1−2 mM) with tetrabutylammonium tetrafluoroborate (0.1 M) as a supporting electrolyte were used in the experiments. The potentials vs NHE were determined by using ferrocene as internal reference.

Electronic spectra of the metal complexes in acetonitrile solutions were recorded on either a Varian Model 2300 spectrophotometer or a Hewlett Packard 84552 diode array spectrophotometer (HP) with an 89500 UV/vis Hewlett Packard ChemStation. Scan ranges: Varian, 300−2200 nm; HP, 190−800 nm. Conductances of the complexes (about 1 mM in acetonitrile) were measured on a YSI Model 35 conductance meter.

Table 2. Force Field Parameters beyond Those Common to MM2/MMP2

(a) Torsional Parameters (kcal/mol)

torsion	V_1	V_2	V_3
C(sp^3)−N(sp^3)−Ni−N(sp^3)	0.00000	0.00000	0.00000
C(sp^3)−N(sp^3)−Ni−N(sp^2)	0.00000	0.00000	0.00000
C(sp^2)−N(sp^2)−Ni−N(sp^3)	0.00000	0.00000	0.00000
C(sp^2)−N(sp^2)−Ni−N(sp^2)	0.00000	0.00000	0.00000
C(sp^3)−C(sp^3)−N(sp^3)−Ni	−0.2000	0.73000	0.80000
H−C(sp^3)−N(sp^3)−Ni	0.00000	0.00000	0.52000
C(sp^2)−C(sp^2)−N(sp^2)−Ni	0.00000	10.0000	0.00000
H−C(sp^2)−N(sp^2)−Ni	0.00000	10.0000	0.00000
C(sp^2)−C(sp^3)−N(sp^3)−Ni	0.00000	0.00000	0.00000
C(sp^3)−C(sp^2)−N(sp^2)−Ni	0.00000	10.0000	0.00000
N(sp^3)−C(sp^3)−C(sp^2)−N(sp^2)	0.00000	0.00000	0.00000
H−C(sp^2)−C(sp^2)−N(sp^2)	0.00000	15.0000	0.00000
C(sp^2)−C(sp^2)−N(sp^2)−C(sp^2)	0.00000	10.0000	0.00000
C(sp^3)−C(sp^2)−N(sp^2)−C(sp^2)	0.00000	10.0000	0.00000

(b) Stretching Parameters

bond	force const (mdyn/Å)	bond length (Å)
Ni−N(sp^2)	0.7480	2.05000
Ni−N(sp^3)[46]	0.68000	2.10000
M−N(sp^2)	1.10000	0.98*l*
M−N(sp^3)[46]	1.00000	*l*

(c) Bending Parameters

bond angle	force constant (mdyn/rad)	bond angle (deg)
N(sp^3)−Ni−N(sp^3)[46]	0.30000	90.000
N(sp^3)−Ni−N(sp^2)	0.00000	90.000
N(sp^2)−Ni−N(sp^2)	0.30000	90.000
C(sp^3)−N(sp^3)−Ni[46]	0.20000	109.00
C(sp^2)−N(sp^2)−Ni	0.20000	120.00
C(sp^2)−N(sp^2)−C(sp^2)	0.43000	120.00

(d) Nonbonded Parameters[47]

atom	WDVR (Å)	ϵ (kcal/mol)
Ni(II)	2.00000	0.20000

Molecular Mechanics Calculations. Molecular mechanics calculations were undertaken using a modified version of Allinger's MM2/MMP2 program on a VAX 9000−210VP computer.[40−43] The results of calculations were visualized in the SYBYL program of TRIPOS Associates, Inc., St. Louis, MO. The crystal structure data[31] for $[NiL^2]^{2+}$ were used as the input for $[NiL^2]^{2+}$ and $[ML^2]^{2+}$, while the molecular mechanics calculations on $[ML^1]^{2+}$ were based on the cystal structure of $[FeL^1]^{2+}$, which will be reported elsewhere. Force field parameters are listed in Table 2. The force constant and ideal bond length for Ni−N(sp^3) were taken from literature,[43] while a bond length of 2.05 Å and a force constant of 0.748 mdyn/Å (10% higher than that of Ni−N(sp^3)) were used for Ni−N(sp^2). All torsional force constants of C−Ni−N−C were set to zero, and the torsional force constants of X−C−N−C(sp^3) (X = H or C) were used to replace those of X−C−N−Ni.[44,45] The Ni^{2+} force constants except the stretching parameters of metal−nitrogen bonds were used to investigate the best fit of M−N distances for L^1 and L^2. The stretching constants of M−N(sp^2) and M−N(sp^3) were set at 1.10 and 1.00 mdyn/Å, respectively. For calculations used to estimate the metal/ligand size-fit, the ratio of the M−N(amine) reference distance to the M−N(Py) reference distance was kept constant. Thus the ideal M−N(sp^2) distance is always about 2% shorter than that of M−N(sp^3). This assumption not only reflects bond lengths in the crystal structures but also reduces the two variables, reference bond lengths of M−N(sp^3) and M−N(sp^2), to one ((M−N(sp^3)). The total steric energies and M−N distances of the hypothetical complexes with different reference M−N distances were computed, and the M−N bond lengths with minimum total energies were obtained for complexes of the ligands L^1 and L^2.

Results and Discussion

Preparation of the Ligand, L^1. The procedure described in the literature[30] was followed in attempts to prepare the new ligand L^1, but that procedure always resulted in mixtures which contained partially substituted compounds and little of the completely substituted L^1. In the literature procedure, the pH of the solution is maintained below 9.[30] 1,4,7-Tris(2-pyridylmethyl)-1,4,7-triazacyclononane can easily be obtained under such conditions. However, 1,5,9-triazacyclododecane has a much higher proton affinity than 1,4,7-triazacyclononane, and the first protonation equilibrium constant K_1[32,33] has a value around 10^{13}, probably because of strong intramolecular hydrogen bonding. During one experiment, the pH of the solution was raised to over 10, and some amount of ligand was isolated from the crude product by column chromatography using acetonitrile and methanol as eluent. Raising the pH of the solution also promoted some side reactions in addition to the formation of the ligand. When the reaction was run with the pH above 9, the solution intermediately turned red. The side reactions were prevented by chilling the solution to 0 °C. At this moderate temperature, the solution did not turn red even at pH > 12. With the pH between 11 and 12, the temperature of the reacting solution was kept at 0 °C for the first 3 days, during which time the product precipitated as a sticky brown oil. This oil is

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Table 3. Effective Magnetic Moments and Molar Conductances[a] of the Complexes of L^1 and L^2

complex	magnetic moment (μ_B)	molar conductance, Λ (Ω^{-1} cm^2 mol^{-1})	ref
$[Fe^{II}L^1](PF_6)_2$	5.68, 4.5	283	this work, 30
$[Fe^{II}L^2](ClO_4)_2$	0.62, 1.20		30, 31
$[Mn^{II}L^1](PF_6)_2$	6.00	291	this work
$[Mn^{II}L^2](ClO_4)_2$	5.82		31
$[Co^{II}L^1](PF_6)_2$	4.38	236	this work
$[Co^{II}L^2](ClO_4)_2$	4.79		31
$[Ni^{II}L^1](PF_6)_2$	3.23	240	this work
$[Ni^{II}L^2](ClO_4)_2$	3.17		31
$[Cu^{II}L^1](PF_6)_2$	2.10	281	this work
$[Cu^{II}L^2](ClO_4)_2$	2.20		31
$[Pd^{II}L^1](PF_6)_2$	diamag	281	this work
$[Pd^{II}L^2](ClO_4)_2$	diamag		31

[a] Note: the molar conductance for 2:1 complexes ranges from 220 to 300 Ω^{-1} cm^2 mol^{-1}.[50]

fairly pure and can be converted to a pure light brown solid, by vigorously stirring for another 3 days at room temperature. Pale brownish needle-like crystals were obtained by recrystallization of the oil-like product from a minimum amount of hot dimethyl sulfoxide.

Preparation of Metal Complexes. $FeCl_2{\cdot}4H_2O$, $MnCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $PdCl_2$, $Cu(CH_3COO)_2$, and $Ni(CH_3COO)_2$ were used in the preparation of the corresponding complexes. The metal salt (in methanol/H_2O for $PdCl_2$, and in methanol for the others) was added to a methanolic solution of the ligand to form the complex. Any insoluble particles in the solution were removed by filtration before a clear methanol solution of ammonium hexafluorophosphate was added to precipitate the complex hexafluorophosphate salt, $[ML^1](PF_6)_2$. The products were usually pure and gave satisfactory elemental analyses without further purification. If necessary, the salt could be recrystallized from a minimum amount of acetonitrile or an acetonitrile/ethanol mixture.

Magnetic Susceptibilities and Molar Conductances. The magnetic susceptibilities of the complexes were measured by the NMR method developed by Evans. All the complexes except $[PdL^1](PF_6)_2$ caused the solvent resonance peak to shift downfield; this indicated that $[PdL^1](PF_6)_2$ is diamagnetic while the other complexes are paramagnetic. The effective magnetic moments of the metal ions are presented in Table 3 along with those of the complexes of the related smaller-ring ligand, $[ML^2](ClO_4)_2$.[31] In $[FeL^1](PF_6)_2$ the iron(II) is high spin with an effective magnetic moment of 5.68 μ_B. This value is somewhat higher than those reported for $[FeL^1](ClO_4)_2$ (4.13 μ_B) and $[FeL^1](AsF_6)_2$ (4.9 μ_B)[30] and more in keeping with expectation for high-spin d^6 in a pseudooctahedral environment.[48] In contrast, the complex with the cyclononane-derived hexadentate ligand, $[FeL^2](ClO_4)_2$, is low spin and its effective magnetic moment has been reported to be 1.20–1.26 μ_B (303–406 K)[30] or 0.24–0.63 μ_B (98–298 K).[31] The latter data are consistent with the residual paramagnetism of a low-spin d^6 species.[49] For the smaller ligand, the counterion had little influence on the spin states since $[FeL^2](PF_6)_2$ is also low spin. The structural difference between L^1 and L^2 is the size of the triaza macrocycle. Since the metal ions are not encompassed by the ring, but rather wear it like a crown, a dramatic ring-size effect might not have been expected. To the contrary, ring size does undoubtedly play a very important role in determining the iron(II) spin state in these complexes.

Table 4. Electronic Spectral Data for L^1 and Complexes of L^1 and L^2 [a]

complex	color	λ (nm (ϵ, M^{-1} cm^{-1}))
L^1	pale brown	262 (8.74×10^3)[b]
$[Fe^{II}L^1](PF_6)_2$	yellow-green	362 (1.27×10^3), 870 (9)
$[Fe^{II}L^2](ClO_4)_2$	brown-red	432 (1.24×10^4)
$[Mn^{II}L^1](PF_6)_2$	colorless	
$[Mn^{II}L^2](ClO_4)_2$	colorless	
$[Co^{II}L^1](PF_6)_2$	dark-brown	1046 (4)
$[Co^{II}L^2](ClO_4)_2$	gray	472 (272)
$[Ni^{II}L^1](PF_6)_2$	green-brown	964 (13)
$[Ni^{II}L^2](ClO_4)_2$	violet	515 (27), 810 (36), 886 sh (24)
$[Cu^{II}L^1](PF_6)_2$	blue	716 (122)
$[Cu^{II}L^2](ClO_4)_2$	blue	695 (121)
$[Pd^{II}L^1](PF_6)_2$	yellow	316 (704)
$[Pd^{II}L^2](ClO_4)_2$	red	453 (76)

[a] Data for ML^2 are from ref 31. [b] Data in parentheses are extinction coefficients.

The molar conductances of the complexes in acetonitrile fall into the range normally observed for 2:1 electrolytes[50] (see Table 3). This further confirmed the coordination structures of the complexes of the ligand L^1.

Electronic Spectra. The wavelengths of absorption maxima and the corresponding molar absorbances from the electronic spectra of the complexes of L^1 and L^2 [31] are given in Table 4. $FeL^1(PF_6)_2$ has absorbance maxima at 362 nm (1.27×10^3) and 870 nm (9); parenthetical numbers are molar absorbances. The high molar absorbance of the first band indicates that it is due to a charge transfer transition, probably from iron(II) to ligand (d–π^*); from its low intensity, the second band can be assigned as the d–d transition.[51] $Mn^{II}L^1(PF_6)_2$ is colorless, and no significant absorbances were found in the scan range, 200–800 nm. Like $Cu^{II}L^2(ClO_4)_2$ and many other Cu(II) compounds, the Cu(II) complex is blue, with an absorbance at 716 nm having an extinction coefficient of 122 cm^{-1} M^{-1}. This absorbance is red-shifted by 21 nm from that of $Cu^{II}L^2(ClO_4)_2$. $Pd^{II}L^1(PF_6)_2$ is yellow with an absorption band at 316 nm. In contrast, $Pd^{II}L^2(ClO_4)_2$ is red and exhibits a band at 453 nm. This suggests the possibility that the two palladium(II) complexes might have different coordination structures. L^2 acts as a pentadentate ligand in $Pd^{II}L^2(ClO_4)_2$, with an uncoordinated pyridyl group. The spectra of both greenish brown $Ni^{II}L^1(PF_6)_2$ and brown $Co^{II}L^1(PF_6)_2$ display very broad and overlapping absorption bands in the ultraviolet and visible ranges. However, both showed weak absorption bands in the near-infrared range, 964 nm for Ni(II) and 1046 nm for Co(II); these afford indications of the ligand field strength of L^1. In contrast, L^2 displays a greater ligand field strength, again traceable to the small triaza macrocycle.

Electrochemistry. Cyclic voltammograms of the L^1 complexes are presented in Figure 3, and the redox potentials and peak separations are listed in Table 5. In order to demonstrate the ring-size effect on the electrochemistry of the complexes, the redox potentials of $[ML^2](ClO_4)_2$[31] are also listed in the Table 5. Since $[FeL^2](ClO_4)_2$ and $[FeL^2](PF_6)_2$ have very similar electrochemical behaviors, any effect of the anion on electrochemistry can be neglected. The results of the electrochemical studies on the complexes of L^1 and L^2 displayed a remarkable triaza-ring-size effect. In general, the complexes derived from cyclododecane $[ML^1](PF_6)_2$ are at least 300 mV more difficult to oxidize than the analogous cyclononane derivatives, $[ML^2](ClO_4)_2$.

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(48) Figgis, B. N. *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966; p 285.

(49) Figgis, B. N. *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966; p 278.

(50) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(51) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 174.

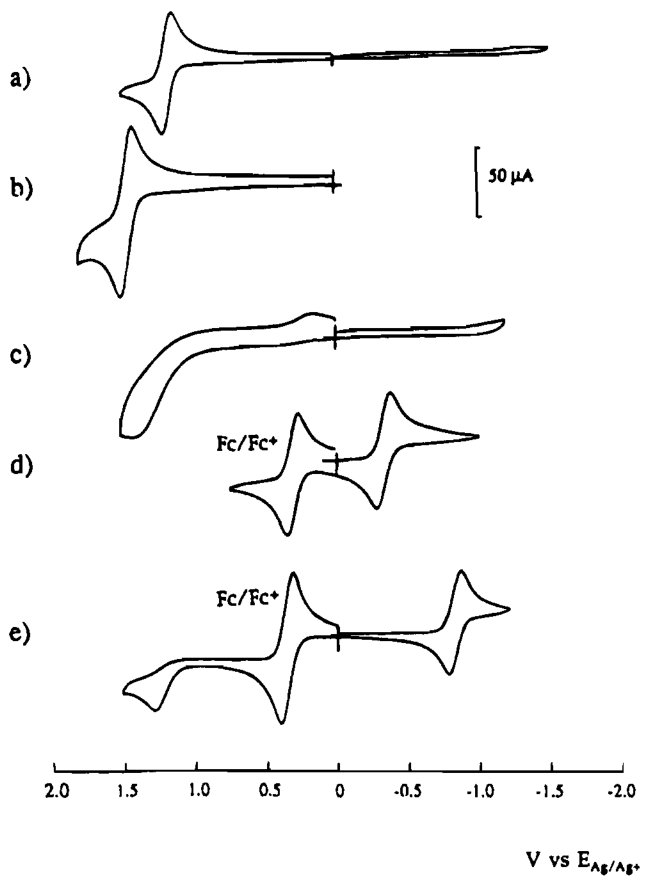

Figure 3. Cyclic voltammograms of $[ML^1]^{2+}$ in degassed acetonitrile (1 mM) with 0.1 M Bu_4NBF_4 as supporting electrolyte (scan rate 100 mV/s): (a) $[FeL^1](PF_6)_2$; (b) $[MnL^1](PF_6)_2$; (c) $[CoL^1](PF_6)_2$; (d) $[CuL^1](PF_6)_2$; (e) $[PdL^1](PF_6)_2$.

Table 5. Redox Potentials (V vs NHE) with Peak Separations (mV) in Parentheses

redox couple	$[ML^1]^{2+}$	$[ML^2]^{2+}$ [31]
Fe(III)/Fe(II)	1.22 (105)	0.76 (70)
Mn(III)/Mn(II)	1.48 (90)	1.18 (245)
Ni(III)/Ni(II)	>1.9 ($E_{p,a}$)[a]	1.42 (105)
Co(III)/Co(II)	0.31 ($E_{p,c}$),[a] 1.49 ($E_{p,a}$)	0.09 (90)
Cu(II)/Cu(I)	−0.21 (90)	
Pd(III)/Pd(II)	1.27 ($E_{p,c}$)	
Pd(II)/Pd(I)	−0.77 (70)	

[a] $E_{p,a}$ and $E_{p,c}$ are the anode and cathode peak potentials for irreversible processes.

From scans over the range from −1.2 to +1.8 V vs Ag/Ag^+, $[FeL^1](PF_6)_2$ and $[MnL^1](PF_6)_2$ in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte exhibited quasi-reversible redox couples at 1.22 and 1.48 V, respectively, vs NHE. When the ligand was changed from L^1 to L^2, the redox potentials for Fe(II)/Fe(III) and Mn(II)/Mn(III) couples shifted to less positive values, from +1.22 to +0.76 V vs NHE for iron complexes and from +1.48 to +1.18 V vs NHE for manganese complexes. It is common experience that iron(II) complexes with high redox potentials are usually low spin, but $[FeL^1](PF_6)_2$ is a rare example of a high-spin iron(II) complex with an unusually high redox potential. The relatively anodic potential of the $[FeL^1]^{3+/2+}$ couple, compared to that of $[FeL^2]^{3+/2+}$, is readily rationalized on the basis of the great selectivity of L^1 for larger ions, as discussed in the section on molecular mechanics studies. In general, first-row transition ions are smaller than the ideal size for L^1. Consequently, the larger ion of any pair, e.g., Fe^{2+} from $Fe^{3+/2+}$, is favored by this ligand, and this is reflected by a redox potential that favors Fe^{2+}.

$[CuL^1](PF_6)_2$ and $[PdL^1](PF_6)_2$ were reversibly reduced to Cu(I) and Pd(I) species at −0.21 V and −0.76 V vs NHE, respectively. The formation of Cu(I) at modest potentials is not surprising, but the generation of Pd(I) species at −0.76 V vs NHE is not expected. In order to confirm the oxidation state of the Pd(I) species, potential step and cyclic voltammograms were performed to determine the number of electrons involved in the process. The experiments demonstrated that the redox reaction is a one-electron process. It is very rare to observe a palladium(I) complex in the absence of strong π-back-bonding donors such as phosphine and carbon monoxide. Since the electrochemical results described above indicated the possibility of obtaining a palladium(I) complex, attempts are underway to synthesize the complex. $[PdL^1]^{2+}$ also exhibited an anodic peak at 1.27 V vs NHE. In contrast to $[PdL^1]^{2+}$, $[PdL^2]^{2+}$ exhibited no peaks in the range −1.5 to +1.7 V vs Ag/AgCl at 20 °C.[31]

The cyclic voltammogram for $CoL^2(ClO_4)_2$ exhibits a reversible redox couple attributable to Co(III)/Co(II) at 0.09 V vs NHE with a peak separation of 90 mV. In contrast to $CoL^2(ClO_4)_2$, $CoL^1(PF_6)_2$ presented an anodic peak at 1.49 V vs NHE and a cathodic peak at 0.31 V vs NHE. The two peaks were suspected of having a common origin since the starting complex showed no electrochemical activity over the scan range from −1.0 to +1.0 V. The peak current remained constant during multiple-scan experiments. These observations might suggest that the electro-oxidation of the Co(II) complex is followed by some chemical reactions to form some other species, which can then be reduced on the electrode to form the original Co(II) complex. As discussed in conjunction with the Fe(II) complex, steric factors might be blamed for the high oxidation potential of the Co(II) complex. Once formed, $[CoL^1]^{3+}$ may be unstable; for example, strain energy may cause the dissociation of one of the pyridyl groups. The contrasting redox behaviors of $CoL^1(PF_6)_2$ and $CoL^2(ClO_4)_2$ dramatizes the ring-size effect. The variation in ring size also affects the electrochemistry of the nickel(II) complexes. Unlike $[NiL^2]^{2+}$, which undergoes a quasi-reversible redox reaction at 1.42 V vs NHE, $[NiL^1]^{2+}$ showed no reversible redox couple; only an anodic peak was observed and that occurred at higher than 1.9 V vs NHE. This suggested that the nickel(III) complex $[NiL^1]^{3+}$ is extremely unstable.

Molecular Mechanics Calculations. The remarkably different physical properties of $[ML^1]^{2+}$ and $[ML^2]^{2+}$ inspired us to model the structures of the complexes. The $[ML^1]^{2+}$ species are oxidized at higher potentials than the analogous $[ML^2]^{2+}$, an observation we attributed to a lower formation constant for $[ML^1]^{3+}$, as compared to that of $[ML^2]^{3+}$. The coordinating atoms in the two compounds are the same, and the only difference is the triaza ring size. The saturated amine nitrogen atoms of the ring coordinate to a metal ion to form in the L^1 complex three fused six-membered chelate rings and in the L^2 complex three fused five-membered rings. Hancock used molecular mechanics calculations to examine stereochemical relationships associated with chelate ring size and concluded that saturated five-membered chelate rings favor binding to large metal ions and that similar six-membered rings favor small metal ions.[7,46] It was pointed out, however, that the size selectivities of the chelate rings might change in structures involving fused rings.[52] We provide here a clear-cut case where fusing rings together reverses their size selectivities. The simple conclusion based on single chelate rings is contradictory to our explanation

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(52) Hancock, R. D. *Pure Appl. Chem.* **1986**, *58*, 1445.

Table 6. Calculated Structures of $[NiL^2]^{2+}$ with Crystal Data[31] in Parentheses (Distances, Å; Angles, deg)

	structure[a]		
	I	II	III
M−N(a)[b]	2.12 (2.11)	2.12 (2.11)	2.12 (2.08)
M−N(p)	2.07 (2.03)	2.07 (2.05)	2.08 (2.11)
N(a)−Ni−N(a′)	84.7 (83.4)	84.3 (83.7)	84.4 (85.2)
N(a)−Ni−N(p)	80.5 (81.1)	80.6 (80.8)	80.2 (80.9)
N(a)−Ni−N(p′)	99.2 (96.8)	98.6 (97.7)	98.7 (98.0)
N(a)−Ni−N(p″)	164.4 (164.4)	164.2 (164.2)	163.9 (165.4)
N(p)−Ni−N(p′)	96.4 (98.7)	97.2 (98.1)	97.4 (96.5)

[a] Minimized structures I−III are based on the three independent molecules in the unit cell in the crystal of $[NiL^2]^{2+}$.[31] [b] N(a) and N(p) stand for amine and pyridine nitrogen atoms.

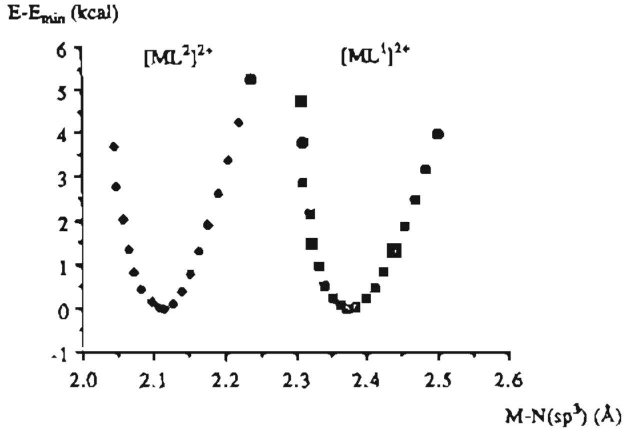

Figure 4. Graph of the difference between the total strain energies and the minimum energies ($E - E_{min}$) as a function of metal−nitrogen bond lengths M−N(sp^3).

of the high oxidation potentials of $[ML^1]^{2+}$ and of the high-spin state of $[FeL^1]^{2+}$. Using Allinger's MM2/MMP2 program, as modified by Lin,[40] the parameters in Table 2, and coordinates from the crystal structure,[31] minimum-energy conformations for $[NiL^2]^{2+}$ were obtained, and the results are displayed in Table 6. Three independent molecules of $[NiL^2]^{2+}$ exist in the unit cell, and three minimizations were calculated. Despite differences in the initial structures, the minimized structures are almost identical. These calculations were extended to estimate the best metal ion size for each of the two ligands L^1 and L^2. In order to find the M−N distances giving minimum energies, the M−N distance parameters were changed incrementally, and the total steric energies and minimized M−N distances were computed. The difference between the energy with a certain arbitrary bond length and the minimum energy ($E - E_{min}$) was plotted against the minimized bond length of M−N(sp^3) (Figure 4). The curves in Figure 4 indicate that the M−N(sp^3) distances giving minimum energies for L^1 and L^2 are 2.37 and 2.12 Å, respectively. Thus, L^1 should be selective toward the metal ions having M−N(sp^3) bond lengths (~2.37 Å) quite a bit larger than those of L^2 (M−N(sp^3) ≈ 2.12 Å). Changing stretching parameters for the M−N bonds did not shift the valley positions of the curves although the curves were made more narrow when the force constants were decreased. The minimum energy was lowered by 0.05 kcal when the stretching parameters were changed to 0.68 from 1.00 dyn/Å and to 0.748 from 1.10 dyn/Å for M−N(sp^3) and M−N(sp^2), respectively. These molecular mechanics calculations support our deduction that L^1 favors larger metal ions than does L^2.

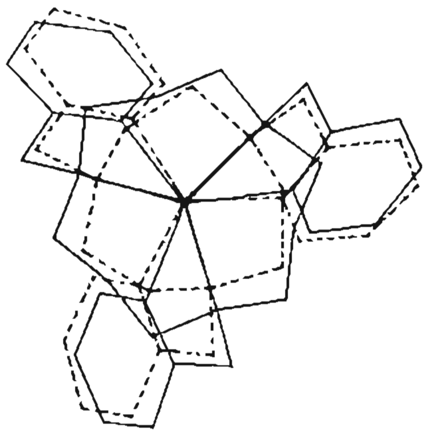

Figure 5. Energy-minimized structures of complexes of 1,5,9-tris-(pyridylmethyl)-1,5,9-triazacyclododecane (solid line) and 1,4,7-tris-(pyridylmethyl)-1,4,7-triazacyclononane (dashed line) with the reference M−N(sp^3) distance of 2.20 Å.

Figure 5 shows the superimposed minimized structures of $[ML^1]^{2+}$ and $[ML^2]^{2+}$ that were derived from calculations in which the M−N(sp^3) distance parameters in both cases were 2.20 Å. This figure dramatizes the fact that the 12-membered triaza ring of L^1 (solid line) produces a much larger coordination geometry than does the 9-membered ring of L^2. It is to be expected that L^1 will greatly stabilize larger ions, and for a redox couple M^{3+}/M^{2+}, where the ions are both high spin, this will be the ion having the lower oxidation state. This accounts very nicely for the dramatic rise in the potentials of the M(III)/M(II) couples in going from the complexes of L^2 to those of L^1. The results also concur with the fact that $[FeL^1](PF_6)_2$ cannot be low spin since the cavity is too big to permit the short bond distances required by low-spin Fe(II). It is suggested that the following generalization is of broad significance: the fusing of chelate rings leads to enormous changes in the size selectivities of the corresponding ligands.

From the preferred M−N bond length of around 2.37 Å that has been predicted by these molecular mechanics calculations, it is suggested that L^1 is not a very good ligand for first-row transition metal ions. Rather, it should display substantial selectivity for large metal ions such as second- or third-row transition metal ions and heavy post transition elements, a possibility that could lead to some practical applications. These are the subjects for ongoing research.

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