4600 *Inorg. Chem.* **1997,** *36,* 4600−4603

Tricationic Metal Complexes ([ML][NO$_3$]$_3$, M = Ga, In) of *N,N′,N″*-Tris(2-pyridylmethyl)-*cis*-1,3,5-triaminocyclohexane: Preparation and Structure

Kerry A. Hilfiker,[†] Martin W. Brechbiel,[‡] Robin D. Rogers,[§] and Roy P. Planalp*,[†]

Departments of Chemistry, University of New Hampshire,
Durham, New Hampshire 03824, and The University of
Alabama, Tuscaloosa, Alabama 35487, and Chemistry
Section, Radiation Oncology Branch, National Institutes
of Health, Building 10, Room B3-B69,
Bethesda, Maryland 20892

Received November 22, 1996

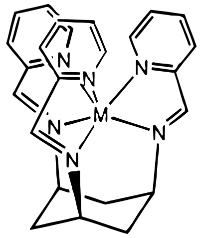
Introduction

Ligands based on the *cis*-1,3,5-triaminocyclohexane (tach) framework have versatility in binding metal ions of varied charge and size.[1−3] We are pursuing derivatization of the triamine framework with *N*-pendant groups in order to prepare chelates for the biological transport of metals. We have recently reported an efficient synthesis of tach and novel derivatives thereof, including tachpy, a hexadentate chelator derived from tach by addition of *N*-pendant 2-pyridylmethyl groups.[4] The metal ions Al^{3+}, Ga^{3+}, and In^{3+} are of interest,[5] Al^{3+} for its toxicity[6,7] and Ga^{3+} and In^{3+} for radiopharmaceuticals.[8,9,10]

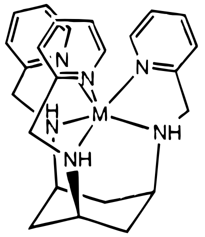
The selectivity and stability of metal ion binding is affected by the nature of the ligand donor atoms and the steric factors of ligand conformation.[11] Another factor is charge on a metal complex, which will affect its biodistribution properties.[12] We have chosen the 2-pyridylmethyl group as a pendant group in order to prepare charged metal complexes. Previously, the parent imine ligand (tachimpy) and metal complexes thereof have been prepared.[13] However, a coordinated imine is subject to hydrolysis in presence of Lewis acids.[14] We report herein the preparation and structure of the first metal complexes of the novel ligand tachpy (Ga(tachpy)$^{3+}$ and In(tachpy)$^{3+}$).

Experimental Section

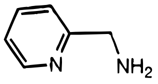
Materials and Methods. Anhydrous grade MeOH was obtained from Fisher. Et$_2$O was distilled from Na/K. Anhydrous grade DMSO and DMF were obtained from Aldrich. Ga(NO$_3$)$_3$·9H$_2$O was from Aldrich and In(NO$_3$)$_3$·5H$_2$O from Alfa. Tachpy was prepared as previously reported.[4]



M(tachimpy)$^{n+}$



M(tachpy)$^{n+}$



ampy

Proton NMR were obtained at 300 MHz with a Varian 300XL instrument or at 360 MHz with a Bruker AM360 instrument. Chemical shifts are reported in ppm on the δ scale relative to TMS (DMSO solutions) or TSP (D$_2$O solutions). Proton chemical shifts are annotated as follows: ppm (multiplicity or spin system, coupling constant if measurable, integral, assignment). Sample temperatures for variable temperature NMR were calibrated with the ethylene glycol chemical shift thermometer.[15] Fast atom bombardment (FAB-MS) mass spectra were obtained on an Extrel 4000. Elemental analyses were performed by Atlantic Microlabs (Atlanta, GA) and Galbraith Laboratories (Knoxville, TN).

Preparation of [Ga(tachpy)][NO$_3$]$_3$·3H$_2$O. Method A. To a solution of tachpy (0.235 g, 5.84 × 10^{-4} mol) in MeOH (3 mL) was added gallium nitrate nonahydrate (0.242 g, 5.80 × 10^{-4} mol) in MeOH (3 mL). A dirty white precipitate appeared on mixing and redissolved after a few seconds of stirring. The solution was warmed to 60 °C for 3 h, allowed to cool, and layered with Et$_2$O (ca. 10 mL). After standing for 12 h, oily white material deposited from the solution. The supernatant was decanted and layered with Et$_2$O, giving additional oily solid. The oily solids were purified by successive redissolution in dry MeOH, precipitation with Et$_2$O, and trituration with Et$_2$O. After several cycles, the product grows clear, colorless prisms by slow diffusion of Et$_2$O into MeOH solution. Yield: 0.198 g (2.78 × 10^{-4} mol, 48%).

Method B. To a cloudy pale yellow solution of tachpy (0.0434 g, 1.08 × 10^{-4} mol) in water (2 mL) was added gallium nitrate nonahydrate (0.0450 g, 1.08 × 10^{-4} mol). The cloudy solution was heated at 80 °C for 20 h with no visible change. Volatile material was removed under reduced pressure and the resulting solid crystallized by diffusion of Et$_2$O into MeOH (3 mL). Yield: 0.060 g (8.0 × 10^{-5} mol, 78%). Anal. Calcd for C$_{24}$H$_{36}$GaN$_9$O$_{12}$: C, 40.47; H, 5.09; N, 17.70. Found: C, 40.79; H, 4.73; N, 17.00. ^{1}H NMR (DMSO-d_6, 300 MHz, 25 °C):[16] δ 8.42, 7.96, 7.70, 7.30 (d, t, d, t, 4H, C$_5H_4$N); 6.73 (m, 1H, N*H*); 4.53 (ABX, 2H, py−C*H*$_2$); 3.57 (s, 1H, cyclohexyl methine H); 2.52, 2.11 (AB, J = 11 Hz, 2H, cyclohexyl methylene H's, diastereotopic). ^{1}H NMR (D$_2$O, pH range 2−8, 300 MHz, 25 °C): δ 8.40, 7.93, 7.67, 7.50 (t, d, t, d, 4H, C$_5H_4$N); 4.79, 4.61 (AB, J = 20 Hz, 2H, py−C*H*$_2$, diastereotopic); 3.78 (s, 1H, cyclohexyl methine H); 2.57, 2.33 (AB, J = 16 Hz, 2H, cyclohexyl methylene H's, diastereotopic). ^{1}H NMR (DMSO-d_6, 360 MHz, 77 °C): slight chemical shift variations relative to 25 °C spectrum but no changes in splitting patterns or linewidths. MS (FAB/thioglycerol): 469 (M − 3H)$^+$. UV (MeOH): $\lambda_{\max}$ 263 nm (8.6 × 10^3).

Preparation of [In(tachpy)][NO$_3$]$_3$·3H$_2$O. Tachpy (0.0411 g, 1.02 × 10^{-4} mol) was dissolved in MeOH (2 mL) to form a slightly yellow solution. In(NO$_3$)$_3$·5H$_2$O (0.0403 g, 1.03 × 10^{-4} mol) was dissolved in MeOH (2 mL) and placed in a sonicator for approximately 5 min to afford a suspension. To this suspension was added the tachpy/MeOH

[†] University of New Hampshire.

[‡] National Institutes of Health.

[§] The University of Alabama.

(1) Hegetschweiler, K.; Ghisletta, M.; Fassler, T.; Nesper, R.; Schalle, H.; Rihs, G. *Inorg. Chem.* **1993**, *32*, 2032.

(2) Bollinger, J. E.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1994**, *33*, 1241.

(3) de Angelis, S.; Batsanov, A.; Norman, T. J.; Parker, D.; Senanayake, K.; Vepsalainen, J. *J. Chem. Soc., Chem. Commun.* **1995**, 2361.

(4) Bowen, T.; Planalp, R. P.; Brechbiel, M. W. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 807.

(5) Burgess, J. *Chem. Soc. Rev.* **1996**, *25*, 85.

(6) Bollinger, J. E.; Mague, J. T.; Banks, W. A.; Kastin, A. J.; Roundhill, D. M. *Inorg. Chem.* **1995**, *34*, 2143.

(7) Liu, S.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1992**, *31*, 5400.

(8) Clarke, E. T.; Martell, A. E. *Inorg. Chim. Acta* **1991**, *181*, 273.

(9) Wieghardt, K.; Bossek, U.; Chaudhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

(10) Ma, R.; Welch, M. J.; Reibenspies, J.; Martell, A. E. *Inorg. Chim. Acta* **1995**, *236*, 75.

(11) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.

(12) Hider, R. C.; Hall, A. D. *Prog. Med. Chem.* **1991**, *28*, 41.

(13) Gillum, W. O.; Huffman, J. C.; Streib, W. E.; Wentworth, R. A. D. *J. Chem. Soc., Chem. Commun.* **1969**, 843.

(14) Liu, S.; Wong, E.; Karunaratne, V.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1993**, *32*, 1756.

(15) Kaplan, M. L.; Bovey, F. A.; Cheng, H. N. *Anal. Chem.* **1975**, *47*, 1703.

(16) Yu, C.; Dumoulin, C. L.; Levy, G. C. *Magn. Reson. Chem.* **1985**, *23*, 952.

S0020-1669(96)01402-4 CCC: $14.00

Table 1. Crystal Data and Structure Refinement for [Ga(tachpy)][NO_3]$_3$·DMF (**1**) and [In(tachpy)][NO_3]$_3$·DMSO (**2**)

	1	**2**
color/shape	colorless/plate	colorless/fragment
empirical formula	$C_{27}H_{37}GaN_{10}O_{10}$	$C_{26}H_{36}InN_9O_{10}S$
formula weight	731.39	781.52
temp, K	173(2)	173(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens	$a = 13.5166(4)$ Å	$a = 13.7848(2)$ Å
	$b = 14.3612(5)$ Å, $\beta = 98.211(1)°$	$b = 14.4516(2)$ Å, $\beta = 98.038(1)°$
	$c = 16.1161(6)$ Å	$c = 15.8678(2)$ Å
orientation matrix and cell dimens	4423 reflns in full θ range	6923 reflns
vol, Å^3	3096.3(2)	3130.01(7)
Z	4	4
density (calcd), Mg/m^3	1.569	1.658
abs coeff, mm^{-1}	0.963	0.893
diffractometer/scan	Siemens SMART/CCD area detector	Siemens SMART/CCD area detector
radiation/λ, Å	Mo Kα (graphite monochrom)/0.710 73	Mo Kα
F(000)	1520	1600
cryst size, mm	0.40 × 0.35 × 0.30	0.35 × 0.35 × 0.45
θ range for data collection, deg	1.84−21.67	1.83−27.91
index ranges	$-13 \le h \le 14, -13 \le k \le 14, -16 \le l \le 16$	$-14 \le h \le 18, -15 \le k \le 18, -20 \le l \le 20$
reflns collected	11 108	18 638
indep/obsd reflns	3630 ($R_{\text{int}} = 0.0684$)/2709 ($I > 2\sigma(I)$)	7364 ($R_{\text{int}} = 0.0396$)/6469 ($I > 2\sigma(I)$)
abs corr	semiempirical form ψ-scans	none
range of relat transm factors	0.9929 and 0.8034	
secondary extinction corr	coeff = 0.0001(3)	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
computing	SHELXTL, Ver. 5[a]	SHELXTL, Ver. 5[a]
data/restraints/params	3624/0/458	7350/0/428
goodness-of-fit on F^2	1.134	1.147
weighting scheme	SHELX-93 weight parameters: 0.0608, 4.4318	SHELX-93 weight parameters: 0.0295, 5.4332
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0503$, w$R_2 = 0.1150$	$R_1 = 0.0368$, w$R_2 = 0.0842$
R indices (all data)	$R_1 = 0.0791$, w$R_2 = 0.1354$	$R_1 = 0.0457$, w$R_2 = 0.0923$
largest diff peak and hole	0.788 and −0.475 e Å^{-3}	0.600 and −1.080 e Å^{-3}

[a] Reference 24.

solution, causing the suspension to take on an orange tint. The mixture was returned to the sonicator for an additional 5 min, causing it to become clearer and pale pink-orange. White needles began to form within 2 min and were allowed to grow for 12 h. The crystals were separated by decantating of supernatant, washed with Et_2O, and dried under reduced pressure. Yield: 0.0340 g (4.49 × 10^{-5} mol, 44%). Anal. Calcd for $C_{24}H_{36}InN_9O_{12}$: C, 38.06; H, 4.79; N, 16.64. Found: C, 38.45; H, 4.57; N, 16.43. ^{1}H NMR (DMSO-d_6, 360 MHz, 25 °C):[15] δ 8.45, 8.35, 7.88, 7.50 (d, t, d, t, 4H, C_5H_4N); 6.63 (m, 1H, NH); 4.41−4.57 (ABX, 2H, py−CH_2); 3.65 (s, 1H, cyclohexyl methine H); 2.53, 2.13 (AB, J = 11 Hz, 2H, cyclohexyl methylene H's, diastereotopic). ^{1}H NMR (DMSO-d_6, 360 MHz, 77 °C): slight chemical shift variations relative to 25 °C spectrum, and the py−CH_2 signal is a sharp multiplet spanning 4.49−4.53 δ. ^{1}H NMR (DMSO-d_6, 360 MHz, 107 °C): the py−CH_2 signal is a sharp doublet, J = 7.2 Hz. MS (FAB/thioglycerol/DMSO): 515 (M − 2H)$^+$. UV (MeOH): λ_{max} 263 nm (8.6 × 10^3).

X-ray Data Collection, Structure Solution, and Refinement for [Ga(tachpy)][NO_3]$_3$·DMF (1) and [In(tachpy)][NO_3]$_3$·DMSO (2). Suitable crystals of **1** were obtained from a DMF solution layered with Et_2O. Suitable crystals of **2** were obtained from a DMSO solution layered with Et_2O. Transparent single crystals were mounted on fibers and transferred to the goniometer. The crystals were cooled to −100 °C during data collection by using a stream of cold nitrogen gas. The space groups were determined from the systematic absences. A summary of data collection parameters is given in Table 1.

The structures were solved by direct methods. The DMF molecule in **1** was found to be disordered over two fractionally separated positions. The "A" model (O10A, N10A, C25A, C26A, and C27A) was refined at 65% occupancy, while the "B" positions were refined at 35% occupancy. The "B" orientation was refined with isotropic thermal parameters only. For both structures, the geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{\text{eqv}}$ (C). The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom ($B = 1.2U_{\text{eqv}}$ (C)). The remaining three hydrogen atoms were located from a difference Fourier map and allowed to ride on the bonded N atoms with $B = 1.2U_{\text{eqv}}$ (N). Refinement of the non-hydrogen atoms was carried out with anisotropic temperature factors (except for O10B, N10B, C25B, C26B, and C27B in **1**). Selected bond lengths and angles are given in Table 2.

Results and Discussion

Synthesis and Solution Behavior. The complex Ga(tachpy)(NO_3)$_3$ may be formed from Ga(NO_3)$_3$ and tachpy in water, while In(tachpy)(NO_3)$_3$ forms only in methanol. It has not been possible to prepare Al(tachpy)$^{3+}$. The proton NMR spectrum of Ga(tachpy)$^{3+}$, measured over the pH range 2−8, shows no change for 4 weeks, whereas In(tachpy)$^{3+}$ decomposes upon attempted dissolution in D_2O. The distortion of tachpy is greater when coordinated to a metal of larger radius (*vide infra*), and this may be the reason for the hydrolysis of In(tachpy)$^{3+}$. Our findings may be compared to those of Hancock *et al.*, who measured stability constants for the association of one molecule of 2-(aminomethyl)pyridine (ampy) to M^{3+} in 0.1 M $NaNO_3$(aq) and found values of log K_1 = 8.4 for Ga(ampy)$^{3+}$ and log K_1 = 7.6 for In(ampy)$^{3+}$ (K_1 = [M(ampy)$^{3+}$]/[M^{3+}][ampy]).[17] However, while it was possible to measure K values for Ga(ampy)$_2^{3+}$ and Ga(ampy)$_3^{3+}$, hydrolysis and precipitation of an indium hydroxide species occurs on attempted formation of In(ampy)$_2^{3+}$.[17] This hydrolytic behavior of the In^{3+}(aq)/ampy system parallels that of In(tachpy)$^{3+}$.

Proton NMR studies of both Ga^{3+} (D_2O or DMSO solvent) and In^{3+} (DMSO solvent) complexes indicate that the coordination spheres are rigid, as shown by the chemical inequivalence of the pyridyl−CH_2−N protons, which form an ABX (H_X is

---

(17) Duma, T. W.; Marsicano, F.; Hancock, R. D. *J. Coord. Chem.* **1991**, *23*, 221.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in $[Ga(tachpy)][NO_3]_3\cdot DMF$ (**1**) and $[In(tachpy)][NO_3]_3\cdot DMSO$ (**2**)

$[Ga(tachpy)][NO_3]_3\cdot DMF$ (**1**)			
Ga−N(1)	2.056(5)	N(3)−C(19)	1.487(7)
Ga−N(2)	2.079(5)	N(4)−C(8)	1.349(7)
Ga−N(3)	2.083(4)	N(5)−C(14)	1.364(8)
Ga−N(5)	2.090(5)	N(6)−C(20)	1.338(7)
Ga−N(4)	2.105(5)	C(7)−C(8)	1.482(8)
Ga−N(6)	2.114(5)	C(13)−C(14)	1.481(8)
N(1)−C(7)	1.494(7)	C(19)−C(20)	1.491(8)
N(2)−C(13)	1.487(7)		
N(1)−Ga−N(2)	91.8(2)	N(4)−Ga−N(6)	92.0(2)
N(1)−Ga−N(3)	92.6(2)	C(7)−N(1)−Ga	112.6(3)
N(2)−Ga−N(3)	87.1(2)	C(13)−N(2)−Ga	112.4(3)
N(1)−Ga−N(5)	98.3(2)	C(19)−N(3)−Ga	111.5(3)
N(2)−Ga−N(5)	80.8(2)	C(8)−N(4)−Ga	114.3(4)
N(3)−Ga−N(5)	163.9(2)	C(14)−N(5)−Ga	114.5(4)
N(1)−Ga−N(4)	80.7(2)	C(20)−N(6)−Ga	114.2(4)
N(2)−Ga−N(4)	169.6(2)	C(8)−C(7)−N(1)	111.7(5)
N(3)−Ga−N(4)	100.4(2)	N(4)−C(8)−C(7)	117.2(5)
N(5)−Ga−N(4)	93.0(2)	C(14)−C(13)−N(2)	112.0(5)
N(1)−Ga−N(6)	168.8(2)	N(5)−C(14)−C(13)	117.2(5)
N(2)−Ga−N(6)	96.4(2)	N(3)−C(19)−C(20)	111.5(5)
N(3)−Ga−N(6)	80.3(2)	N(6)−C(20)−C(19)	117.7(5)
N(5)−Ga−N(6)	90.5(2)		
$[In(tachpy)][NO_3]_3\cdot DMSO$ (**2**)			
In−N(1)	2.222(2)	N(3)−C(19)	1.481(4)
In−N(5)	2.234(2)	N(4)−C(8)	1.339(4)
In−N(4)	2.238(2)	N(5)−C(14)	1.345(4)
In−N(2)	2.248(2)	N(6)−C(20)	1.346(3)
In−N(3)	2.253(2)	C(7)−C(8)	1.505(4)
In−N(6)	2.257(2)	C(13)−C(14)	1.502(4)
N(1)−C(7)	1.474(4)	C(19)−C(20)	1.507(4)
N(2)−C(13)	1.479(4)		
N(1)−In−N(5)	106.24(8)	N(3)−In−N(6)	75.92(8)
N(1)−In−N(4)	77.02(8)	C(7)−N(1)−In	112.4(2)
N(5)−In−N(4)	99.61(9)	C(13)−N(2)−In	111.7(2)
N(1)−In−N(2)	89.50(9)	C(19)−N(3)−In	110.6(2)
N(5)−In−N(2)	76.36(9)	C(8)−N(4)−In	114.9(2)
N(4)−In−N(2)	164.37(8)	C(14)−N(5)−In	115.6(2)
N(1)−In−N(3)	90.11(8)	C(20)−N(6)−In	115.0(2)
N(5)−In−N(3)	154.20(9)	N(1)−C(7)−C(8)	113.6(2)
N(4)−In−N(3)	103.51(8)	N(4)−C(8)−C(7)	118.8(3)
N(2)−In−N(3)	84.13(8)	N(2)−C(13)−C(14)	113.1(2)
N(1)−In−N(6)	161.43(8)	N(5)−C(14)−C(13)	118.7(2)
N(5)−In−N(6)	91.23(8)	N(3)−C(19)−C(20)	112.8(2)
N(4)−In−N(6)	94.17(8)	N(6)−C(20)−C(19)	118.3(3)
N(2)−In−N(6)	100.96(8)		

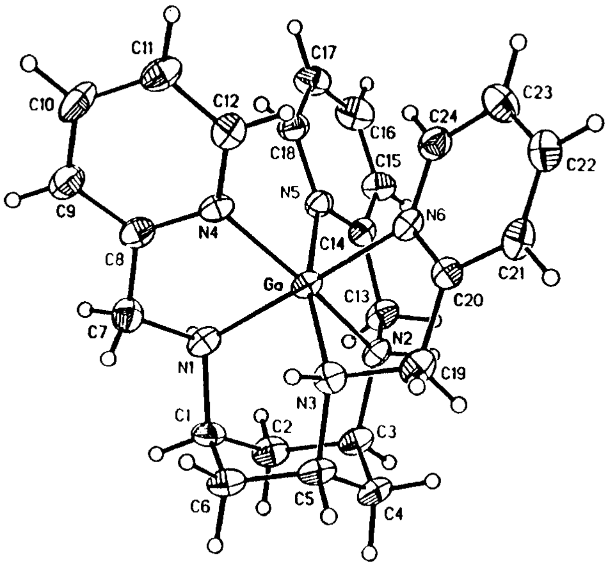


Figure 1. Molecular structure (50% probability ellipsoids) of the metal complex cation of $[Ga(tachpy)][NO_3]_3\cdot DMF$ (**1**).

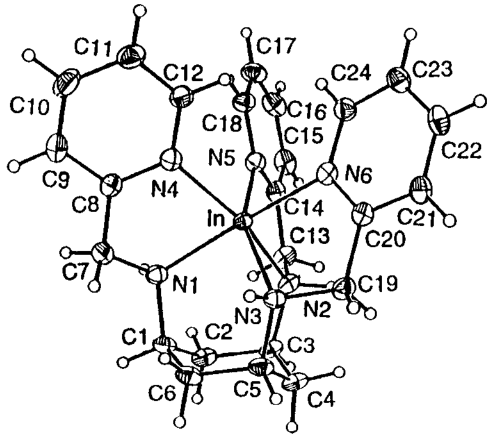


Figure 2. Molecular structure (50% probability ellipsoids) of the metal complex cation of $[In(tachpy)][NO_3]_3\cdot DMSO$ (**2**).

the amine hydrogen) spin system at room temperature. This is assumed to be due to a complex of C_3 symmetry with twisted pyridylmethyl pendant arms which may assume either the Λ or Δ configuration, as described by Hancock *et al.* for *N,N′,N″*-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, a ligand that is analogous to tachpy in that it has three 2-pyridylmethyl arms on a triamine framework.[18,19] At ca. 107 °C, the methylene signal of $In(tachpy)(NO_3)_3$ collapses reversibly to a doublet, while that of $Ga(tachpy)(NO_3)_3$ is unchanged, suggesting an interconversion of the chelate rings between Λ and Δ forms in the In^{3+} compound and consistent with a lesser rigidity of the indium complex, due to the longer In−N bonds. $In(tachpy)^{3+}$ also has a coordination geometry closer to trigonal prismatic (*vide infra*), which geometry is the presumed energy maximum in the $\Lambda-\Delta$ interconversion.[7]

Structural Studies. X-ray structures of $[Ga(tachpy)][NO_3]_3\cdot DMF$ (**1**) and $[In(tachpy)][NO_3]_3\cdot DMSO$ (**2**) are depicted in Figures 1 and 2. The structures of **1** and **2** are isomorphous. Each complex crystallizes as the pair of configurational enantiomers (Λ and Δ), as described above. Structural parameters of **1** and **2** are summarized and compared in Table 3. Bond lengths M−N are larger for **2**, reflecting the difference in six-coordinate ionic radii between In^{3+} (0.93 Å) and Ga^{3+} (0.76 Å).[20,21] In both substances, the amine hydrogen associates the complex cation to the nitrate anions through three hydrogen bonds (N−H···O).

The tachpy ligand adapts to the change in metal radius through a conformational change in the pyridylmethyl arms, which may be seen in the twist angle α (Figure 3), which averages 22.40° for **1** and 18.23° for **2**. As the metal radius increases, the pyridylmethyl arms straighten out, bringing the pyridyl nitrogens to a position farther from the corresponding amine nitrogen, to accommodate the longer M−N bonds. Accordingly, two nitrogens come closer to eclipsed (as viewed along the pseudo-3-fold axis), and the metal coordination geometry approaches trigonal prismatic (Table 3). Complexes of *N,N′,N″*-tris(2-pyridylmethyl)-1,4,7-triazacyclononane show similar structural features.[18,19,23]

---

(18) van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489.

(19) van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 1208.

(20) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925.

(21) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(22) Choquette, D. M.; Buschmann, W. E.; Olmstead, M. M.; Planalp, R. P. *Inorg. Chem.* **1993**, *32*, 1062.

Table 3. Comparison of Structural Parameters in [Ga(tachpy)][NO$_3$]$_3$·DMF (**1**) and [In(tachpy)][NO$_3$]$_3$·DMSO (**2**)

parameter	[Ga(tachpy)][NO$_3$]$_3$·DMF	[In(tachpy)][NO$_3$]$_3$·DMSO
M−N bond distances, Å	2.056(5), 2.079(5), 2.083(4), 2.090(5), 2.105(5), 2.114(5)	2.222(2), 2.234(2), 2.238(2), 2.248(2), 2.253(2), 2.257(2)
twist angles α, deg	22.58(21), 22.66(22), 21.98(22) av 22.40	19.04(10), 18.00(10), 17.93(11) av 18.23
C−C−C−C torsion angles of cyclohexyl framework, deg	52.4(7), 55.2(6), 55.0(6), 51.9(6), 49.5(7), 49.7(7) av 52.28	49.7(3), 52.4(3), 52.3(3), 49.3(3), 46.8(3), 47.0(3) av 49.58

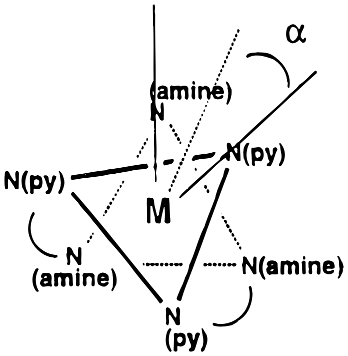


Figure 3. The twist angle defined for the coordination sphere of M(tachpy)$^{n+}$.

There is also a small effect of metal radius on the cyclohexanetriamine framework. The cyclohexyl ring is distorted by the expansion of the cyclohexyl nitrogens out from axial positions, which is naturally greater in the In^{3+} complex, as illustrated with the superposition plot of Figure 4. Thus, the C−C−C−C torsion angles of the cyclohexyl ring are decreased in **2** (average 49.58°) relative to **1** (average 52.58°) due to the greater distortion caused by the larger In^{3+} ion (Table 3). Similar distortions in metal alkoxide derivatives of the oxygen analog of tach, *cis*-1,3,5-cyclohexane trialkoxide, have been described in the cyclopentadienyltitanium complex.[22]

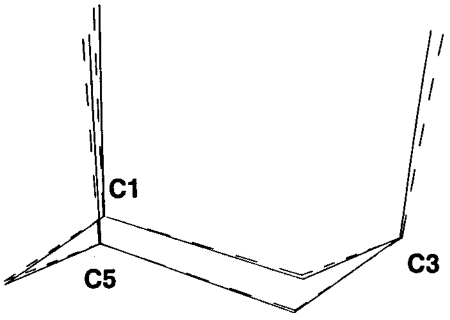


Figure 4. A superposition plot of the cyclohexyl rings and axial nitrogens of [Ga(tachpy)][NO$_3$]$_3$·DMF (solid lines) and [In(tachpy)][NO$_3$]$_3$·DMSO (dashed lines).

Conclusion. The ligand *N*,*N*′,*N*″-tris(2-pyridylmethyl)-*cis*-1,3,5-triaminocyclohexane exhibits minimal distortion in forming complexes with Ga^{3+} and In^{3+}. The versatility in coordination mirrors that observed with other tach-based ligands.[1,2] Studies of complexation chemistry of a variety of pendant-arm derivatives of tach are in progress.

Acknowledgment. We thank Dr. Derk Wierda for useful comments on the manuscript. R.P.P. thanks the NIH for financial support. K.A.H. acknowledges the UNH Undergraduate Research Opportunities Program for summer support (SURF program).

Supporting Information Available: Tables of all bond distances, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, and H-atom coordinates for [Ga(tachpy)][NO$_3$]$_3$·DMF (**1**) (Tables 1S−4S respectively) and [In(tachpy)][NO$_3$]$_3$·DMSO (**2**) (Tables 5S−8S, respectively) (16 pages). Ordering information is given on any current masthead page.

IC9614024

---

(23) Twist angles of d^{6-8} metal complexes of ligands more rigid than tachpy, having a tris(diimine) linkage to the pendant groups (e.g., tachimpy), have been investigated: Larsen, E.; La Mar, G. N.; Wagner, B. E.; Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652.

(24) *SHELXTL*, Version 5; Siemens Industrial Automation, Inc., Analytical Instrumentation Business Unit: Madison, WI, 1995.